COST
Materials, Physical and Nanosciences

COST Action 532

TRIBOSCIENCE AND TRIBOTECHNOLOGY
SUPERIOR FRICTION AND WEAR CONTROL IN ENGINES AND TRANSMISSIONS

SCIENTIFIC FINAL REPORT

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Content:

CHAPTER 1 SUMMARY

By Kenneth Holmberg, Action Coordinator

The COST 532 Action has focused European research work to solve friction, wear and lubrication related problems in engines and transmissions. The work was carried out in three working groups:
WG1 – ES Engine System with research and development activities focusing on low friction engines, chemical factors in engine wear, microsurface triboeffects, wear reducing coatings and environmental impact reduction.
WG2 – TS Transition Systems with research and development activities focusing on development of oil-free power train, contact fatigue and fracture, PVD/CVD coatings for energy reduction, high performance lubricants and development of new tribological solutions for components such as clutches, gears, brakes and springs.
WG3 – CH Tribochemistry with research and development activities focusing on lubricant-hard coating interaction, additive surface interaction, water contaminant effect on fatigue, oxidation effects, tribocorrosion, nanostructured coatings and self lubricating materials and coatings.

Major scientific results:

- A scientific breakthrough was to clarify the basic mechanisms related to carbon-based low friction coatings in lubricated contacts. The one micrometer thick vacuum deposited diamond-like carbon surfaces can in dry conditions reduce the friction with up to two orders of magnitude. Now their interaction with lubricants and additives has been explained and new coating-additive chemical compositions were developed. The results were reported in 33 journal articles. Projects: CH5, CH7, TS2, TS4.
- New nanocomposite, doped structured, multilayer and duplex coated surfaces for low wear applications in tools, machine parts and medical implants were developed, 34 journal articles, CH1, CH13, CH14, ES3, TS15, TS17.
- New methods for coated surface optimisation by microFEM modelling and simulation, 9 journal articles, TS3.
- New lubricant formulations for low friction, 13 journal articles, CH2.
- new tribocorrosion surface protection methods, 8 journal articles, CH6, CH10.
- New lubricant contamination and degradation (water, oxidation etc) control methods, 4 journal articles, CH3, CH4.
- Improved tribological properties of environmentally adaptable lubricants, 17 journal articles, CH2, CH4, CH5, CH11, ES6, TS2.

Much work was focused on improving the understanding of environmentally adaptable fluids in engines and transmissions. New techniques for emission reduction in engines by use of biogas, advanced lubricants, coatings and light weight materials were developed.

Major technological solutions:

- A detailed theoretical and experimental study on a new piston-ring design where the hydrodynamic microlubrication was generated by a textured topography containing microdimples resulted in 4 % fuel consumption reduction in engine tests, ES8.
- Transmission systems were redesigned to improve the frictional conditions resulting in a power loss reduction of up to 74 %, TS1.
- Improved understanding of engine friction and wear control by additive tribochemistry, fuel chemistry, contamination rate, surface texturing, ES1, ES2, ES5, ES8.

- Fuel consumption and emission reduction in engines by use of biogas, advanced lubricants, coatings and light weight materials, ES6.
- Tribological guidelines for improved wet clutch and brake performance, TS7, TS9, TS13.
- New electromagnetic oil free cylinder head design, TS1.
- New tribolgically improved grease composition for sliding springs in mechanical watches, TS11.

The results are benefited in new industrial products and improvements in production methods in the 103 companies directly involved in the research work. The 42 projects carried out have already by now when the 5 year Action comes to an end resulted in 32 industrial improvements in commercial use.

The Action included a total work effort of 260 person years in 42 projects. The total funding was 12.093.000 Euro distributed as 43 % public, 27 % industrial and 30 % own funding and 103 companies, 58 universities and research institutes from 27 countries were involved in the project research work.

The technical and scientific results from the action are in detail reported in:

- This Scientific Final Report, 346 pages,
- The proceedings of the final reporting event, the ECOTRIB 2007 International Conference held in Ljubljana, Slovenia, 13-15.6.2007, 1078 pages,
- Special Issue of the international refereed journal Wear, to appear 2008,
- Special Issue of the international refereed journal Tribology International, to appear 2008,
- Special Issue of the international refereed journal Tribotest, to appear 2008,
- The proceedings of the Workshop in Ghent 18-19.10.2004, 289 pages,
- The proceedings of the Workshop in Porto 13-14.10.2005, 248 pages,
- 166 articles in International refereed journals,
- 318 papers at international conferences and
- 144 national research papers.

A complete list of published reports is found in the Scientific Final Report for each project and at the Action web page.

CHAPTER 2 TRIBOCHEMISTRY, CH

2.1 Summary

By Sture Hogmark and Bojan Podgornik, Coordinators of WG3

Number of projects: 14 (From Sweden 4, Poland 3, Romania 2, Spain 2, Germany, Portugal and Slovenia 1 each) 11 projects are finalised (100%), the other three are at 90%, 85% and 30% of finalisation, respectively. WG3 has resulted in 206 reports of which 91 are internationally refereed journal papers, 66 are international conference papers and 49 are national reports. They have generated 8 industrial improvements already in use. Additionally 4 improvements are being evaluated.

The activities within the 14 projects can be classified in five *themes*.

Lubricants and greases

New thin coatings

Oxidation and corrosion

New materials

Testing and equipment

All 14 projects have chemical aspects and tribology (Tribochemistry) as common denominators. It concerns the chemical reactions occurring on the mating surfaces under the frictional heating and mechanical stresses occurring under the tribological action. Actors are elements and species in the surface materials or coatings and constituents in the atmosphere or lubricant. Physical and chemical reactions are stimulated under tribological contact. Several projects are confined within more than one of the five themes. Most of the projects are concerned with reduction of friction and wear in the boundary and mixed lubrication regimes, i.e. where the load is carried by mechanical contact between the mating surfaces or partly by the lubricant and partly by mechanical contact, respectively.

Lubricants and greases is the largest theme. It involves the projects CH2, CH3, CH4, CH5, CH7, CH11 and CH12, and has primarily been concerned with characterisation and development of additives for reduced friction and wear. Environmental aspects including biodergadability are emphasised. CH5, CH7, CH11 and CH 12 report on new products in commercial use as a result of the projects.

New thin coatings have been the main theme in CH1, CH5, CH7, CH10, CH13 and CH14. CH1 is promoting a commercial spin-off of new coatings, CH5 has reported on new coating composition in commercial use as a result of the project, and CH13 has developed commercial equipment for coating deposition.

Oxidation and corrosion was the focus of CH1, CH4, CH8 and CH10.

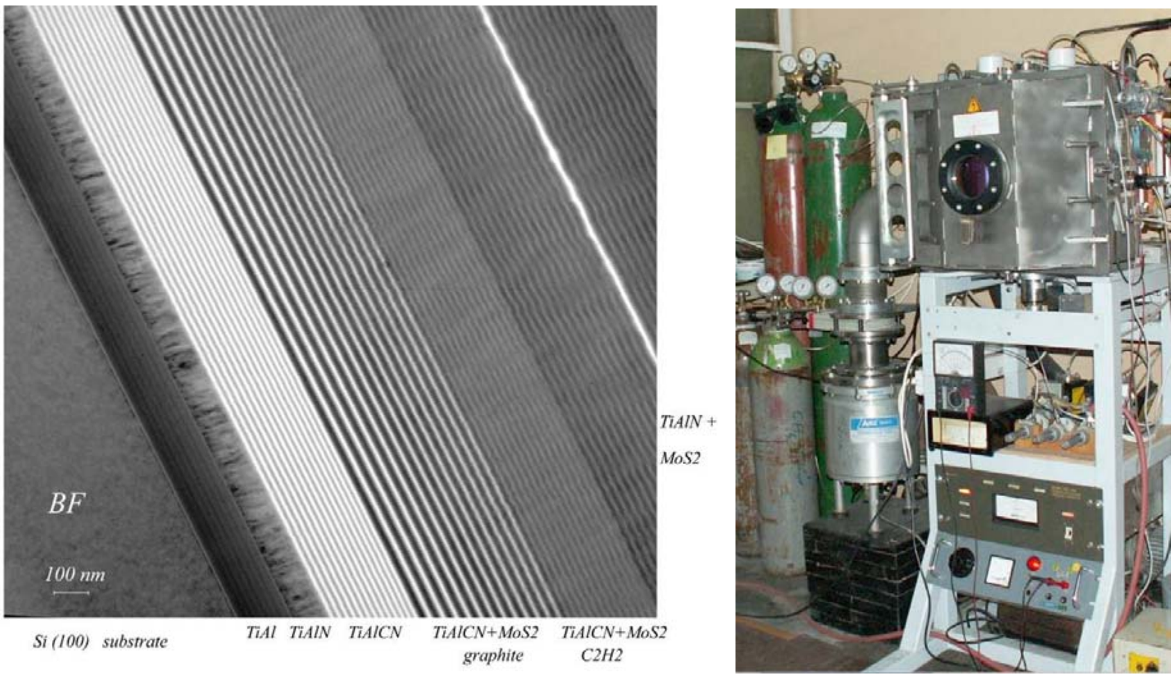
New materials were developed in CH8 and CH9. In CH9, a new epoxy-based composite material including Fe-powder, aramid fibres, graphite and MoS_2 fillers was developed for use for temperatures below 150°C. A company will apply the material.

Testing and equipment were themes in CH6 and CH 13, respectively. Both projects have gained results and equipment for commercial use.

Below, three highlights will be given, emphasising the combination of high scientific level and useful results. The three examples represent new coating materials for mechanical components, evaluation of chemical interaction between new coating materials and lubricant constituents, and, finally, adaptation of lubricants by chemical additives.

New self-lubricating coatings

Very advanced self-lubricating coating materials were developed in CH11 together with process equipment, deposition process and new top-of-the-line coating materials were developed. Coatings from the TiAlN/CrN/MoS_2 multilayer system were prepared by unbalanced magnetron reactive co-sputtering from alloyed Ti/Al: 50/50 at.%, pure chromium and MoS_2 sputter sources. The deposition was performed in Ar-N_2 mixture atmosphere of 0.22 Pa working pressure. The fine nanoscale multilayered structure is seen in Fig. 1a. A versatile semi-industrial batch coating multi-cathode *UM* magnetron sputtering system (Fig. 1b) was designed and constructed in co-operation with the *SME* industrial end-user partner. Coatings will be tried out for components in a sewing machine.



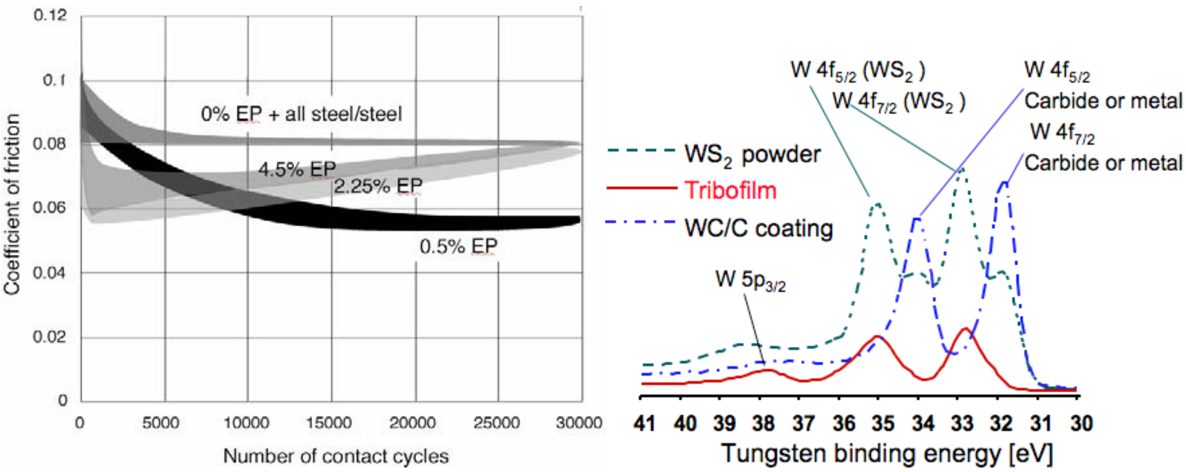
a) b)

Fig. 1. a) Bright-field transmission electron micrograph showing the cross section image of self-lubricated MoS_2 doped TiAlCN coating developed in nano-scale multi-layer structure. b) Overview picture on the newly constructed UM magnetron sputtering system.

The self-lubricated multilayers were characterized in 50 % humid air atmosphere for sliding friction coefficients ranged from 0.08 to 0.12 and micro-Vickers hardness values evaluated from $HV_{0.025}$=850 to $HV_{0.025}$=2500, which were sensitive influenced by the MoS_2 crystalline phase amount and its distribution in the nanostructured coatings.

Interaction between coatings and lubricants

The interaction diamond like carbon (DLC) coatings have been the focus of CH5 and CH7. When applying DLC coatings in components lubricated with oils containing traditional additives, only one of the two mating surfaces should be coated. Also, the amount of additives can be reduced in DLC/steel contacts compared to steel/steel contacts, see Fig. 2.



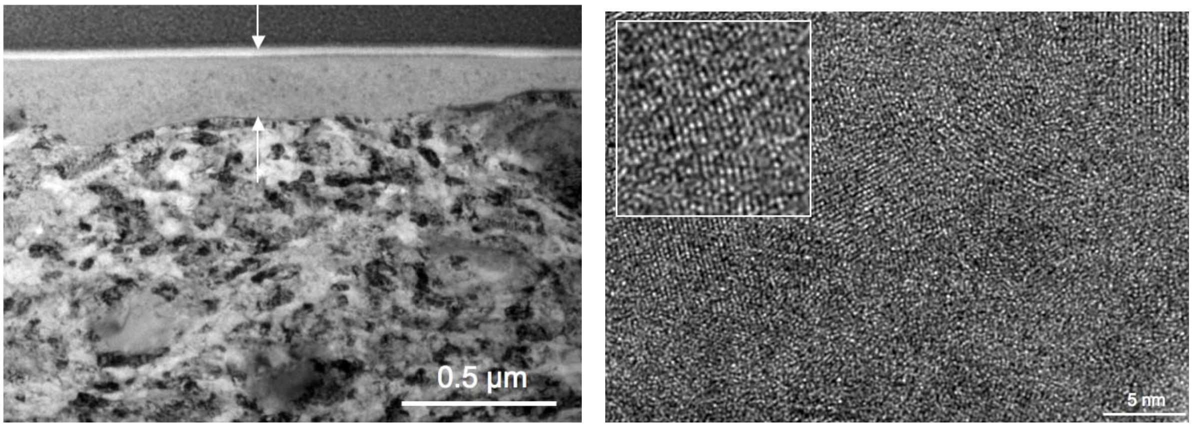
a) b)

Fig. 2. a) Friction vs. number of test cycles for lubricated DLC coating against steel in the Load Scanner. By optimising the amount of EP additive the minimum friction can be reduced and the lifetime of the coating prolonged. The steel against steel case is added for reference. b) ESCA spectrum comparing W4f binding energies of a typical tribofilm from a lubricated DLC/steel contact with that of the as deposited DLC coating (WC/C) and a reference WS_2 powder.

High-resolution transmission electron microscopy (HR-TEM) of tribofilms from DLC/steel contacts were performed in order to understand the mechanisms of their formation and performance. An example of a cross-section through the surface layer of a ball-bearing steel rod tested against W-doped DLC is seen in Fig 3. A thin and relatively homogeneous film with characteristic fullerene like crystallites is revealed, and as indicated in Fig. 2a, composition of these crystallites is WS_2, and they are been formed by a chemical reaction between W in the DLC coating and sulphur in the lubricant. WS_2 is known as a material that often generates low friction.

Thus, the WC/C not only supply wear protection and low friction through its inherent properties, used with sulphur-additivated lubricants it can react chemically to further reduce friction in boundary lubricated situations. Similar advantages were observed with Mo-doped DLC coatings

This knowledge has been used industrially both through optimized DLC coating for common-rail diesel injection systems in terms of composition, multilayer structure and thickness, and by adopting lubricants for DLC/steel contacts used in hydraulics equipment in the forestry and farming.



a) b)

Fig. 3. a) TEM image of cross-section of the contact surface of a tested steel rod run against a W-doped DLC. b) HR-TEM of the tribofilm material.

Adoptation of lubricants

Lubricants have been studied in CH11 and CH12 with respect to molecular structure and aging. The aim of CH11 was to increase the understanding about how molecular parameters are related to the physical behaviour of lubricants, and to study the additive response mechanisms for environmentally adapted base fluids. From such knowledge it is possible to make "tailor-made" lubricants, i.e. to develop lubricants with optimum properties for certain application. The project has resulted in new guidelines for selection and additivation of environmentally adapted base fluids, and new guidelines for fine-tuning of machined surfaces properties.

The principal aim of CH12 was to investigate the feasibility of replacing currently employed mineral oils with environmentally adapted lubricants through an investigation of their impact on components in tribological contacts in terms of friction and wear. Aging of the adapted lubricants was a prime concern, see Fig. 4. The conclusions are:

- All three tested fluids continue to show acceptable performance even at high acid number. This precludes the occurrence of catastrophic failure of the lubricant during normal operational use.
- Coefficient of friction appears to reduce with fluid age (thicker, more viscous fluids).
- The formation of agglomerated wear particle "sludge" occurs to varying extents with the "fresh" fluids and for aged oil B but is not seen after ageing for the esters.

The question from the end-users was whether or not an existing commercially available product will function over an extended period of time in a given application. This has been shown to be so. In this sense, an industrial improvement has been achieved in an already commercially employed product.

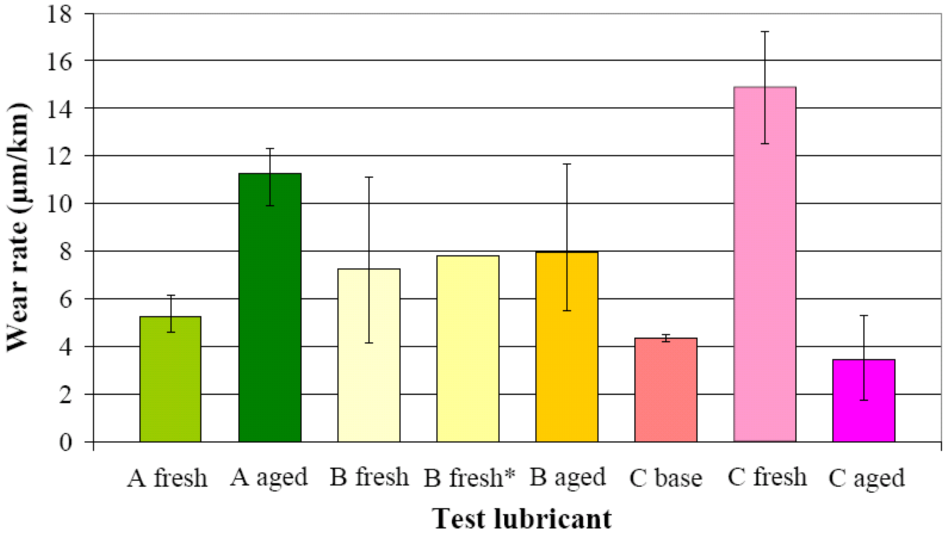


Fig. 4. Wear rates in terms of sliding distance for tests performed with fresh and aged samples of the three oils. Data for fresh oil B from a separate study (B fresh) is also shown in this diagram to assist comparison of test methods.*

2.2 Project result reports

CH1 - DEVELOPMENT OF SELF-LUBRICATING COATINGS OF THE W-S-C/N SYSTEM FOR MECHANICAL APPLICATIONS

Co-ordinator and partners

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Partners: There is no "direct" partners in this project although in other projects on the same subject some companies and research institutes are present.

Project status and schedule

Finished
Starting – 1st November 2003 and ending – 31st March 2007

Project aims

The main objective of this project is to develop self lubricating nanocomposite W-S coatings doped with C and N, that satisfy simultaneously: high wear resistance (wear coefficients lower than $10^{-16} m^3/N.m$), low friction coefficients (<0.1) in a great variety of environments (from vacuum to dry and humid air), high hardness (>10GPa) and high loading bearing capacity (films must withstand 100N loads during tribological testing). Recently, it was decided to extend the study to other transition metal dichalcogenides. Preliminary tests were performed with Mo-Se-C system. The project is finished concerning the W-S-C system.

Project results

This report describes the research activities developed during this project based on the alloying of transition metal dichalcogenides (TMD) with C. In order to be possible to summarize all the obtained results, this report is presented as a compilation of papers being referred the main achievements in each main task on which the project is based as follows:

Deposition of coatings of the W-S-C, W-S-N and Mo-Se-C systems

In task one, coatings of W-S-C and W-S-N systems were initially deposited. Three different approaches were followed for incorporating C or N in the W-S films: (1) by a reactive process using CH_4 or N_2 during the deposition which, by varying their partial pressure in the chamber, allowed to achieve different N and C contents in the coatings; (2) by a co-deposition process using the two available cathodes in the sputtering equipment, one for the C and the other for the WS_2 targets, to which different powers were applied in order to vary the final composition in C; and (3) using a C target with incrusted C pellets which, depending on their total number, permitted achieving different C contents. It was also decided to perform some depositions with another TMD system based on $MoSe_2$, for comparison purposes. In this case the used process was the one which permitted achieving the best tribological behaviour with W-S-C system, i.e. the co-deposition from a C target with WS_2 pellets.

The results concerned with this task were published in the following items:

- W-S-C deposition in reactive process – References: [1], [2], [3], [11], [12]
- W-S-N deposition in reactive process – References: [1], [2], [3]
- W-S-C deposition by co-sputtering from separate targets – References: [5], [11], [12]
- W-S-C deposition by co-sputtering from a C target with WS_2 pellets – References: [8], [9], [10], [11]
- Mo-Se-C deposition by co-sputtering from a C target with $MoSe_2$ pellets – References: [14], [15] and [16]

Characterization of coatings of the W-S-C, W-S-N and Mo-Se-C systems

The chemical composition varied from 0 up to 70at.% of C or 35at.% of N. The addition of C permitted to achieve nanocomposite structures with very compact morphologies in comparison with low C/N content films. Typically, the films without C had a very porous morphology, columnar which became progressively denser with C addition. At the same time, the surface roughness was progressively decreasing. There were not significant differences among the influence how the different methodologies of deposition led to the C incorporation. The results for N were very similar in these properties as for C.

W-S coatings were crystalline with asymmetric diffraction peaks, feature attributed to the "turbo-stacking" structure of hexagonal WS_2 phase. With the C or N introduction there was a decreasing of the crystallinity as shown by the broadening of the diffraction peaks and loss of their intensity. In some cases, it was possible to detect some specific features in the XRD patterns which could be indexed as W-C phases. The coatings deposited by co-sputtering from separate targets were amorphous. The use of high resolution transmission electron microscopy (HRTEM) showed that in the films with high C content there was a nanocomposite structure formed by nanocrystals of W-C e W-S phases embedded in an amorphous C-based matrix. The formation of these phases was confirmed by X-ray photoelectron spectroscopy (XPS) that showed, undoubtedly, the presence of W-C, W-S and C-C bonds. It is important to remark that in the case of Mo-Se-C films the presence of Mo-C bonds was not detected, suggesting the non-formation of carbide phases in this system.

Both the addition of C and N led to a significant improvement of the hardness from 0.5 GPa in W-S film up to values one order of magnitude higher in the films alloyed with C or N. This increase was not so high in the case of Mo-Se-C films, probably due to the non-formation of carbide phases.

As for the hardness, also the adhesion / cohesion determined by scratch-testing increased significantly with the addition of those elements (critical load from 5 N up to more than 25 N). The analysis by HRTEM showed that the increase in the critical load would be related with the formation of TiC carbides (coming from the Ti interlayer) in the interface between the interlayer and the W-S-C film.

The papers published which show results on the subjects above summarized are:
- Chemical composition – References: [1], [2], [4], [5], [8], [11], [12]

- Morphology– References: [2], [4], [5], [11]
- Structure – References: [2], [4], [5], [11]
- Hardness – References: [5], [8], [9], [11], [12]
- Adhesion / Cohesion – References: [3], [5], [11], [12]

Tribological characterization of coatings of W-S-C, W-S-N and Mo-Se-C systems

The influence of the C and N addition was determinant on the properties of W-S-C/N and Mo-Se-C coatings, either in unidirectional or reciprocating pin-on-disk tests. The best tribological behaviour (friction coefficient, $\mu < 0.03$ and wear, $K < 5.10^{-7} m^2/N$) was achieved with N-alloyed films. However, these coatings only had good results in dry atmospheres. This was the reason why these coatings were not so studied as those alloyed with C. For some deposition conditions of this last case, the achieved values are remarkable in both dry and humid environments, having been reached wear coefficients which are two orders of magnitude lower than for W-S films with similar friction coefficients. The tribological results allowed to draw the following conclusions:

1. The friction coefficient decreases significantly with the applied load in the test. For the highest applied load μ dropped from ~0.2 (this value depended on the C content) down to values lower than 0.1. It is important to remark that the same values could be achieved if the tests were of long duration even if the applied load was as low as 5 N. There were no significant changes in the wear coefficient with the increase of the applied load.

2. As it would be expected, there was a significant decrease of the friction coefficient when the humidity rate was decreased in the testing environment. This decrease was not so evident in the coatings with the highest C contents. However, even in 50% RH atmospheres the friction coefficient could be kept at values lower than 0.1 if either the load or the number of cycles was very high.

3. The test at high temperature showed that the coatings were stable in some cases up to temperatures of 350 ºC. After heating at 100 ºC, μ dropped abruptly for values lower than 0.05. The best behaviour was observed for coatings with C contents in the range from 40 to 50 at.%.

The study of the Mo-Se-C system showed similar trends to W-S-C but with μ values still more reduced. In humid atmospheres and with high loads or high number of cycles, μ could reach values as low as 0.015. Unfortunately, in spite of the lower μ values, the Mo-Se-C system presented a lower thermal resistance (200 ºC as maximum temperature) and wear coefficients higher than W-S-C coatings.

With the aim of studying the applicability of these coatings, long duration tests up to 200,000 cycles were applied, value which is quite high when self lubrication in humid atmospheres is concerned. Furthermore, tribological tests in varying atmospheres from dry to humid (50% RH) were performed with a Mo-Se-C film having been observed that the friction coefficient did not vary more than in the range from 0.015 to 0.03. Finally, one W-S-C coatings was tested in a reciprocating pin-on-disk machine with 1000 N applied load, resisting during 10 min at 20 Hz.

The papers published with tribological results are:

- W-S coatings alloyed with N – References: [1], [3], [7]
- W-S coatings alloyed with C – References: [1], [7], [8], [9], [10], [11], [12], [13]
- Mo-Se coatings alloyed with C – References: [14], [15] and [16]

- Reciprocating wear tests– References: [3]
- Tests for industrial applications – References: [9], [10] e [14]

Study of the sliding wear mechanisms for W-S-C, W-S-N and Mo-Se-C systems

The study of the wear mechanisms was performed by the synergetic analysis of the results obtained with optical and electron microscopies and by Auger and Raman spectroscopies. The analysis of the transfer layers allowed concluding that the low friction coefficients could not be attributed to the same mechanisms as it is usual for this type of coatings. Thus, it was decided to analyse in more detail the wear tracks in the coated worn surface. Using Raman technique it was possible to detect an enrichment of W-S amount in these zones in relation to the initial composition. Auger spectroscopy in depth, with successive eroded steps, showed that the superficial layer (a couple of nanometers) is exclusively formed by W-S without any C, to which was attributed the influence in the very low friction coefficients. In fact, in the case when μ was higher than 0.1, the formation of this surface W-S rich layer was not observed.

The papers published in this subject were
- References: [10], [14], [15] and [16]

<u>Project co-operation</u>

A new project is under preparation for extending the interpretation of the tribological results at nanoscale level. This project will be submitted to the Portuguese National Science Foundation.

Several communications were presented in many different scientific events and laboratories, as follows:

- *Study of self lubricant coatings of the W-S system*, A. Cavaleiro, COST Action 532 "Triboscience and Tribotechnology: Superior friction and wear control in engines and transmissions" 19-20 February 2004, Brussels
- *W-S-C sputtered films: Influence of the carbon alloying method on the mechanical properties,* M. Evaristo, A. Nossa, A. Cavaleiro, Poster presented at the PSE2004 at Garmisch-Partenkirchen, 13-17 September 2004
- *Self-lubricating coatings based on tungsten disulfide,* Invited Talk at EMPA – Duebendorf, Switzerland, 12th January 2005
- *Nanocomposite self lubricating W-S-C/N coatings with high loading bearing capacity*, A. Cavaleiro, A. Nossa, Invited talk at W-15 Surface Engineering for Hard Coatings, 4-8 June 2004, Avila, Espanha
- *The influence of the addition of Ti on the mechanical properties of W-S-Ti coatings,* M. Evaristo, A. Nossa, A. Cavaleiro, Poster presented at Materiais 2005, Aveiro University, April 2005
- *Tribological behavior of W-S-C Films In Humid Air and Dry Environments,* A. Nossa, A. Cavaleiro, IBERTRIB 2005, Minho University, July 2005
- *Tribological behavior of reactive and co-sputtered W-S-C coating,* M. Evaristo, A. Nossa, A. Cavaleiro, IBERTRIB 2005, Minho University, July 2005
- *Self-lubricating W-S-C coatings* M. Evaristo, A. Nossa, T. Polcar, A. Cavaleiro, Invited talk at AEPSE 2005, Qingdao, China, September 2005
- *Tungsten as a versatile element for thin coatings for mechanical applications,* A. Cavaleiro Invited talk at MIIC 2006 – 16 - 18 March 2006, Mikkeli, Finland

- *Development of self-lubricating coatings of the W-S-C/N system for mechanical applications, A. Cavaleiro,* “COST 532 "Triboscience and Tribotechnology: Superior friction and wear control in engines and transmissions", April 2006, Dubrovnik, Croatia
- *High temperature tribological behaviour of self-lubricating Mo-Se-C sputtered coatings,* M. Evaristo, A. Nossa, T. Polcar, A. Cavaleiro, ICMCTF 2006 – International Conference on Metallurgical Coatings and Thin Films”, May 2006, San Diego, USA
- *High temperature tribological behaviour of nanocomposite carbon containing transition metal dichalcogenide (C-TMD) self-lubricating coatings,* M. Evaristo, A. Nossa, T. Polcar, A. Cavaleiro, Invited talk at ESF Exploratory Workshop on Carbon-Based Nanostructured Composite Films, Organized under the auspices of the E-MRS, 30 August – 1 September 2006, Gdansk, Poland
- *Nanocomposite transition metal-dichalcogenides sputtered self-lubricating coatings alloyed with carbon,* T. Polcar, M. Evaristo, A. Nossa, A. Cavaleiro, Invited talk at EMRS 2006 Fall meeting, Symposium A - Nanostructured composite films: Synthesis, characterization, properties and applications, 4-6 September 2006, Warsaw, Poland
- *Tribological behaviour of C-alloyed transition metal dichalcogenides (TMD) coatings in different environments*M. Evaristo, T. Polcar and A. Cavaleiro, Mechanics and Materials in Design (M2D’ 2006) 24-26 July Porto Portugal
- *The tribological behaviour of W-S-C films in pin-on-disk testing at high temperature* M. Evaristo, T. Polcar,, A. Cavaleiro, 6th Iberian Vacuum Meeting and ETCHC-4, Salamanca, 26-28 June 2006, Spain
- *Friction of self-lubricating W-S-C sputtered coatings sliding under increasing load,* T. Polcar, M. Evaristo, A. Cavaleiro, M. Stueber, S. Ulrich, PSE2006, September 2006, Garmisch-Partenkirchen, Germany
- *The effect of C addition on the tribological behaviour of TMD sputtered self-lubricating coatings*, A. Cavaleiro, University of Groningen, December 2006, Groningen, The Netherlands
- *Comparative study of the tribological behaviour of self-lubricating W-S-C and Mo-Se-C sputtered coatings*
- T. Polcar, M. Evaristo, A. Cavaleiro, to be presented at ECOTRIB 2007 Joint European Conference on Tribology and Final conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007, Ljubljana, Slovenia
- *Synthesis, mechanical and tribological properties of sputtered Mo-Se-C coatings*, T. Polcar, M. Evaristo, A. Cavaleiro, to be presented at ECOTRIB 2007 Joint European Conference on Tribology and Final conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007, Ljubljana, Slovenia
- *Self lubrication materials: what can be expected when sputtered coatings are deposited combining tmd and dlc?,* A. Cavaleiro, Invited Talk at MATERIA 2007, Morelia, Mexico
- *The potential of C-alloying of transition metal dichalcogenides for self-lubricating application,* T. Polcar, M. Evaristo and A. Cavaleiro, Invited talk at ISOPE 2007, Lisbon, Portugal

<u>Publications were project results are reported</u>

1. Behaviour of Nanocomposite Coatings of W-S-C/N System Under Pin-on Disk Testing, A. Nossa, A. Cavaleiro, Materials Science Forum, 455-456 (2004) 515.
2. Chemical and physical characterization of C(N)-doped W-S sputtered films, A.Nossa, A. Cavaleiro, Journal of Materials Research 19 (8) (2004) 2356-2365.
3. Revestimentos auto-lubrificantes do sistema W-S dopados com C / N, Ana Nossa, Dissertação de Doutoramento, Faculdade de Ciências e Tecnologia da Universidade de Coimbra, 2004.

4. On the microstructure of tungsten disulfide films alloyed with carbon and nitrogen, A. Nossa, A. Cavaleiro, N.J.M. Carvalho, B.J. Kooi, J.Th.M. De Hosson, Thin Solid Films, 484 (2005), 389-395.
5. W-S-C sputtered films: Influence of the carbon alloying method on the mechanical properties, A.Nossa, A. Cavaleiro, M. Evaristo, Surface and Coatings Technology, 200, (2005) 1076-1079.
6. The influence of the addition of Ti on the mechanical properties of W-S-Ti coatings, M. Evaristo, A. Nossa, A Cavaleiro, Materials Science Forum Vols. 514-216 (May 2006) pp687-691.
7. Tribological Behaviour of C(N)-alloyed W-S Films, A. Nossa, A. Cavaleiro, Tribology Letters (accepted for publication).
8. Tribological behaviour of C-alloyed transition metal Dichalcogenides (TMD) coatings in different environments, M. Evaristo, T. Polcar, A. Cavaleiro, submitted (under review) to International Journal of Mechanics and Materials in Design.
9. The tribological behaviour of W-S-C films in pin-on-disk testing at elevated temperatures, T. Polcar, M. Evaristo, A. Cavaleiro, accepted for publication in Vacuum.
10. Friction of self-lubricating W-S-C sputtered coatings sliding under increasing load T. Polcar, M. Evaristo, A. Cavaleiro, Plasma Process & Polymers (in press).
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13. Tribological Behaviour of W-S-C Films in Humid and Dry Environments, A. Nossa, A. Cavaleiro, Proceedings IBERTRIB 2005.
14. The effect of C addition on the tribological behaviour of TMD sputtered self-lubricating coatings, A. Cavaleiro, University of Groningen, December 2006, Groningen, The Netherlands.
15. Comparative study of the tribological behaviour of self-lubricating W-S-C and Mo-Se-C sputtered coatings, T. Polcar, M. Evaristo, A. Cavaleiro, to be presented at ECOTRIB 2007 Joint European Conference on Tribology and Final conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007, Ljubljana, Slovenia.
16. Synthesis, mechanical and tribological properties of sputtered Mo-Se-C coatings, T. Polcar, M. Evaristo, A. Cavaleiro, to be presented at ECOTRIB 2007 Joint European Conference on Tribology and Final conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007, Ljubljana, Slovenia.

Planned or achieved industrial improvements in commercial use

The results of the project are now being evaluated for a spin off action by old students of the University of Coimbra for developing a new enterprise.

CH2 - INTERACTIONS OF LUBRICANT ADDITIVES AND MATERIALS OF RUBBING ELEMENTS

Co-ordinator and partners

Co-ordinator:
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Project status and schedule

Finished
Starting and ending dates: 2003-2005

Project aims

This project aims at elaborating both theoretical and technological principles of a priori creation of surface and subsurface layer properties in a tribosystem. The main point is here the elaboration of prognosis of interactions between active components of lubricant and friction pair material.

This project was realized according to the established plan. The investigations have included:

- selection of approaches to the planned studies and preparation of rubbing system elements,
- preparation of model base lubricants composed with different additives and investigation their physic-chemical properties,
- determination of antiwear (AW) and extreme pressure (EP) characteristics of the prepared tribosystems (metal-lubricant); statistical processing of obtained results,
- investigation of chemical reaction products of lubricant active components formed during friction,
- investigation of rubbing surface microstructure; identification of wear mechanisms,
- investigation of chemical structure of boundary layers forming during friction; identification of chemomechanical interaction mechanisms,
- investigation of active elements distribution in depth of surface layer; identification of element migration phenomena as well as processes of structural rearrangement of surface layers,
- elaboration of the obtained results; determination of relationships between components of the tribosystem.

Project results

This final report describes only some main aspects of the realized investigations and drawn conclusions.

Model base lubricants (SAE 30/95, PAO-4, PRIOLUBE 3970) were composed with vegetable-originated unconventional lubricant additives. As the additives were used products of chemical and thermooxidative modifications of vegetable oils:

- product of sunflower oil thermooxidation at 120^oC during 15h (denoted as DE),
- product of Diels-Alder reaction of rape-seed oil (denoted as KE).

The used additives were the most effective at 2,5% by weight concentration in base oil. The obtained results were verified based on lubricants containing 2,5% by weight conventional multifunctional additive based on ZDDP (denoted as ACX).

Tribological tests were performed using ball-on-disk tester with steel-steel elements of the friction pair. Figures 1-3 show comparison of AW/EP properties of lubricants containing selected synthetic and natural additives (2,5 % w/w). Model tests were verified based on lubricants containing ACX.

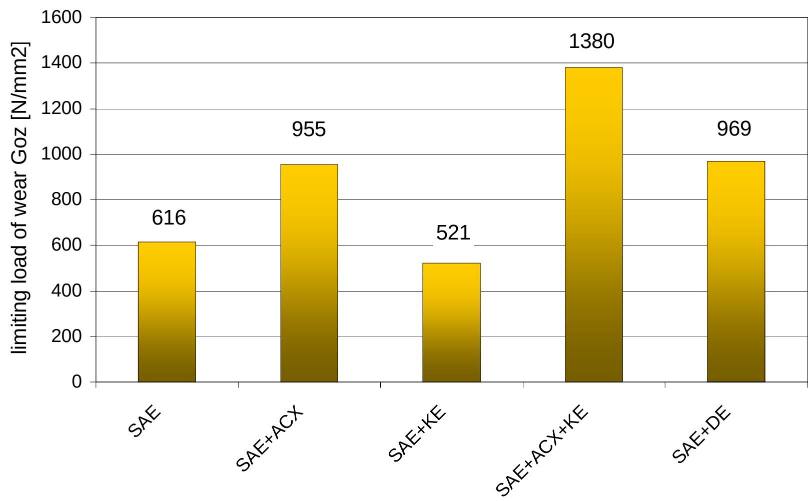

Fig. 1. Influence of the used additive type in mineral oil SAE on limiting load of wear.

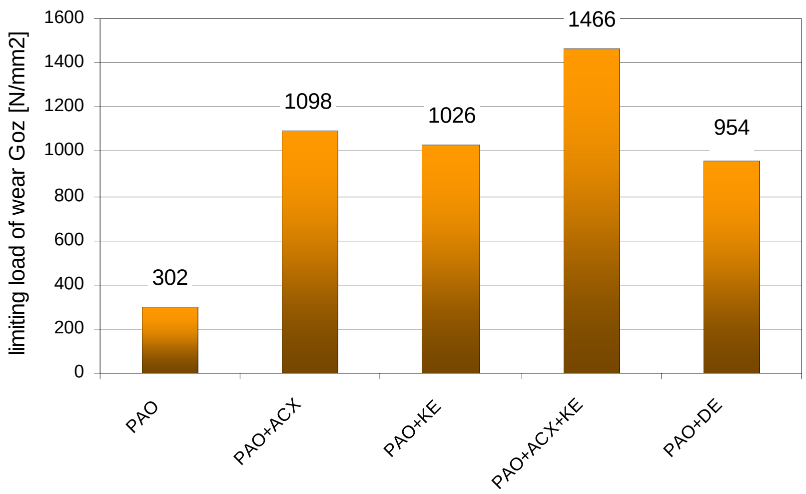

Fig. 2. Influence of the used additive type in synthetic oil PAO on limiting load of wear.

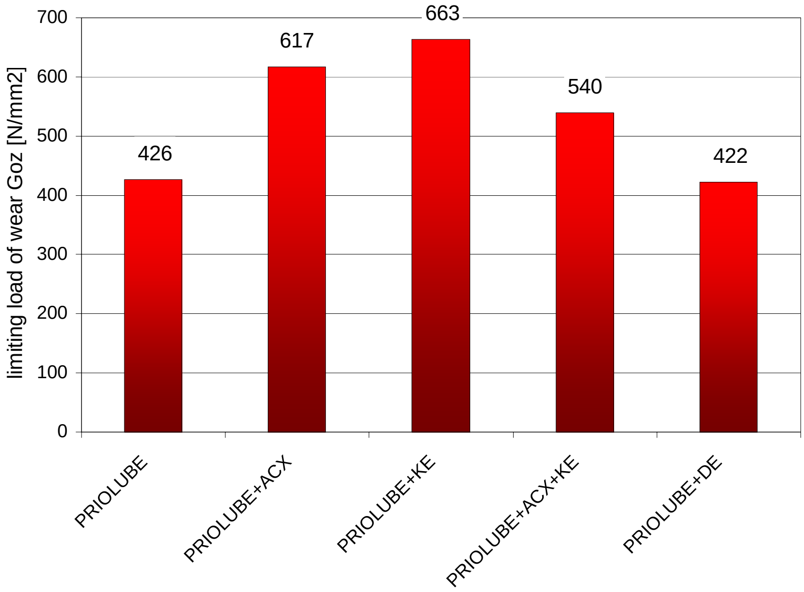

Fig. 3. Influence of the used additive type in synthetic oil PRIOLUBE on limiting load of wear.

As show in Figures 1-3 PAO-based compositions have the best properties contrary to lubricants based on PRIOLUBE and SAE. Whereas ecological KE product has proved the most efficient additive in all investigated both mineral and synthetic base oils. It has been also observed synergetic effect between KE and ACX in SAE and PAO.

In order to investigation of rubbing surfaces microstructure and identification of suitable wear mechanisms SEM analysis, optical microscope and profilographic measurements were performed. For example Figure 4 presents images of wear scar on the balls lubricated during tribological tests in four-ball machine by SAE, PAO and PRIOLUBE as well as their compositions containing KE additive. In all presented images - except one (see Figure 4c) - abrasive wear is visible. However application of the KE additive caused elimination of adhesion tackings characteristic for PAO base oil and reduction of the wear.

Since FTIRM and EDS techniques cannot be sensitive enough to analyse monolayers, the sliding surfaces have been examined by means of X-ray photoelectron spectroscopy. XPS is very sensitive for investigating not only the chemical composition but also the chemical environment of the atoms in a molecule.

After running a survey profile of the disk lubricated during friction at 20^{o}C with PAO+KE (see Figure 5), the regions for high-resolution spectra of iron 2p, oxygen 1s and carbon 1s photoelectrons were selected (see Figure 6).

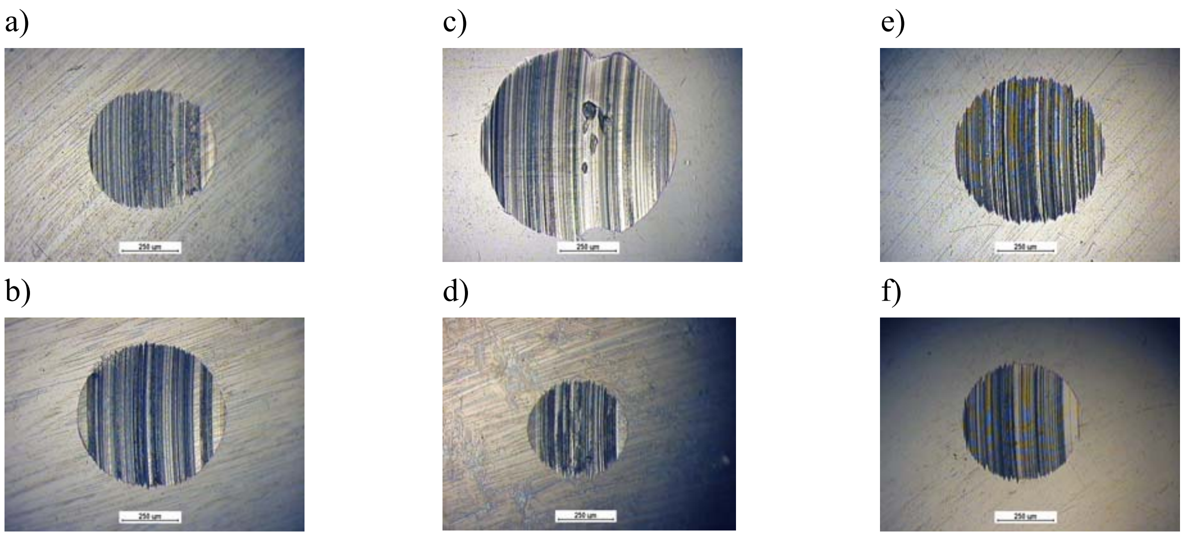

Fig. 4. Optical microscope images of the wear scars on the balls lubricated during friction by: a) SAE, b) SAE+KE, c) PAO, d) PAO+KE, e) PRIOLUBE, f) PRIOLUBE+KE.

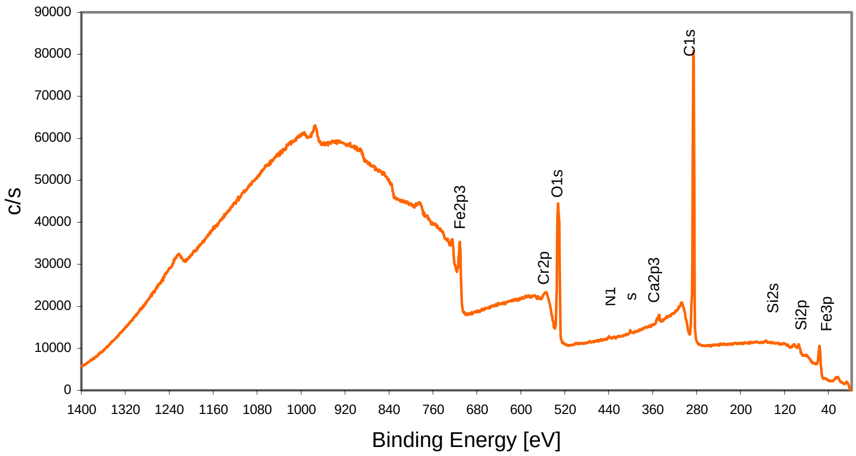

Fig. 5. XPS survey profile of the steel disk lubricated during friction with PAO+KE.

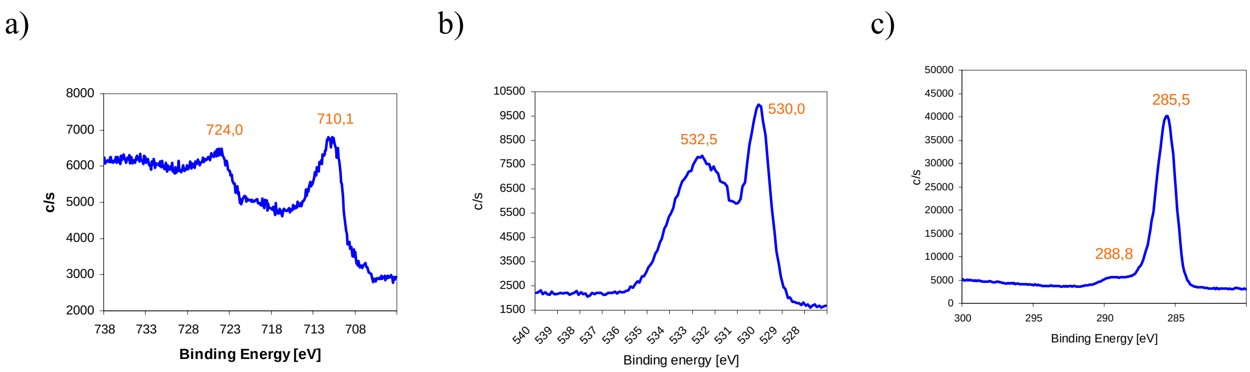

Fig. 6. Typical XPS spectra of: a) Fe2p, b) O1s and c) C1s photoelectrons recorded on the sliding steel surface after friction at 20°C lubricated with PAO+KE.

Presented in Figure 6a the spectrum of Fe2p photoelectrons has a peak at 724 eV (beyond the interpretative iron 2p region) and at ~710,1 eV assigned to iron compound formation (elemental iron binding energy is 706-707 eV). The last one is typical for Fe-O bond, for example in such compounds as oxides, hydroperoxides and carboxylates.

In the oxygen region (see Figure 6b) a multiple peak at 532,5 eV and 530 eV.

The peak at 532,5 eV is typical for C=O as well as C-H bond in organic compounds. Whereas the low binding energy of 530 eV is characteristic location for oxide oxygen. The C1s photoelectron spectrum (see Figure 6c) contains peaks at 285,6 eV assigned to the C-O bond and at 288,8 eV assigned to the C=O bond in carboxylates.

The same microregion of the investigated surface was subjected to an ion sputtering. Obtained results are shown in Figure 7. Spectra of the iron, oxygen and carbon regions revealed shift in binding energy values. Comparison of Fe2p spectra shows progressive reduction of Fe_2O_3 amount (~710 eV) in favour of metallic iron (~707 eV). Besides in successive spectra of O1s photoelectrons the peak at 532,5 eV disappearing, while the peak at ~530 eV remains. This means that organic compounds are presence on the rubbing surface and in depth of steel only iron oxides are detected. In the carbon photoelectron region shift of the peak at ~285,5 eV takes place in direction of lower energy due to chemical bonding, typical for some cyclic hydrocarbons, whereas 283,5 eV – iron carbide.

a) b) c)

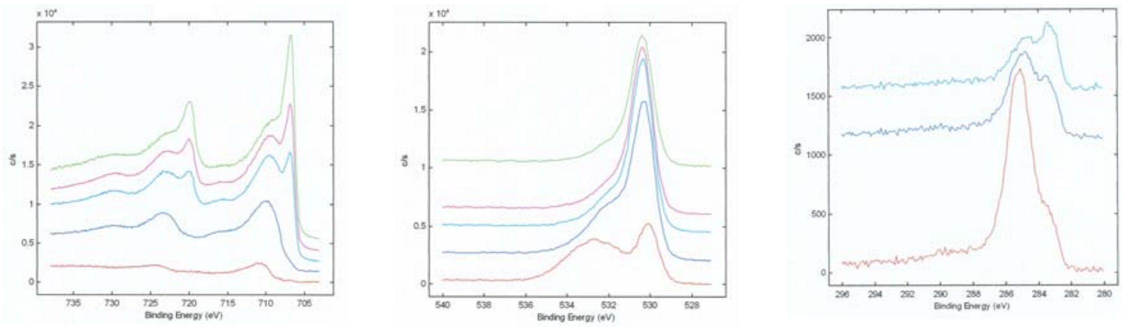

Fig. 7. Typical XPS spectra of: a) Fe2p, b) O1s and c) C1s photoelectrons recorded during sputtering the sliding steel surface lubricated with PAO+KE.

Summarizing, instrumental surface analyses of the wear tracks lubricated with PAO containing KE additive at ambient temperature allowed the chemistry of formed reaction products in the sliding contact area to be determined. The obtained analytical data indicate the possible presence of carboxylates in the analysed deposits as well as in depth cyclic hydrocarbons, complex compounds of iron and iron oxides.

It is hypothesized that at ambient temperature reactions are mostly initiated by the mechanical action of the tribological system.

Conclusions

Basing on the results obtained in this work it has been concluded that the tested lubricants undergo chemomechanical reactions during friction which lead to organic compounds formation. Among them carboxylates and complex compounds of iron are predominant.

Antiwear efficiency of the selected lubricants was very high. For example PAO-based lubricants containing ecological additive (product of chemical modification of rapeseed oil) were more effective under different friction conditions than conventional mineral lubricants.

The obtained results and the set of specialized analytical procedures that have been developed constitute a theoretical basis to forecast the character and consequences of the interactions between active components of lubricant and friction pair material as a function of the time and working conditions.

Project co-operation

Mention the forms of co-operation used:

- e-mail contacts (the co-operation consists in exchanging of scientific experiences);
- presentation of results on COST kick-off meeting in Radom (02.10.2003);
- presentation of results on Working Group Meetings in Prague (17.02.2005);
- paper at COST 532 Conference integrated with NIST Conference in Porto (12-14.10.2005);
- paper submitted to ECOTRIB 2007 Joint European Conference on Tribology and Final Conference of COST 532 Action: Triboscience and tribotechnology in Lubljana (12-15.06.2007).

Planned or achieved industrial improvements in commercial use

Authors of this work have described a package of their own methods for investigation of chemomechanical interactions between active components of lubricant and friction pair material. Among them there are both methods for identification of the chemical reaction products in a bulk lubricant and methods for the identification of chemical structure of boundary layers formed during friction on the steel surface. These methods can be implemented in diagnostic systems to determine the application range of new lubricants and in quality inspection of specialized lubricants assigned to specific technical applications.

The principal achievement of the study was also the elaboration of bases for the prediction of surface layers properties as a result of controllable interactions between suitable chosen lubricant and material of friction pair. Application of the obtained results in the practice will enable to design kinematic pairs with assumed operational properties. It can also improve operation of elementary machines and devices.

Publications were project results are reported

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10. MAKOWSKA, M. AND MOLENDA, J., 2005. Interactions of selected lubricant additive and material of rubbing surfaces. *Proc. of COST 532 Conf. integrated with NIST Conf.,* Porto, Portugal, 187-193.
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12. MAKOWSKA, M., MOLENDA, J. AND SIWIEC, E., 2005. Evaluation of antiwear efficiency of ecological additive in synthetic base oil. *Tribologia*, 203 (5), 141-150. (In Polish).
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17. *COST 532 Project Results Report*. COST 532 Tribology Conference, Ghent, Belgium, 18-20.10.2004.
18. *COST 532 Project Results Report*. Working Group Meeting, Brussels, Belgium, 19-20.02.2004.
19. *COST 532 Project Results Report*. Working Group Meeting, Praha, Czech Republic, 17.02.2005.
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CH3 - THE INFLUENCE OF WATER CONTAMINATION ON ENDURANCE LIFE

Co-ordinator and partners

Co-ordinator:
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Partners: Professor Stathis Ioannides
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Project status and schedule

Running with full funding
Starting and ending dates 04-2001 to 06-2005.

Project aims

To quantify the rolling bearing lifedecrease caused by water contamination in oil by:
Quantifying hydrogen transport into and in steel as a function of stress variation.
Quantifying influence of surface shear stress on hydrogen transport.

Project results

Preliminary results have been produced using five different experimental set-ups:

1. Rotating bending beam experiments with different geometry (smooth, notched) under different chemistries at the surface, and with and without rubbing contacts at the surface. The experimnets showed that the hydrogen moves around in the steel as a function of stress variations.
2. Tensile tests in an Instron machine. The tensile test specimen with water (wet cloth) in contact with the surface accumulated hydrogen during the stress variations. (Tensile stresses from zero to a maximum.)
3. Tests, using a hydrogen analyser, shows that the hydrogen in steel is absorbed at theree different energy levels. This indicates at least three different types of positions in the steel, where the hydrogen is located.
4. Helium ion accelerator tests (ERDA) have shown that the hydrogen distribution in soft and hardened 52100 ball bearing steel is very different from each other. The soft steel had a rather evenly distributed hydrogen concentration, while hardened steel had large hydrogen concentration variations within a fraction of a millimeter.
5. Ball bearing tests in atmospheres with different relative humidity to measure hydrogen ingress and endurance life.

Project co-operation

The forms of co-operation used: e-mail contacts, meetings, seminars, researchers visits.

Industrial improvements in commercial use

The results will be used by SKF in their rolling bearing theories and manufacturing.

Publications where project results are reported

Two papers were published in the NORDTRIB conference 2004. One paper is published by WEAR ("Quantifying diffused hydrogen in AISI-52100 bearing steel and in silver steel under tribo-mechanical action: Pure rotating bending, sliding-rotating bending, rolling-rotating bending and uni-axial tensile loading", Imran, Jacobson and Shariff, Wear 261 (2006), pp 86-95), one paper was published in the proceedings of Leeds-Lyon Symposium 2005. PhD Thesis "Effect of Water Contamination on the Diffused Content of Hydrogen under Stress in AISI-52100 Bearing Steel", ISRN-LUTDN/TMME-1018-SE.

" Effect of water contamination on the diffused content of hydrogen under stress in AISI-52100 bearing steel [COST532-CH3] " submitted to ECOTRIB 2007 Joint European Conference on Tribology and final conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007. Ljuljana, Slovenia).

CH4 - OXIDATION STABILITY OF NON-TOXIC GREASES

Co-ordinator and partners

Co-ordinator:

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Project status and schedule

Running with partial funding Finished
Starting and ending dates 01. 2003-12. 2005

Project aims

The scientific aim of the project is the assessment of oxidation resistance of on ecological grease based on a vegetable oil with an antioxidants. A modification of the vegetable oil will be performed to obtain a dispersion phase of the grease showing an improved thermal-oxidative resistance. An effectiveness of various antioxidants in the oil will be investigated.

Project results

In view of above, there is a real need for research on equivalents of petroleum and development of new technologies for production of lubricants according to the most advanced, 'ecological' trends. It seems that the most perspective approach is to focus on alternative, renewable, widely available, natural resources, for example vegetable oils.

Vegetable oils are a potential source of environmentally friendly base oils. They exhibit excellent lubrication properties but are limited as potential lubricants due to low thermal and oxidation stability. This is a reason for application of antioxidants in formulations of vegetable oils, being the dispersion phase of greases. Base oil is a major component in grease. It typically represent 80-90% of the finished product volume.

Good lubricating properties of vegetable oils and a high degree of their biodegradation were decisive for using them as the dispersion phase of lubricating greases.

The assessment of physico-chemical properties of a base oil and formulations using such an oil with an antioxidant will be performed on the ground of parameters describing structural stability and resistance to oxidation. Lubricating properties of the prepared oils and - in turn - greases will be tested using standardised procedures for determination of AW/EP properties and fatigue life. For this purpose an analysis of physicochemical and tribological properties of selected vegetable oils was carried out. The base oils is characterized by beneficial set of physical, chemical, tribological parameters and biodegradation degree.

The useful lifetime of vegetable oils and greases is determined largely by their ability to resist oxidation. Different Scanning Calorimetry – DSC provides a rapid method for predicting the oxidative stability of these lubricating. DSC is a viable alternative to oven aging because requires small samples and evaluation are complete in several hours or less.

Vegetable oils rapeseed with antioxidant were oxidized in the cell of a differential scanning calorimeter (DSC). From the resulting DSC exotherm the characteristic parameters were extracted and used for assessment of the oxidative stabilities of the oils (Fig.1).

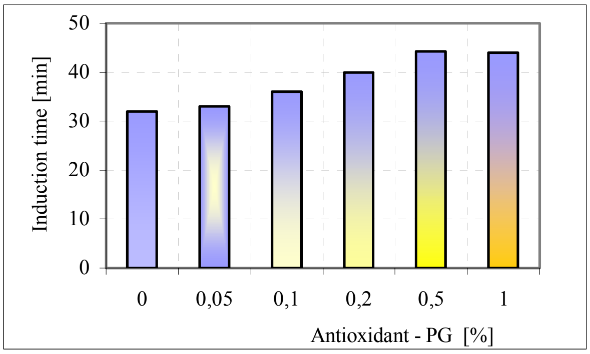

Fig. 1. The effect of antioxidant concentration on the oxidation stability of rapeseed oil.

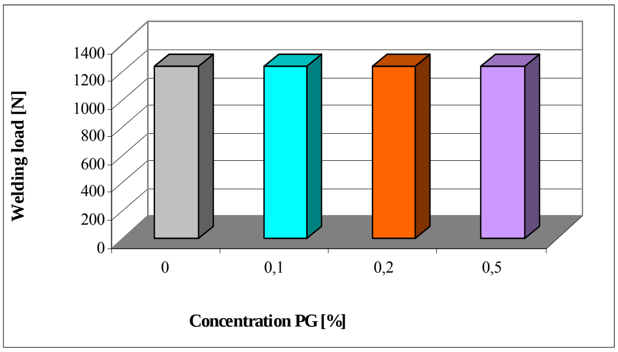

Fig. 2. Welding load of model lubricating with PG.

Lubricating properties of base oil were assessed on the basis of the normalised four-ball test with turns of a movable ball equal to 1500 rpm. On the basis of executed experiments the value of welding load P_z (Fig.2) and limiting load of wear $G_{oz,}$ were assigned. They were assessed on the basis of an hour's test with the load 392,4 N (Fig. 3, 4). Measurement of lubricating properties was broadening by results of investigations of wear indexes with a linearly increasing load obtained on the modified Four-Ball–Machine.

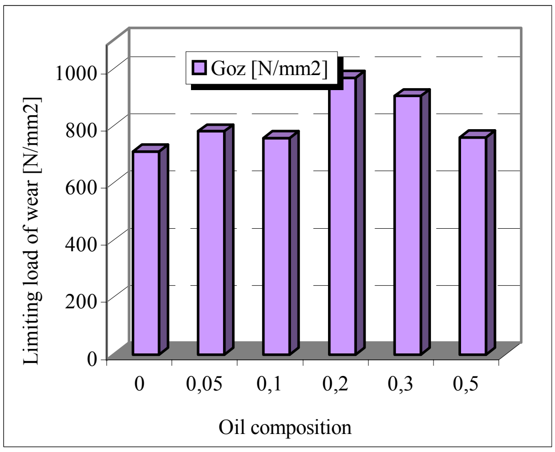

Fig. 3. Anti-wear properties of base oils after wear test.

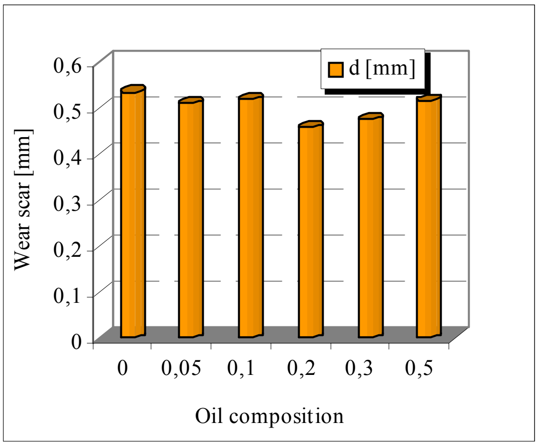

Fig. 4. Wear scar of base oils.

Obtained results, presented in Fig. 3 and Fig. 4, shows that antiwear properties depend on oil composition. In all these cases, the use of the antioxidant resulted in the better couple protection. Composition with 0,2% PG (A3) shows the best wear protection.

On the ground of the results obtained, a model base oil showing the best oxidation resistance and the best tribological properties will be selected. This oil will be the dispersive phase for formulation of an ecological grease.

The chosen rapeseed oil and his compositions with the addition PG one used as the oil - phase at working out of the grease.

The oil composition with the best thermal stability and with favorable tribological properties will be use as a dispersing agent in this grease. At this point of schedule on the basis of the vegetable oil with antioxidant PG at level 0,1÷0,2% w/w developed greases. The grease consists of modified vegetable oil as base fluid, Lithium Stearate as thickener and polymer additive.

The estimation the propriety the physics-chemical the grease one executed on the ground the measurement parameters characterizing the structural persistence and resistances on the process of the oxygenation. The method DSC became put-upon to the estimation of the dynamics of the course of the process oxidized of the grease during the oxidation in the atmosphere of the oxidative gas. These research let on the delimitation of oxidation stability of received vegetable greases.

The vegetable grease (rapeseed) were oxidized in the cell of a differential scanning calorimeter (DSC). The useful lifetime of greases are determined largely by their ability to resist oxidation. Different Scanning Calorimetry – DSC provides a rapid method for predicting the oxidative stability of these lubricating. The effective of the antioxidants in grease was investigated. From the resulting DSC exotherm the characteristic parameters were extracted and used for assessment of the oxidative stabilities of the inhibited greases. The results of the trials are shown in Fig. 5. The Fig. 5. represents the comparison of the oxidation stability of the vegetable grease with the non-toxic grease PB of the white oil.

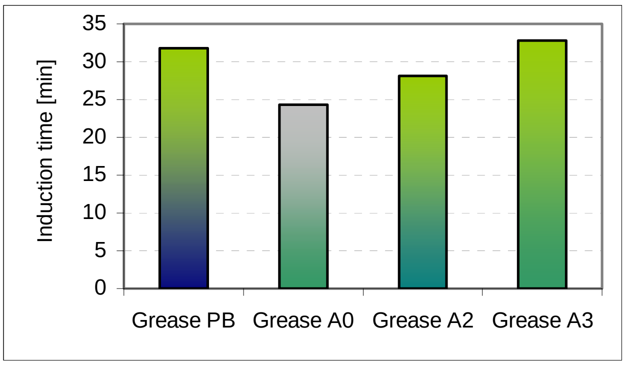

Fig. 5. The oxidation stability of mineral and rapeseed greases.

The vegetable grease with the addition 0,2%PG shows the comparable oxidation resistance to the mineral grease. Tribological test were carried out using four-ball extreme-pressure tester. The influence of antioxidant concentration on the antiwear and antiseizure greases properties was determined using values of PN-76/CC-04147 standard parameters. The elaborated greases (A 0 – non-modified, A2, A3 – modified) underwent standard investigations, in particular assessment of their lubricating properties (fig. 6, 7).The greases are based on non-toxic components and vegetable base oil. From tribological point of view the developed grease meets requirements for typical bearing greases.

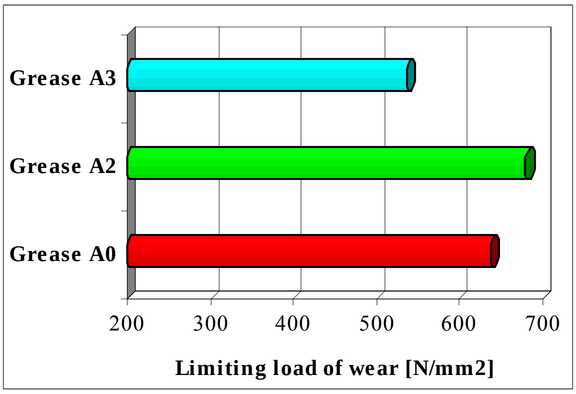

Fig. 6. Anti-wear properties of greases after wear test.

Fig. 7. Wear scar diameter of greases.

Here presents the results of research of vegetable grease influence on the fatigue live. An influence of the oils and the elaborated grease on the fatigue life (resistance to pitting) were assessed in a modified four-ball tester (rolling contact) according to IP 300/82 procedure. The tribological tests were carried out using T-03 four-ball tester under high load conditions. It has been stated that:

1. The L_{10} life of tribological coups lubricated with non-toxic greases and typical bearing grease,
2. The rolling-contact L_{50} life of non-toxic greases and typical bearing grease.

In the second group of lubricants three greases have been examined vegetable grease (grease A0), mineral grease (grease PB), typical bearing grease.

Here the results of the surface fatigue life experiments are given. The tests have been performed, under conditions stated above, on the T-03 Four-Ball Pitting Tester of the ITeE.

The quantiles L_{10} and L_{50} of the fatigue life have been shown in Figures 7 and 8.

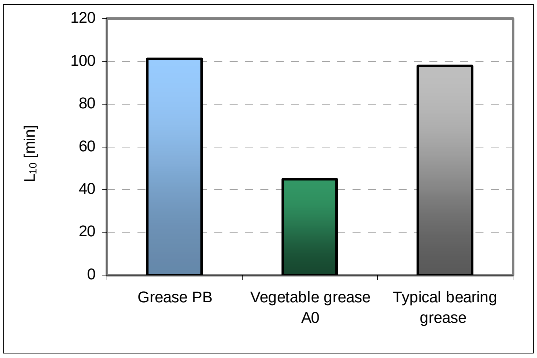

Fig. 7. The L_{10} quantile of the pitting fatigue life for the greases /PB, A0, typical bearing/ tested

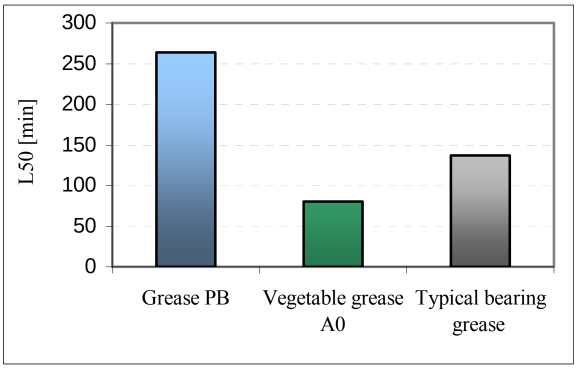

Fig. 8. The L_{50} quantile of the pitting fatigue life for the greases /PB, A0, typical bearing/ tested

From the above given figures it is evident that the white oil based grease PB is, in respect to their anti-pitting action, very similar to the successfully used commercial ball-bearing greases. When taking into account the median (L_{50}) of the fatigue life, the grease PB is better than the verified in the engineering practice bearing grease and vegetable grease. The quantiles (L_{10} and L_{50}) of the pitting fatigue life for the vegetable grease A0 are worse than the verified in the non-toxic grease PB and typical bearing grease. The antioxidant not influence on the anti-pitting properties vegetable greases. Research of the influence of the tribological additives of vegetable greases on the surface fatigue life of the rolling bearing will be continued.

Ecological character of the vegetable grease will be proved during complex research on toxicological and biodegradation degree. The biodegradability was marked according to the test CEC L-33-T-82 in which qualified is the fall of the concentration of hydrocarbons in the sample containing investigated matter in the mineral basis grafted microorganisms originating from sewage of the refinery after the mechanical brush-up. Toxicity of the grease was checked according to the rules of ecological evaluation, i.e. on the base of investigation of its action on mammals, fish and microorganisms, and on the ground of chemical analyses.

The results of the biodegradability have been shown in table 1.

Table 1. Comparison of biodegradability of used dispersion phases and greases tested according to CEC-L-33 T-82 standard.

Kind of the dispersion phase and lubricating grease	Biodegradability [%]	Category of biodegradability according to the three-stage scale
BASE OIL – VEGETABLE		
Rapeseed oil	94	easily biodegradable
VEGETABLE GREASES		
Grease I (A0)	87	easily biodegradable
Grease II (A3)	89	easily biodegradable

Toxicity of the grease was checked according to the rules of ecological evaluation, i.e. on the base of investigation of its action on mammals, fish and microorganisms, and on the ground of chemical analyses (Table 2).

Table 2. Toxicity of the grease – Grease II (A3).

The kind of the test	The kind of test - organisms	*The coefficient of the estimation*
The enzymes test	With relation to of microorganisms *Lumistox-Microtox* with luminescence bacteria *Vibro fisheri*	$LC(EC_{50}) = 39{,}9$[mg/l]
The test with young forms of invertebrata	With relation to of invertebrata Toxikit with invertebrata *Thamnocephalus platyurus*	$LC_{50}/_{24h} > 500$ [mg/l]
The test with relation to of fish	The test with fish *Lebistes reticulatus*	$LC_{50}/_{96h} = 160{,}4$ [mg/l]

According to criteria of the toxicity USEPA (Environmental Protection Agency - USA) one ascertained that worked out grease substances belong to relationships about the not large harmfulness for water organisms.

Conclusion

The basic objective of the carried out experiments was to elaborate grease with a higher degree of biodegradation than the grease made on the base of the mineral oil.

Elaboration of new generation lubricants with elimination or considerable reduction of contents of toxic chemical compounds was the first stage of undertaken work. Achievement of this aim was possible thanks to use of the non-toxic oil base, ecologically safe thickeners as well as modifiers improving useful properties.

This grease is based on non-toxic components and vegetable base oil. The useful lifetime of vegetable oils are determined largely by their ability to resist oxidation. Vegetable oils were oxidized in the cell of a differential scanning calorimeter (DSC). The insufficient oxidation stability of vegetable oils demands introductions antioxidants.

The non-toxic grease is characterized by beneficial set of tribological and ecological parameters. It has high useful standard and it is not hazard for ecosystem therefore this grease can be applied in food industry and in other branches of industry too.

Because of elaborated lubricants' destination for application in the food industry and possibility of the direct contact with food, the used dispersion phases and greases underwent ecological assessment. Then their biodegradability was assigned.

The final effect of the work execution is ecological, both non-toxic and biodegrading greases, meeting requirements concerning greases meant for use in friction pairs, low and high loaded and at the same time not threatening the ecosystem, even when products of wear will get to the environment.

Publications were project results are reported

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7. Report for the Management Committee of the COST 532 project, May 2004.
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10. DRABIK, J., PAWELEC, E., 2005: Oxidation stability of non-toxic greases. European Conference on Calorimetry and Thermal Analysis for Environment ECCTAE, 6-11 September 2005.

11. Report for the Management Committee of the COST 532 project, January 2005.
12. Report for the Management Committee of the COST 532 project, September 2005.
13. DRABIK, J., PAWELEC, E., 2005: Metody oceny środków smarowych w aspekcie wymagań ekologicznych. Konferencja Pojazd a Środowisko, pp. 59-65. (In Polish).
14. DRABIK, J., PAWELEC, E., 2005: Tribological characteristics of the non-toxic greases for the food industry. Biodegradable Lubricants, VIT, pp. III 5 – III 7.
15. Final Report for the Polish Committee for Scientific Research, December 2005. (In Polish).

Planned or achieved industrial improvements in commercial use

As a result of this project, fully ecological greases are expected to be formulated. These products can be substituted for commercial bearing greases based on mineral ingredients.

The application of the developed ecological greases, planned in food industry, industry agriculture and forestry.

CH5 - INTERACTIONS BETWEEN HARD COATINGS AND LUBRICANTS

Co-ordinator and partners

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Project status and schedule

Starting and ending dates 26.6.2003 – 26.6.2006

Project aims

Aim of this project is to define relationships between surface properties (i.e. surface tension, surface free energy, contact angle) and tribological properties of the lubricated hard coated contact. With obtained results and knowledge the most suitable modification of the hard coating, leading to improved tribological properties and adsorption, and without hampering mechanical properties of the coating, should be determined.

Project results

Experimental

As a reference material 100Cr6 steel was selected in this investigation, with "pure" DLC coating (a-C:H) and W doped DLC coating selected as representative coatings, which are regularly used in real applications. Liquid phase was paraffinic mineral oil and vegetable based sunflower oil, used as base and EP/AW additivated oil, respectively.

Surface tension, surface free energy and contact angle measurements were performed by Wilhelmy plate method, which is based on a pulling force measurement (Fig. 1).

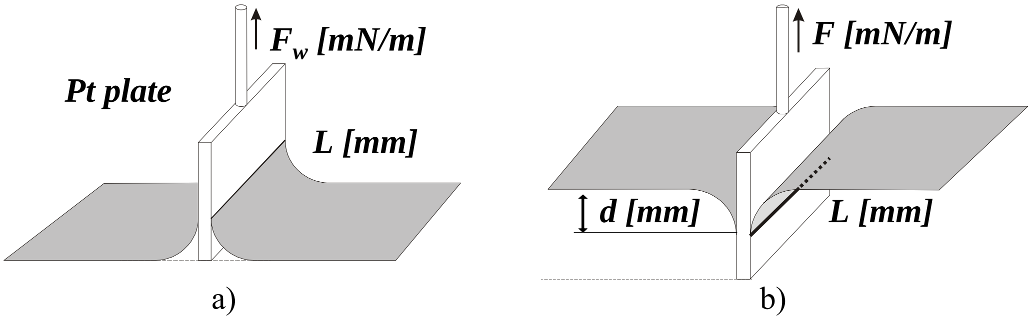


Fig. 1. Wilhelmy plate method; (a) surface tension determination and (b) contact angle measurement.

Tribological evaluation of investigated solid/liquid systems was performed in a load-scanner, where two crossed cylinders (10mm in diameter) are forced to slide against each other in such a way that normal load is gradually increased during forward stroke and correspondingly decreased during reversed stroke. Due to a specific configuration each point along the contact path corresponds to a specific contact pressure. For each system the same contact surfaces were used for both contacting partners (both coated or both uncoated). Boundary lubricated tests were performed at a sliding speed of 0.1 m/s, contact pressure in the range of 1.5 - 3 GPa and for a sliding distance of 1m. Additionally, influence of additive type and concentration, as well as contact conditions on the tribological behaviour of boundary lubricated DLC coatings was determined on a high frequency SRV test rig. The upper, oscillating specimens were standard 10 mm diameter steel ball bearings, which were loaded against coated stationary discs. Tests were performed in the contact pressure range of 1.0 to 3.0 GPa, sliding speed range of 0.01 to 0.15 m/s and testing temperature range of 20 to 200°C. In SRV tests pure poly-alpha-olefin oil (PAO) was used as a base fluid, which was consequently mixed with a sulfurized olefin polysulfide EP, or diamine monohexyl phosphate and amine dihexyl phosphate mixed AW additive, using additive concentrations between 0.01 to 10%.

Results

Surface tension of liquid phase

Surface tensions (σ_L) of liquid phases investigated; base sunflower oil (S), sunflower oil with EP/AW additive (S+A), base mineral oil (M) and mineral oil with EP/AW additive (M+A), are summarized in Fig. 2. More important then absolute value of the surface tension are its polar and disperse components or shares, determined by the use of PTFE plate. Base sunflower oil displayed surface tension of 33 mN/m, with 6% polar share. On the other hand, paraffinic mineral oil has completely dispersed nature, as shown in Fig. 2. In agreement with literature, addition of additive increased polar share of surface tension for both base oils, increasing polar share for sunflower oil to 22% and for mineral oil to 7.5% (Fig. 2).

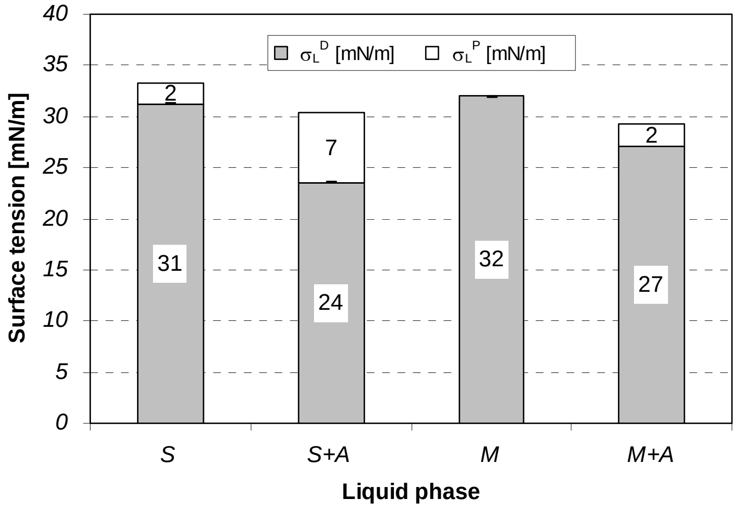


Fig. 2. Surface tension of a liquid phase.

<u>Surface energy of solid phase</u>

Comparison of coated and uncoated surfaces showed similar surface energies of about 30 mN/m for all surfaces investigated. However, uncoated steel surface displayed only 7% polar share, as compared with non-modified DLC coating with 35% and modified W-DLC coating with over 60% polar share of the surface energy (Fig. 3). In the case of uncoated steel surface some disagreements with literature occurred when looking at the polar share of the surface energy. However, present investigation indicated that the type of steel surface preparation and cleaning procedure has an influence on the surface energy measurement results and should be investigated further.

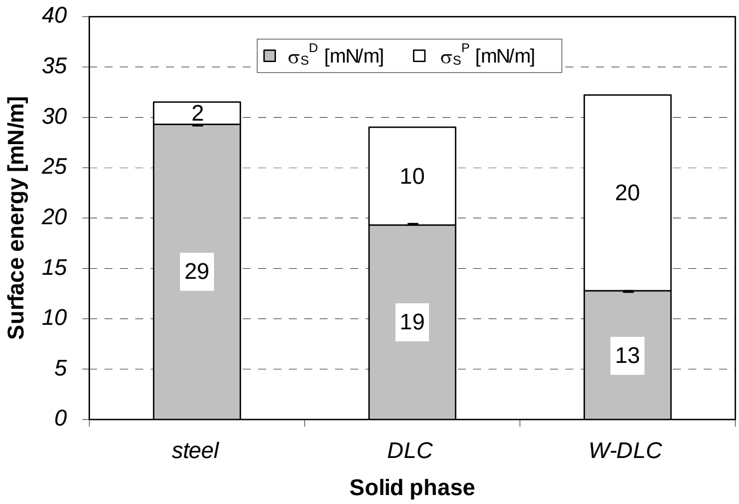


Fig. 3. Surface energy of a solid phase.

<u>Contact angle</u>

Figure 4 shows contact angles between solid and liquid phases included in the investigation, also determined with the use of Wilhelmy plate method. The lowest contact angles, indicating the best wetability, were obtained in the case of doped DLC coating (W-DLC). Contact angles between sunflower oil and W-DLC coating were ~20° and for paraffinic mineral oil ~25°. Analysis with pure oil and oil with additives did not revealed any significant difference in contact angles, when using W-DLC coating, as shown in Fig. 4. Uncoated steel surface displayed higher contact angles values (~28°). However, large standard deviations of the measured results prevented comparison between different oils. In agreement with surface energy measurements (Fig. 3), W-DLC coating with high polar share of surface energy displayed better wetability than DLC coated or uncoated steel surfaces. Furthermore, for W-DLC coated and uncoated steel surfaces use of sunflower oil with higher polar share of surface tension resulted in lower contact angles. However, contact angle measurements on non-modified DLC coating did not show any correlation between contact angle and surface energy measurements, with the highest contact angles observed for base sunflower oil and the lowest for oils with additives, as shown in Fig. 4. The reason for that may well lie in the sensitivity of the method and in large scattering of the measured results.

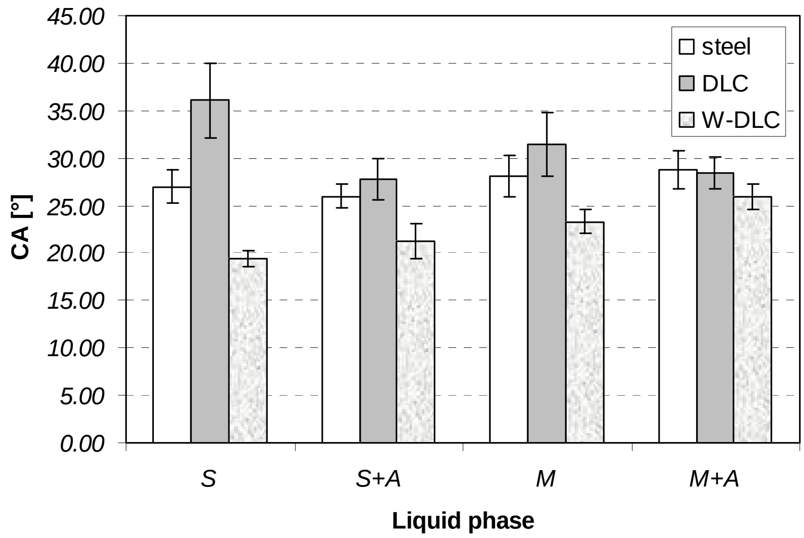


Fig. 4. Contact angles of different liquid phases (oils) in combination with coated and uncoated steel surfaces.

<u>Tribological properties</u>

Load-Scanner test

Steady-state friction values for different surface/lubricant combinations, investigated in Load-scanner are shown in Fig. 5. For all conditions pure DLC coatings showed the lowest friction, with the DLC/mineral oil combination showing 10-20% lower friction as compared to DLC/sunflower oil combination. This finding was true for base oils as well as for oils with the addition of EP/AW additive. On the contrary, use of sunflower oil in combination with uncoated steel surfaces or W-DLC coated ones yield lower friction then mineral oil. While W-DLC coated and uncoated steel surfaces showed similar friction under boundary lubrication when lubricated with mineral oil, being 30-50% higher as compared to non-modified DLC coating, steel surfaces showed better friction properties for sunflower oil (Fig. 5). For all surfaces investigated addition of EP/AW additive resulted in steady-state friction increase.

EDS analysis of worn surfaces did not show any tribofilms formed on coated surfaces (DLC or W-DLC). However, in the case of uncoated steel surfaces P-based tribofilms were detected on contact surface, as indicated by P-peak in EDS spectra.

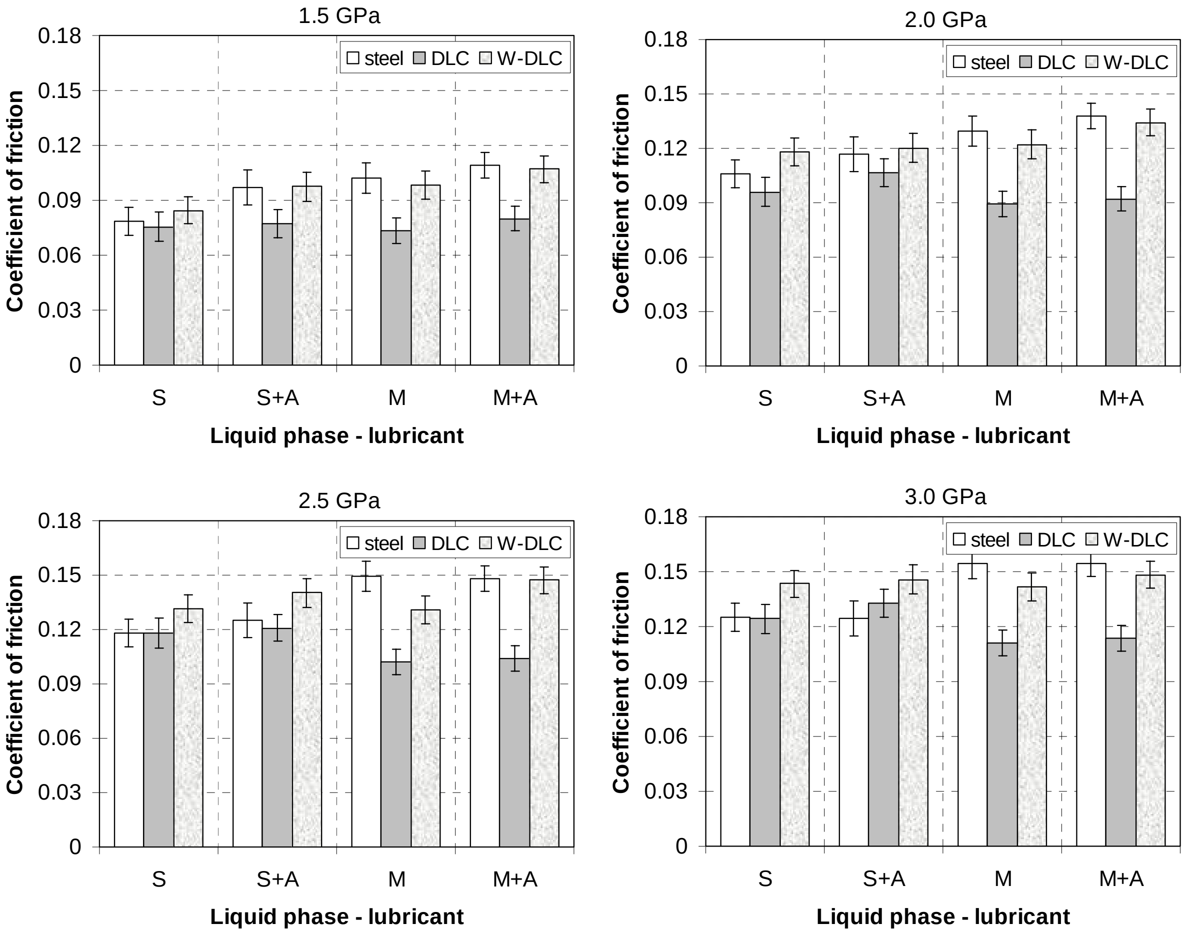


Fig. 5. Steady-state friction recorded in Load-Scanner at 0.1 m/s sliding speed.

Influence of oil-additive type and concentration

Influence of oil-additive type and concentration on tribological behaviour of DLC coated surfaces under boundary lubrication was determined on SRV test rig, with standard 10 mm diameter steel ball loaded against DLC coated stationary discs. Tests were performed at a sliding speed of 0.02 m/s, maximum Hertzian contact pressure of 1.5 GPa and operating temperature of 50°C.

a) Coefficient of friction

Figure 6 shows friction curves for W-DLC coatings running against uncoated steel ball in PAO oil with different EP additive concentrations. In the case of pure PAO oil and for very low EP additive concentration, the coefficient of friction was in the range between 0.12 and 0.15. Increasing the amount of EP additive to about 0.1% resulted in reduction of friction, with the coefficient of friction dropping to a value of 0.12. After approximately 15,000 cycles the coefficient of friction started to rise again, shortly reaching values observed for pure PAO oil (~0.13). Similar reductions in friction in the early stages of sliding were observed for 0.5% and 1% EP additive concentrations. However, after the initial 10,000 – 15,000 cycles the coefficient of friction was further reduced, attaining a value of ~0.08. Concentrations of 2.5% and 5% gave the smoothest and lowest friction coefficient of about 0.08, obtained from the very begging of sliding and maintained for up to $6 \cdot 10^6$ cycles. Increasing the amount of EP additive over 5% did not result in any further reduction of friction. On the contrary, 10% of EP additive caused an increase in friction, with the coefficient of friction reaching a steady-state value of about 0.11, as shown in Fig. 6. The influence of the AW additive on frictional behaviour of W-DLC coatings running against steel was not so pronounced as for the EP additive. AW additive concentrations below 0.5% gave the same friction of about 0.13 as pure PAO oil. Increasing the AW additive concentration over 0.5% led to increased friction, with the coefficient of friction being in the range between 0.15 and 0.17. Similar frictional behaviour was observed when both contact surfaces were coated (W-DLC/W-DLC). However, even at 2.5% and 5% EP additive concentrations a certain number of cycles was needed before low friction behaviour with a coefficient of friction as low as 0.08 was reached. In the case of pure DLC coatings additive type and concentration had only minor effect with the steady-state friction being in the range of 0.13 - 0.15.

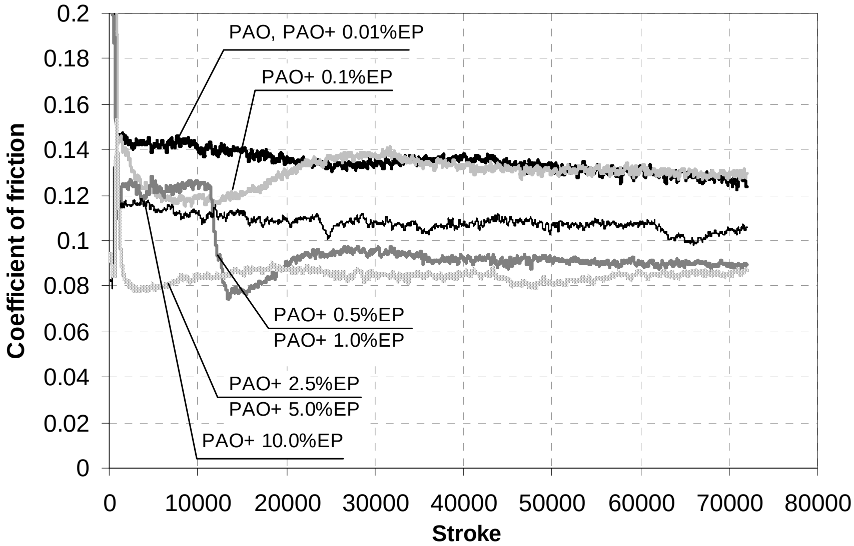


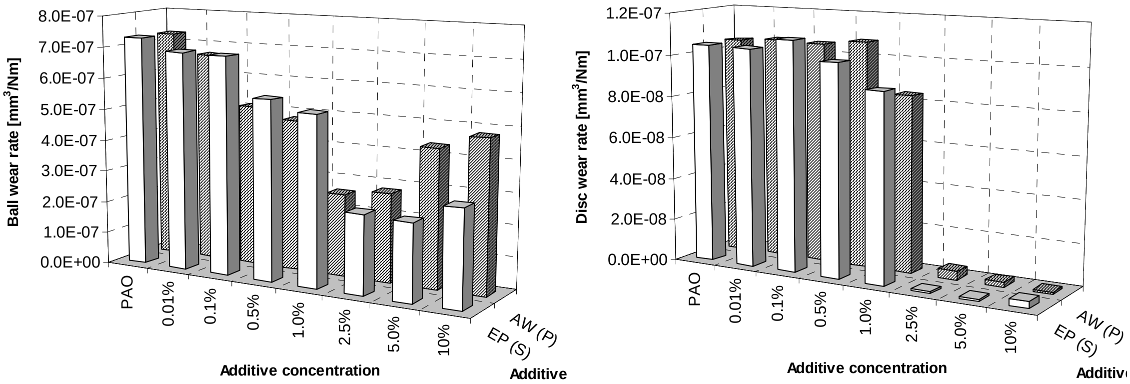
Fig. 6. Coefficient of friction curves for the steel/W-DLC combination running in EP additivated PAO oil.

b) Wear

Average wear rates for uncoated steel balls and W-DLC coated discs after 72,000 sliding cycles under boundary lubrication, using different EP and AW additive concentrations are shown in Fig. 7. In the case of the EP additive, an increase in additive concentration resulted in reduced ball wear, reducing its wear rate from ~$7.3 \cdot 10^{-7}$ mm^3/Nm for PAO oil to ~$5.3 \cdot 10^{-7}$ mm^3/Nm when using EP additive concentration of 1%. Higher concentrations (2.5% – 5%) gave more pronounced reduction, with the ball wear rate being reduced even down to ~$2.4 \cdot 10^{-7}$ mm^3/Nm. However, as in the case of the coefficient of friction, too high EP additive concentrations showed increased wear rates, as shown in Fig. 7a.

Similar wear behaviour was observed for AW additive, with the lowest ball wear rate of about $2.8 \cdot 10^{-7}$ mm^3/Nm obtained at 2.5% AW additive concentration. Further increase in AW additive concentration also led to increased ball wear rates, reaching values of ~$5.0 \cdot 10^{-7}$ mm^3/Nm (Fig. 7a). In the case of W-DLC coated discs both additives had the same influence on the disc wear rate. For additive concentrations from 0 to 1% the disc wear rate was ~$1.0 \cdot 10^{-7}$ mm^3/Nm, with the coating being removed from the contact surface. However, when using additive concentrations above 1%, almost no measurable wear of the disc could be detected, as shown in Fig. 7b.

Comparison of uncoated steel surfaces with pure and doped DLC coatings showed similar wear rates for the case of oil with the AW additive. Furthermore, for the steel/DLC combination coated disc (~$1.0 \cdot 10^{-8}$ mm^3/Nm) as well as steel ball wear rates (~$3.2 \cdot 10^{-7}$ mm^3/Nm) were more or less independent on the type and concentration of the additive used and generally lower then for steel/W-DLC combination.



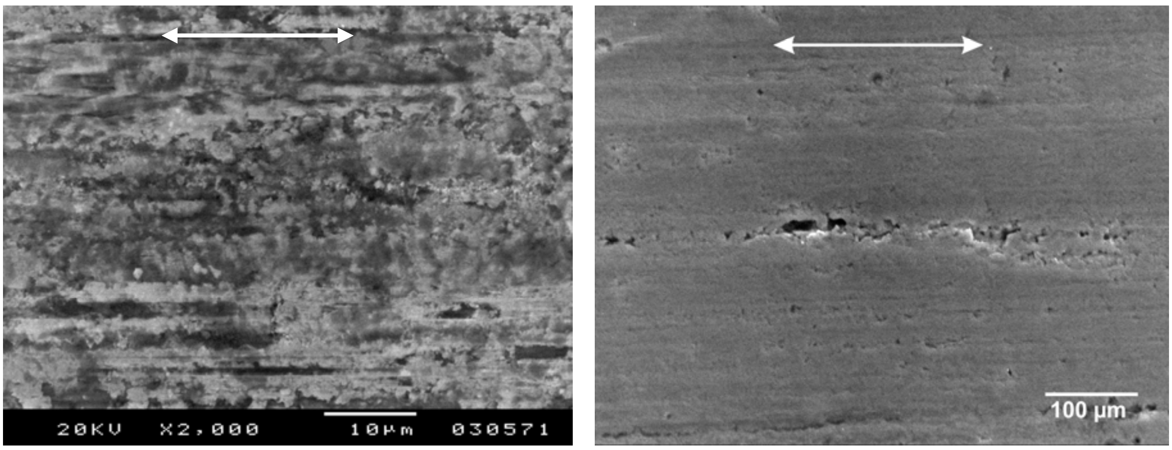
a) b)

Fig. 7. Wear rates vs. additive concentration for (a) steel ball and (b) W-DLC coated disc after 72,000 sliding cycles under boundary lubrication.

c) Surface analysis

For both DLC coatings no reaction products or tribofilms were detected on the coating surface. However, tribofilms formed on the steel counter-surface or on the exposed steel substrate were additive type and concentration dependent. Reciprocating sliding in pure oil or oil with low EP (<0.1%) and AW additive (<1.0%) concentration resulted in transfer of coating material from the coated disc to the steel ball. In the case of AW additive concentrations above 1.0%, the AW additive started to react with the uncoated or revealed steel surface, forming phosphorus-rich tribofilms typical for uncoated steel surfaces.

In the case of EP additive and W-DLC coating transfer of coating material (WC) is followed by formation of a new type of tribofilm on uncoated or revealed steel surfaces, consisting of transferred coating material (WC) and reaction products from the S-based additive. For low EP additive concentrations (≤1.0%) tribofilm of about 15-20 nm was found to consist mostly of transferred WC, with sulphur compounds being formed locally at the surface (Fig. 8a). At higher EP additive concentrations reactive tribofilm became thicker (up to 300 nm) and denser, with the XPS analysis clearly indicating the presence of WS_2 compounds (Fig. 8b).



(a) (b)

Fig. 8. SEM micrographs of steel ball after 10,000 sliding cycles against a W-DLC coated disc in (a) 0.5% and (b) 2.5% EP additive concentration

Influence of contact conditions

a) Contact pressure

Influence of contact pressure on coefficient of friction and wear rate for steel/W-DLC material combination is shown in Fig. 9. In the case of a contact pressure of 1 GPa drop in friction during first 5,000 cycles was followed by an increase in the coefficient of friction, which reached steady-state value of ~0.18 after about 15,000 cycles (Fig. 9a). Ball and disc wear rate after 36,000 sliding cycles was in the range of $3 \cdot 10^{-7}$ mm^3/Nm, with the uncoated steel ball showing one order of magnitude higher wear than coated disc. Increase in contact pressure led to change in friction behaviour and increased wear rate, as shown in Fig. 9. For a contact pressure of 1.5 GPa initial friction of about 0.13 was followed by additional drop to ~0.1, similarly as caused by an increase in EP additive concentration (Fig. 6). Further increase in contact pressure did not caused considerable change in tribological behaviour, but in general, higher contact pressures give higher wear rates and lower steady-state coefficient of friction, which is obtained in shorter time.

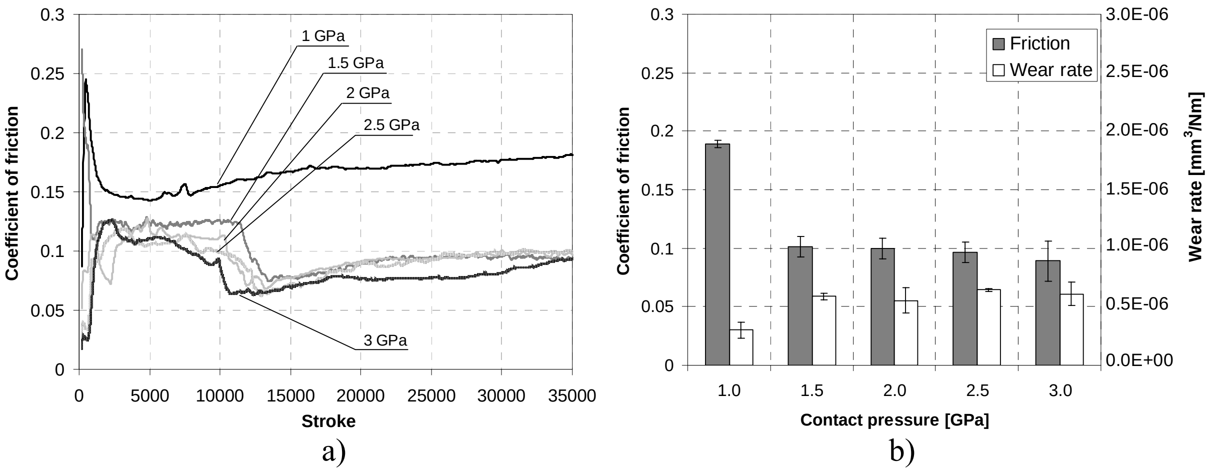


Fig. 9. Influence of contact pressure on (a) friction behaviour, and (b) steady-state friction and wear rate of steel/W-DLC combination (PAO+1%EP, v_s = 0.02 m/s, T = 50°C).

b) Sliding speed

In contrast to contact pressure, increase in sliding speed from 0.01 to 0.15 m/s leads to increased steady-state friction but reduced wear rates after two hours of sliding. Furthermore, with increased sliding speed number of cycles needed for the coefficient of friction to reach low level (~0.1) was increased from approx. 7,000 cycles for sliding speed of 0.01 m/s to more than 20,000 for 0.1 m/s, as shown in Fig. 10. And while sliding speeds of up to 0.1 m/s still show distinctive drop in friction and presence of WS_2-type tribofilm this was not the case for sliding speed of 0.15 m/s. In the case of 0.15 m/s sliding speed gradual decrease toward steady-state friction of about 0.12 was observed during first 200,000 – 300,000 cycles and only transferred coating material (WC) was detected at the steel ball surface.

c) Operating temperature

For pure PAO oil coefficient of friction of ~0.13 and ball and disc wear rate of ~$6 \cdot 10^{-7}$ mm^3/Nm were independent on oil temperature up to 200°C, as shown in Fig. 11a. At 200°C drop in steady-state friction to 0.1 occurred, which is probably caused by coating decomposition. However, when using PAO oil with 1% EP additive increase in temperature had similar effect on friction as increase in EP additive concentration, giving shorter response time in terms of friction reduction and up to 40% lower friction (Fig. 11b).

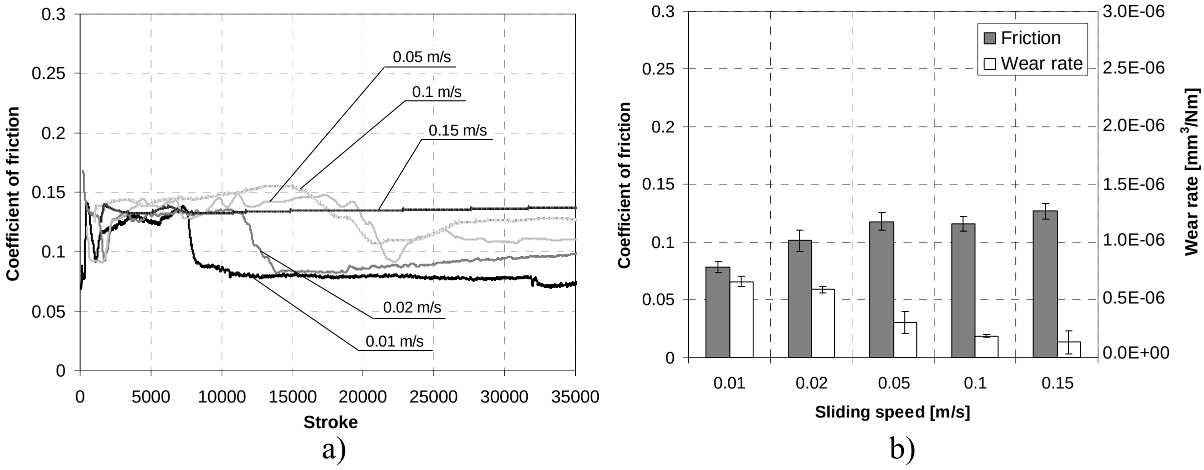


Fig. 10. Influence of sliding speed on (a) friction behaviour, and (b) steady-state friction and wear rate of steel/W-DLC combination (PAO+1%EP, p_H = 1.5 GPa, T = 50°C).

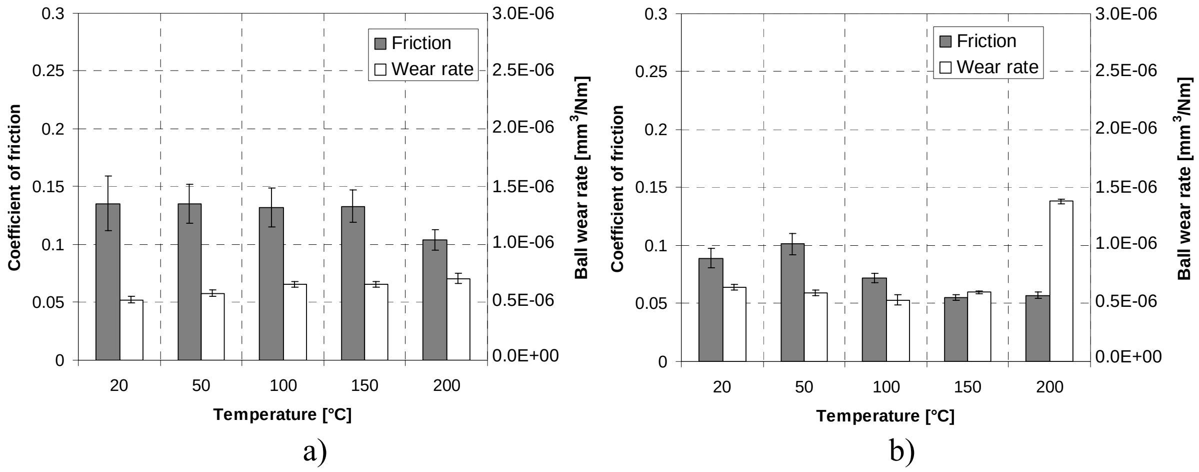


Fig. 11. Influence of test temperature on tribological behaviour of steel/W-DLC material combination running in (a) pure PAO and (b) in PAO with 1%EP additive concentration (p_H = 1.5 GPa, v_s = 0.02 m/s).

EDS analysis of contact surfaces exposed to higher contact pressures and elevated temperatures showed similar tribofilms on steel ball as observed for room temperature, at the same time displaying higher sulphur content, see Fig. 12. Increase in contact pressure and/or operating temperature increases activation energy thus accelerating W-S reaction kinetics, which results in faster and more pronounced response in terms of friction reduction.

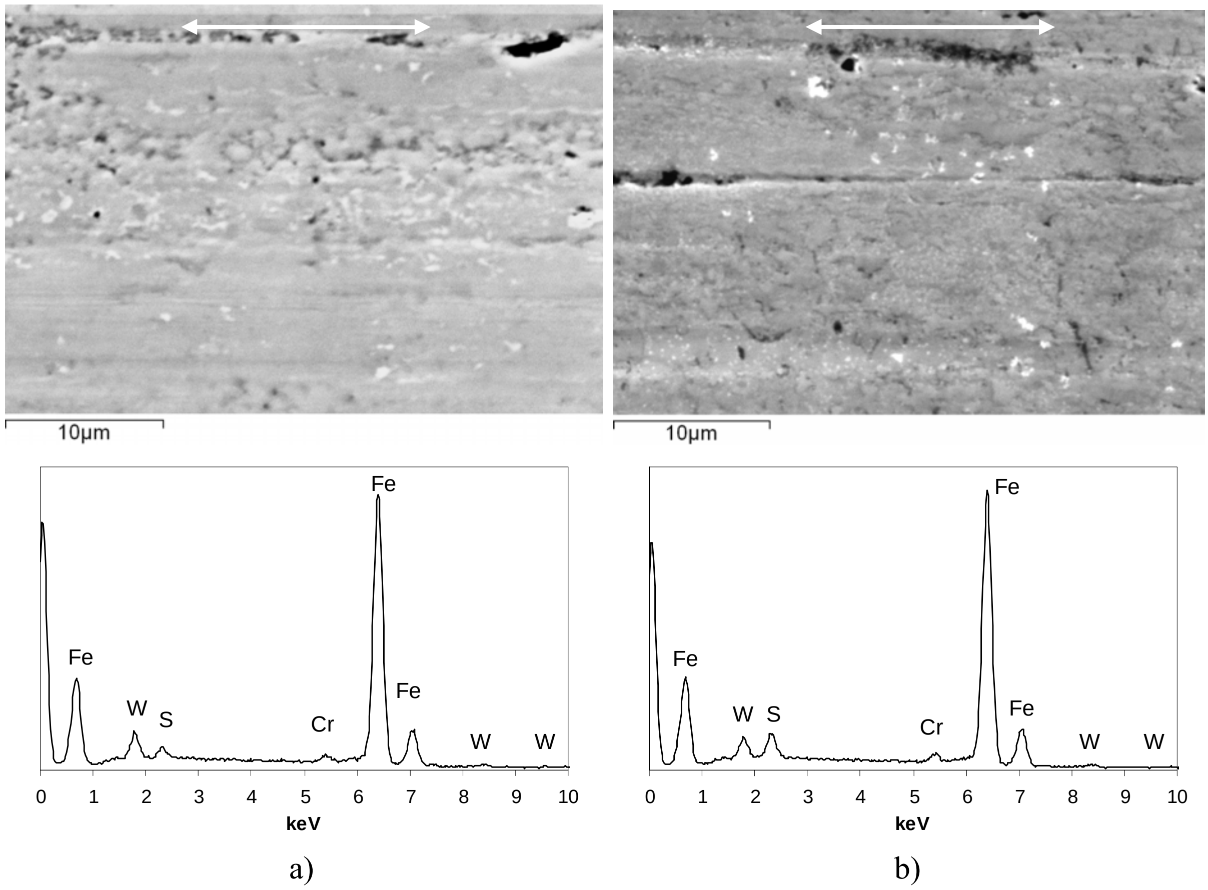


Fig. 12. SEM micrographs and corresponding EDS specters of steel ball tested against W-DLC coating at (a) 20°C and (b) 150°C (PAO+1%EP, p_H = 1.5 GPa, v_s = 0.02 m/s).

Summary

Current results does not show any direct correlation between surface energy of solid phase, surface tension of liquid phase, their polar shares and wettability of the surface, and tribological performance of lubricated surface. Change in surface morphology undoubtly leads to change in surface energy and its polar share, which in combination with proper lubricant can improve solid surface wettability, but these are not the only factors influencing its tribological performance. However, results of the investigation indicate that surface properties of solid and liquid phase (surface energy, surface tension and especially their polar shares) influences solid surface wettability and its tribological performance. Therefore, further tribological investigations on molecular level are needed, which together with investigations in the field of surface energies will be crucial for the successful application of hard coatings in machine component applications.

Regarding influence of oil-additive type and concentration investigation results show that in the case of pure and low additivated PAO oil the frictional behaviour of boundary lubricated DLC coatings is determined by transfer of coating material from the coated surface to the steel counter-surface or exposed steel substrate. In the presence of S-based EP additives tungsten transferred from the W-DLC coating starts to react with the additive, thus forming low-friction tribofilms composed of WS_2 nanocrystals.

Contact pressure and sliding speed have the opposite effect on the tribological behaviour of W-DLC coatings when running in oil with EP additive. Higher contact pressures and/or higher temperatures, which correspond to higher energy input and thus higher potential for WS_2-tribofilm formation, accelerate the process of friction reduction and result in lower friction. On the other hand, increase in sliding speed has the opposite effect due to more effective removal of generated frictional heat.

Project co-operation

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Meetings: University of Maribor (LCPP) – 10.12.2003 & 22.4.2004
Centre for Tribology and Technical Diagnostics – 26.6.2004
OLMA – 15.6.2005
Balzers – 1.-2.9.2005
Balzers – 6.2.2006
Centre for Tribology and Technical Diagnostics – 29.5.2006
Balzers – 7.3.2007

STSM Visits: Uppsala University, Sweden – 20.-30.1.2004

Presentations: Smart surfaces in tribology, September 2003, Switzerland
COST 532 Joint Working Group Meeting, February 2004, Brussels
COST 532 Joint Working Group Meeting, October 2004, Ghent
1st Balzers surface technology forum in Asia, March, 2005, Kanagawa, Japan.
ICMCTF 2005, May 2005, San Diego, USA
International Tribology Conference 2005, Kobe, Japan
COST 532 Joint Working Group Meeting, October 2005, Porto
COST 532 Working Group Meeting, April 2006, Dubrovnik
ICMCTF 2006, May 2006, San Diego, USA
International Forum on Advanced Material Science and Technology, Xiangtan,China, June 2006
COST 532 Joint Working Group Meeting, November 2006, Uppsala
SKF Research Centre, February 2007, Amsterdam

Planned or achieved industrial improvements in commercial use

Optimized DLC coating for common-rail diesel injection systems. Coating optimized in terms of composition, multilayer structure and thickness

Publications where project results are reported

1. B. Podgornik, J. Vižintin, S. Strnad, K. Stana-Kleinschek, Correlation between surface energy and tribological properties of boundary lubricated surfaces. Book of abstracts of a european conference on recent developments in additive technology and surface coating for the reduction of wear and friction on moving surfaces: Smart surfaces in tribology - advanced additives and structured coatings, Zurich, Switzerland, September 10-12, 2003, p. 30.
2. B. Podgornik, J. Vižintin, S. Strnad, K. Stana-Kleinschek, Influence of surface energy on the interactions between hard coatings and lubricants. Proceedings: COST 532 conference: triboscience and tribotechnology : superior friction and wear control in engines and transmissions. Ghent, Belgium, October 18-19, 2004, 52-61.

3. B. Podgornik, J. Vižintin, S. Jacobson. S. Hogmark, Tribological behaviour of WC/C coatings operating under different lubrication regimes. Surface and Coatings Technology, Vol. 177/178 (2004) 558-565.
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5. B. Podgornik, D. Hren, J. Vižintin. Low-friction behaviour of boundary-lubricated diamond-like carbon coatings containing tungsten. Thin solid films, Vol. 476 (2005) 92-100.
6. B. Podgornik, J. Vižintin, S. Strnad, K. Stana-Kleinschek. Low friction coatings and interaction with lubricant. Recent developments in the field of medical and technological interfaces : cooperation within the EU future region, Friday, Seggau – Graz, Austria, 22 April 2005, p. 7.
7. B. Podgornik. Tribological reactions between oil additives and DLC coatings for automotive applications. Book of abstracts: International Conference on Metallurgical Coatings and Thin Films, San Diego, California, May 02 - 06, 2005, p. 49.
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CH6 - DEVELOPMENT OF ENGINES AND TRANSMISSION SIMULATION TESTS TO CHARACTERIZE FRICTION, WEAR AND CORROSION-WEAR BEHAVIOR

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Project status and schedule

Running with partial funding

Project aims

- To perform comparative tests in different test benches to simulate the behaviour from materials and lubricants in testing conditions that simulate the working conditions of the critical components of the engines and transmissions.
- To develop detection methods to evaluate the friction, wear and wear-corrosion behaviour for the in situ characterization of the degradation in sliding contacts.

- To develop guidelines for test rigs operation suitable for the control of friction, wear and corrosion-wear on engines and transmission systems.

- To develop and validate a prototype test rig for investigation at laboratory scale of friction, wear and corrosion-wear on low friction parts of engines and transmission systems.

Project results

Publication presented in COST 532 in Dubrovnik and Slovenia.

During the last months, we have been involved in four projects that we are developing in the COST 532 frame. One of then, about corrosion – wear behaviour of cast iron and aluminium, was exposed in EUROCORR 06 after been improved by Prof. Celis and by Juan Damborenea from CENIM. Another work carried out in collaboration with Damborenea, was about the development and characterization of nanostructured coatings for improve corrosion and wear resistance of transmission components. Finally, we are working too in the development of high corrosion and wear resistance PVD coatings, for the replacement of hard chromium in engines and blades components for the aeronautical industry. Actually we are starting a new initiative that consists of the participation in a Inter-laboratory experience on electrochemical methods for the characterization of CoCrMo biomedical alloys in simulated body fluids. In this initiative laboratories of all the world take part.

Now on, we summarize the work carried out in each project.

Comparative behaviour of cast iron and aluminum under corrosion-wear conditions

Aluminium and cast iron are materials commonly used in the manufacturing of pump wheels. To compare corrosion and tribocorrosion behaviour of both materials, several tests have been carried out using mechanized discs from a real pump wheel. Corrosion tests were realized in different corrosive environments: H_2SO_4 0.5M, NaCl 3.5%, and NaClO (lye 10%), and the electrochemical techniques used were open circuit potential measurements, electrochemical impedance spectroscopy and linear sweep voltammetry. The experimental procedure followed in corrosion test has consisted in open circuit potential measurements during the first seconds of the immersion time. Next, an electrochemical impedance spectroscopy was recorded at the open circuit potential and finally, potentiodynamic polarization method was carried out to derive the dependence of current on the electrode potential. In tribocorrosion tests, the pump wheel discs were disposed in a "ball on disc" configuration and immersed in NaCl to 5% solution. The counter body was a ceramic ball of silicon nitride and the applied load was set at 5 and 10 N. The experimental procedure followed in this case has consisted in open circuit potential measurements under load and unload conditions and a electrochemical impedance spectroscopy measure before and after the mechanical interaction.

The results obtained show that, in corrosion test, both materials present a bad behaviour in the corrosive environments studied, with high corrosion rates in all the cases. The high roughness of the discs surface makes to suppose the presence of more than one interface material-electrolyte, which influences notably in the whole tribocorrosion process. The best behaviour of both materials takes place in NaCl solution. In alkaline medium, the anodic reaction converts the cast iron surface into a thin protective solid layer of iron (II) hydroxide oxidized by dissolved oxygen to the red-brown hydrated iron (III) oxide.

From the open circuit potential measurements in tribocorrosion tests we could observe clearly the passive and active behaviour of both materials. Whereas the aluminium remains in passive state in absence of mechanical load, cast iron remains in active state during the whole test and dissolves continuously in presence of the chloride media.

The impedance measurements provide information on state of both materials before and after sliding. In the case of aluminium discs after unloading, when the open circuit potential returns close to the initial value, the different size of impedance diagrams reveals that, after friction, the initial surface state was not restored. The passive film in the active area does not have its initial properties. The polarization resistance decreases in both cases after friction, with the consequent increase of corrosion current density and corrosion rates. The results indicate the absorption of reactive species (probably on the wear track area) in case of aluminium and the formation of corrosion products layer (ferrous and ferric hydroxides) on the cast iron surface.

Corrosion and wear behaviour of multilayer Cr/CrN PVD coatings in transmissions components

The new tendencies in industrial PVD coatings to improve its properties, are focused in the development of multilayer and nanostructured coatings. These layers improve the tribological properties of whole coating and enhanced corrosion resistance in comparation with the traditional monolayer coatings. The background of this type of coatings consists of the stacking up of several layers with good individual tribological and mechanical properties, but every individual layer has a thickness that can be from hundreds of nanometers up to only 5-10 nm. The properties of these nanostructured coatings have a great dependence on the thickness modulation of every individual layer. In this work, three Cr/CrN multilayers of different thicknesses of individual layer have been deposited on a typical gear steel substrate, F1272. The corrosion and tribocorrosion behaviour of these coatings have been analyzed in sodium chloride environment. Wear tests have been realized using a reference biolubricant.

The Cr/CrN films were deposited by means of cathodic arc PVD process. Because of the low hardness of the substrate steel, all the samples were nitrurated prior to apply the coatings.

Hardness and roughness of the coatings were evaluated using a Fischer indenter device and a profilometer. To analyze the composition and the depth of the layers, we have used a GD-OES instrument. These analysis revealed a multi layer structure in all the coatings studied.

After characterization step, tribocorrosion and wear tests were carried out in order to compare the wear and corrosion resistance of the coatings developed with the substrate.

Friction and wear tests have been realized in an tribometer SRV under wear and extreme pressure conditions. Oscillatory test with point contact , " ball on disc" was the configuration chosen for these type of tests. For simulate lubricated conditions, we have employed a reference biolubricant.

Tribocorroison tests were performed in sodium chloride 0.05M media, under aerated conditions and at room temperature. The equipment is composed of a tribometer with ball on disc configuration added to a standard electrochemical cell of three electrodes. Open circuit potential and friction coefficient were registered in load and unload periods. Two electrochemical impedance spectroscopies were registered, one just before applying the load and the other one at the end of the tribocorrosion test.

Initial characterization showed the existence of multilayer structure in the three coatings developed. The layers were of alternative chromium and chromium nitride. The bilayer periods measured were of 1100 nm, 270 nm and 110 nm respectively. The highest hardness values were obtained in case of the coating with a bilayer period of 270 nm.

In friction and wear tests, we have noted a repetitive and similar behaviour in all the coatings. The wear tracks are less depth in case of coated surfaces. In the extreme pressure experiments we have not obtained significant differences between the three coatings. All the coated surfaces showed a maximum load resistance of about 400-600 N.

Tribocorrosión results are in agreement with friction and wear tests. The developed coatings improve corrosion and wear substrate resistance. Nevertheless, localized corrosion have been found in all the samples as consequence of coatings porosity and microdefects. The wear track area showed the highest pitts concentration of the whole surface exposed. Substrate dissolution have taken place through the coatings pores inducing the steel substrate degradation in localized areas whereas in substrate sample, we have observed uniform corrosion and a quick metal dissolution

Corrosion studies on PVD coatings for aeronautical applications

One of the greatest environmental problems in the aeronautic world is the current replacement of chromium VI, present in numerous processes including anodizing and hard chromium plating as well as mastic or paint type ingredients used in the aeronautic, military and space industries.

One alternative for the substitution of this material on steel substrates is the application of PVD coatings. PVD coatings can increase the lifetime and steel substrate service quality, due to enhanced tribological and corrosion resistance properties.

In this work, we have study corrosion and wear behaviour of a CrN- PVD coated nickel based alloy (Inconel 738). Electrochemical measurements such as electrochemical impedance spectroscopy and dynamic polarizations have been employed as analysis tools. These techniques can provide a wide information about the effect of the coating structure (pores and defects) on the corrosion processes that take place when the material is in contact with an aggressive environment.

The samples of inconel 738 were coated by means of cathodic arc process. Before experimental tests, the coating were characterized by means of hardness, thickness and roughness measurements. The results of this previous characterization revealed the excellent coating properties. A very thick film of 6.84 um, 1438.47 Kg/mm^2 of hardness and 0.15 um of roughness was obtained.

Corrosion, wear and tribocorrosion tests were carried out in order to compare the behaviour of this coating with the typically employed electroless chromium one.

Corrosion tests were carried out at room temperature under aerated conditions. The electrochemical techniques employed were electrochemical impedance spectroscopy and cyclic polarizations. The electrochemical measurements were carried out in a conventional cell of three electrodes where the reference one was Ag/AgCl (0.207 V vs SHE), the counter one was a platinum wire and the working electrode, the sample under study. The samples were immersed during a total time of two weeks. Impedance diagrams were registered at 24h, 72h, 96h, 7 days and 14 days. Polarization scans were registered after two weeks of immersion time.

Tribocorrosion tests were carried out on each material in a tribometer adapted for this type of measurements, with ball on disc configuration. As counterbody we have employed corundum balls of 3mm of diameter. The applied load was set at 10N and the sliding rate $2.5x10^{-3}$ m/s. Potential and coefficient of friction were measured simultaneously before, during and after the sliding test. Impedance spectroscopy was registered before and after the mechanical interactions to compare the evolution of the surfaces state due to the wear effects. Before measurements start, the samples remained immersed in the solution for 20 hours to reach a stable open circuit potential.

The results of this study show that, corrosion tests carried out in saline environments at room temperatures, do not assure an improvement in corrosion properties of the substrate by applying the studied coatings, due to the excellent corrosion resistance of Inconel 738. Nevertheless, with PVD coating have been obtained the highest values of corrosion resistance, of the order of 10 MOhm.

Wear tests were carried out under fretting conditions at high temperature. The coefficient of friction and the material wear loss, were measured for both coatings and Inconel substrate. Results show an improvement in friction and wear behaviour of the two coatings respect the substrate. The CrN- PVD coating has a bit lower mean friction coefficient value. However, the wear measured was similar in CrN and hard chromium coatings.

Under corrosion and wear conditions, both coatings improve substrate properties. Hard chromium and PVD-CrN layers show similar wear resistance in corrosive media under the specific mechanical conditions studied. Differences between tribocorrosion behaviour of both coatings are minimal, so PVD layers could be in certain situations, an acceptable clean alternative to electroless chromium.

Inter laboratory investigation on Electrochemical methods for the characterization of CoCrMo biomedical alloys in simulated body fluids

Interaction of non- biological surfaces and body fluids, is one of the priorities in the development of new biomaterials. A better understanding of the interactions between biological entities and non-biological structures is of central importance for functionalized materials and systems such as the development of new bones substitutes. Assure biocompatibility of biomaterials, requires a fundamental comprehension of electrochemical interactions in the body fluids; in fact electrochemical dissolution of metals is one of the key factors in the improvement of the performance of new biomaterials. Corrosion of biomaterials is critical because it can adversely affect biocompatibility and mechanical integrity.

Classical electrochemical methods (potentiodynamic curves) have been widely used for description of general and localized corrosion. Electrochemical impedance spectroscopy has proved to be very favorable for the characterization of the interface surface/electrolyte; moreover it represents a very sensitive method for the study of adsorption of organic and biological molecules as well as for characterization of protein adsorption. The aim of this inter laboratory investigation is to evaluate the scope of destructive and non-destructive electrochemical techniques for biomedical alloys characterization in simulated body fluids.

This initiative, also pretends to give the first step in the development of a common protocol of testing biomaterials and defining their interaction in a biological environment. Establishing the experimental conditions for the description of the chemical interaction between the biomaterials and biological media is necessary for the understanding of more complex systems such as tribocorrosion. The laboratory network may help to establish a first connection for FP7. For this purpose, the biotribology of materials in artificial hip and knee joints, the mechanisms of lubrication, wear and corrosion, the methods of in vitro simulation and testing, and the resulting biocompatibility and biological reactions to the wear products have to be investigated.

The specific idea is to compare results obtained in a simple way with two different techniques: polarization curves “dc”, and Electrochemical impedance spectroscopy “ac” on a CoCrMo alloy, commonly used in MoM joints, in a simulated body fluid. The alloy is selected according to its excellent corrosion and mechanical properties and biocompatibility; therefore it is considered at the moment one of the best alternatives for MoM joints.

The project will be a first step for deeper collaborations, we would like to have the results no later than June-July 2007 in order to obtain, at least preliminary results, for next EuroCORR 07, and probably the whole study for the next COST Action meeting in Eibar.

The essential objectives of this inter laboratory activity are:

- To evaluate the scope of different electrochemical techniques for biomedical alloy characterization, in which the experimental conditions and data interpretation may be especially controversial.
- To establish the first step for the creation of testing protocol for biomedical materials. To provide basis for characterization of chemical interaction between any substrate (coated or non-coated) and the biological media in order to obtain significant results in further tribological studies, biocompatibility, or in-vivo testing.
- To provide an overview of the European network involved in alloys characterization in the biological field.

Acknowledgements

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Project co-operation

A Short Term Scientific Mission has been setup in the frame of COST 532. Ana Ortega from TEKNIKER visited Prof. Celis Univ. Leuven. She try to collaborate in setup a standard in tribocorrosion. She is now closely collaborating with the company from engines GUASCOR. Also another Short Term Scientific Mission has been setup in the frame of COST 533. Raquel Bayón from TEKNIKER visited CRSA to Prof. Ponthiaux trying to setup tribocorrosion tests in biological media.

Planned or achieved industrial improvements in commercial use

Partners selling tribocorrosion machines for example FALEX will benefit from the results of this article.

Publications

The results of this work will contribute to the Doctoral Thesis from Raquel Bayón.

Other related publications:

1. Igartua, A. Ortega, R. Bayon, "Corrosion and tribocorrosion in biological media", COST 533 Workshop of Biotribology, Helsinki, 28, 29th October 2005.
2. Igartua, X. Fernández, P. Shashkov, S. Usov, I. Illarramendi and J. Landa, "Plasma Electroxidation coatings for magnesium piston applications, COST 532-NIST Conference, Proceedings 207-215, 12-14 de Octubre 2005, Porto, Portugal. EUROMAT, 5-8 Septiembre 2005, Praga, República Checa.

3. Igartua, R. Bayón, “Corrosión and tribocorrosion of aluminium and cast iron materials”, COST 532 Symposium of Tribology, 20-21st April 2006, Dubrovnik, Croatia.
4. Igartua, R. Bayón R. Zabala, P. Zabala, V. País, J. Damborenea, J.-P. Celis, “Comparative corrosion-wear behaviour of cast iron and aluminium”, EuroCorr 06 Conference, Maastrich, 25-28th September
5. R. Bayon, A. Igartua, G. Mendoza, J. P. Celis, “Corrosion and corrosion-wear study of CoCr alloy AND CoCr TiCN – DLC COATED in biological environments”; Workshop COST 533, Warsaw, Poland, 6-7th October 2006
6. R. Martínex, R.J. Rodríguez, J. A. García, A. Igartua, R. Bayón, X. Fernández, A. de Frutos, M. A. Arenas, J. de Damborenea, “Comportamiento frente a corrosion y desgaste de recubrimientos PVD multicapa Cr/CrN para aplicaciones de transmisiones”, Iberotrib, 21-22 Junio 2007, Bilbao, España.
7. R. Bayón, I. Ciarsolo y A. Igartua, “Estudio del efecto del substrato en el comportamiento frente a corrosión y tribocorrosion de recubrimientos DLC en medios biológicos”, Iberotrib, 21-22 Junio 2007, Bilbao, España.
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10. A.Igartua, R. Bayón, G. Mendoza, X. Fernández, A. Alberdi, I. Ciarsolo, E. Aramburu. A.Sanchez, J.C. del Hoyo, J. Martorell, J.Larrea, L.M. del Rio “Corrosion and wear behaviour of multilayer Cr/CrN PVD Coatings”, Sevilla Workshop, "Surface Treatments and Coatings for Mechanical and Aeronautical Applications (WSS-2007)", 28-30 marzo del 2007.

CH7 - COATING MATERIALS OPTIMISED FOR LUBRICANT CONTACTS

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Project status and schedule

Running with sufficient funding
Starting and ending dates: 01 07 2003 – 03 31 2007

Project aims

This project aims at investigating the role of low friction coatings in lubricated sliding and rolling contacts, and the physical and chemical action of lubricant additives.

Background

Earlier studies by EDS revealed that conventional EP and AW additives do not react chemically with DLC (WC/C) coatings. However, the presence of a DLC coating, especially if covering only one of the two mating steel surfaces, significantly reduced the friction in the boundary and mixed lubrication regimes. A mechanical intermixing of coating constituents in the tribo-film was believed to be part of the explanation to this phenomenon.

This project aims at further studies of the tribochemistry of DLC-coated lubricated contacts. In addition to WC/C, VC- and TaC-doped carbon coatings will be included. The chemical analysis is often performed by XPS. A FIB/SEM-instrument is used to study selected areas of the tested friction surfaces. This instrument allows well controlled cross sectioning by ion beam milling, followed by SEM and EDS investigation. TEM-studies of selected samples have also been performed.

The tribological tests are mainly performed in a ball-on-disc apparatus and in the Uppsala Load Scanner. The latter equipment comprises two cylindrical test rods that are forced to slide against each other under well-controlled load scanning conditions, see last years report.

Selected results

One successful theme of the project has been to investigate the possibilities to optimise the coating material with respect to:

- Wear resistance
- Running-in properties, specifically the ability to smoothen the counter surface and also itself run-in to a smooth appearance.
- Ability to form stable, low friction inducing tribofilms on the counter surface.

Friction reduction with Cr-alloyed DLC-coatings

Very interesting results have been obtained, see figure 1, indicating very high potential for solutions much better than current commercial systems. The work must now also include wear life improvements of the coatings, since many of the currently tested systems rely on a quite rapid transfer of coating material to the counter surface, which naturally limits the life of the coating.

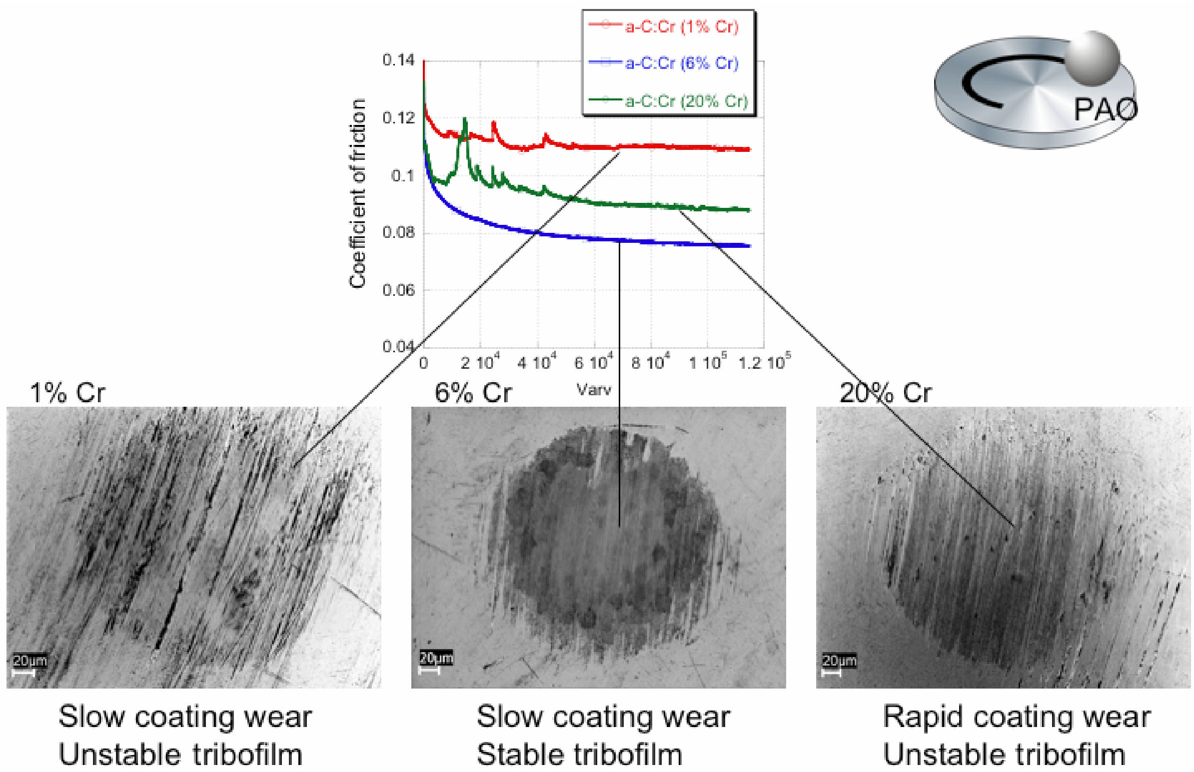


Fig. 1. Results from a pin-on-disc test of Cr alloyed carbon films. The amount of Cr has a significant impact on the friction level by influencing both the coating wear, the running-in of the coating and the steel counter surface and on the formation of stable tribofilms.

Optimised lubricant formulation

Another theme has involved extended testing in the load scanner. To further investigate the possibilities to optimise lubricant formulations for DLC coated components. Recent results indicate that DLC coating make it possible to reduce the friction coefficient in boundary lubricated friction considerably. However, optimum results require some running-in of the contact and an adjustment of the amount of EP additive to suit the DLC/steel combination, see Fig. 2. Initial results indicate that the amount of additive can be significantly reduced from the levels currently used in uncoated steel components. This opens very promising opportunities for reducing the negative environmental and health impact of lubricants, which is directly coupled to some of the more aggressive additives.

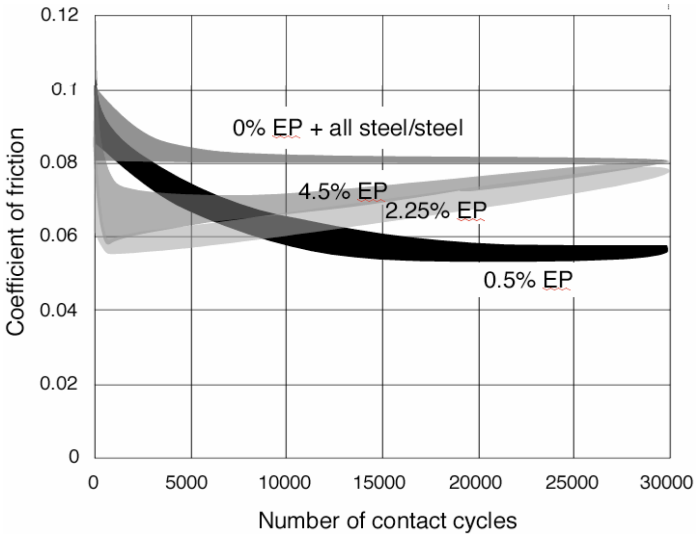
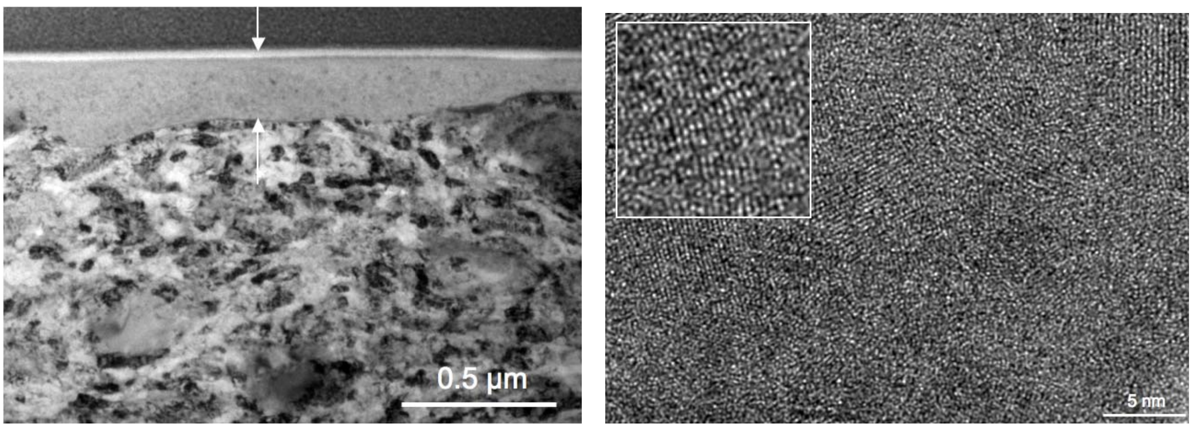


Fig. 2. Friction vs. number of test cycles for lubricated DLC coating against steel in the Load Scanner. By optimising the amount of EP additive the minimum friction can be reduced and the lifetime of the coating prolonged. The steel against steel case is added for reference.

Composition and structure of tribofilms

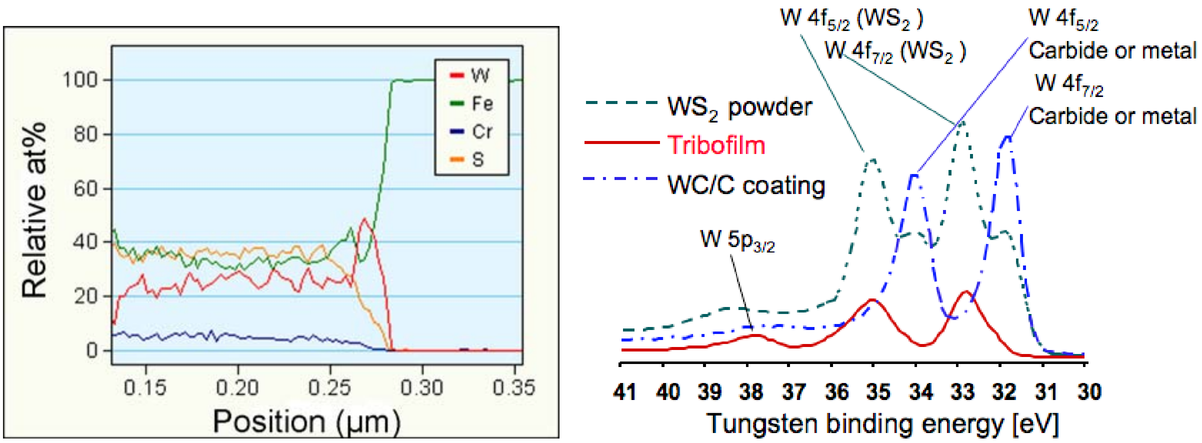
Yet another theme has been to perform high-resolution transmission electron microscopy (HR-TEM) of the above tribofilms in order to understand the mechanisms of their formation and performance. Load Scanning tests were performed with rods coated with DLC-coatings doped with W and Cr, respectively. An example of a cross-section through the surface layer of a BBS rod tested against W-doped DLC is seen in Fig 3. A thin and relatively homogeneous film with characteristic fullerene like crystallites is revealed.

The chemical composition is revealed in Fig. 4



b)

Fig. 3. a) TEM image of cross-section of the contact surface of a tested BBS rod run against a W-doped DLC. b) HR-TEM of the tribofilm material.



a) b)

Fig. 4. a) EDS elemental depth profile across a film obtained with the W-doped coating. b) ESCA spectrum comparing the same film with that of the DLC coating (WC/C) and a reference WS_2 powder.

In high magnification in TEM it is seen that the film from BBS run against the W-doped coating contains small (5 – 10 nm) crystals with a lattice spacings that suggest that the composition is a mixture of WS_2 and FeS.

Me-doped DLC-coatings

This results above encouraged us to explore metal-doped DLC coatings with other metals than W, hoping for the same type of reaction to occur in a lubricated tribological contact. Coatings alloyed with elements such as Mo, V, Ta and Sn were investigated, both theoretically by EkviCalc calculations, and experimentally by ball-on-disk tests. EkviCalc can give information about possible stable compounds at equilibrium as a function of temperature, see Fig. 5. Note that the “low friction” MoS_2 is stable in significant amounts in the whole 100 – 800°C temperature range.

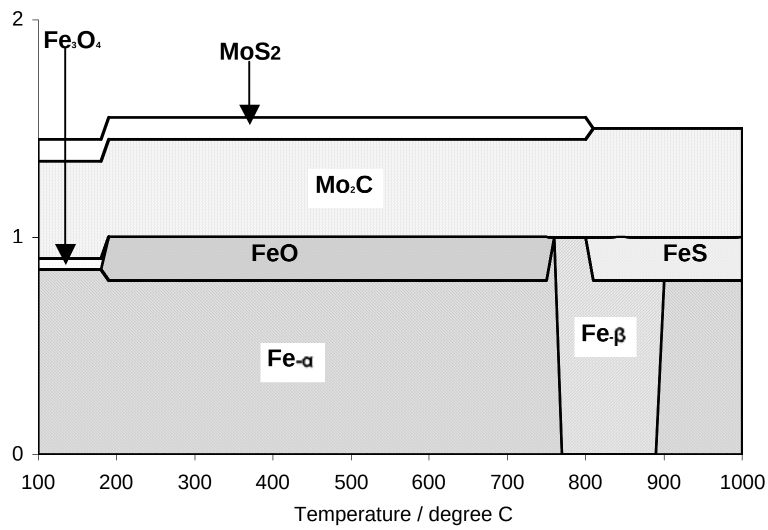


Fig. 5. Stable compounds at equilibrium vs. temperature for a carbon coating doped with Mo.

Conclusions

Low friction tribofilms containing nanosized particles of WS_2 and MoS_2 are found in lubricated contacts between steel and DLC-coatings doped with W and Mo, respectively. These particles are believed to contribute to low friction, strong cohesion and high wear resistance of the tribofilm.

The Ti-Al-C system

A completely new theme is to explore the Ti-Al-C system. When part of the Ti content in a pure TiC coating is substituted with Al, some of the carbon will form free graphite. Al simply "steels" some of the covalent Ti-C bondings, which leaves some excess graphitic carbon in the structure, cp. Fig. 6. The intention is to create a new coating that combines the hardness and wear resistance of TiC with a low friction potential.

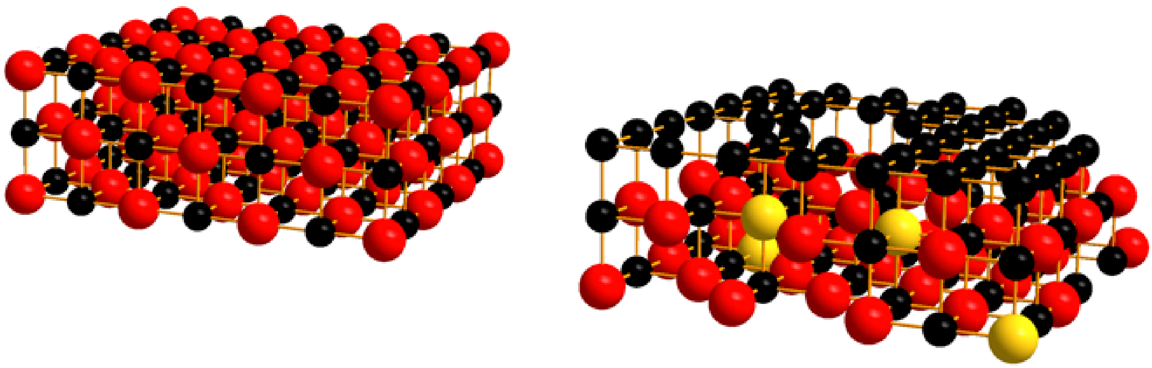


Fig. 6. Crystallographic models of TiC (left) and TiC + C (right).

Project co-operation

A co-operation with Centre of Tribological Development (CTD) at the University of Ljubljana is now fully established. Project leaders from Uppsala and Ljubljana (Hogmark and Podgorik) planned details of the co-operation during a meeting in Ljubljana in September 1, 2003.

There is an active interest in the project also from Swedish industries, and contact (visits, mails, phone calls) occurs with Scania (trucks), Volvo (trucks, cars and construction equipment), Balzers Sandvik (coatings), SKF (bearings), Erasteel (speciality steels) and Hagglunds (hydraulic motors/pumps). Dedicated bench testing in cooperation with Hagglunds has been performed (last reporting meeting at Hagglunds in Mellansel Sept, 2005), Balzers Sandvik and Bodycote (several meetings in Uppsala and elsewhere during 2005) produce some of the coatings, SKF and Erasteel supply the test rod substrates.

A meeting at Scania in Stockholm 25-26 October 2005, where the latest results from CH 7 were reported attracted more than 100 people from academia and industry.

In 2004, a new company, *Primateria*, was formed by three former PhDs from the Uppsala Tribomaterials Group. They all have industrial experience from several years together with Balzers Sandvik Coating AB. In Primateria they work as consultants in surface engineering, and cooperate frequently with the tribologists at Uppsala University.

Publications were project results are reported

International Journals: (11)

1. D. Nilsson, F. Svahn, U. Wiklund and S. Hogmark, Low-friction carbon-rich carbide coatings deposited by co-sputtering, Wear, 254, (2003) 1084-1091
2. F. Svahn, Å. Kassman-Rudolphi and E. Wallén, The influence of surface roughness on friction and wear of machine element coatings, Wear, 254, (2003) 1092-1098
3. Podgornik, B., Jacobson, S., and Hogmark, S., "DLC coating of boundary lubricate components – advantages of coating one of the contact surfaces rather than both or none." *Tribology International*, 36 (2003). 843–849.
4. Podgornik, B., Jacobson, S., and Hogmark, S. "Influence of EP and AW additives on the tribological behaviour of hard low friction coatings." Surface and Coatings Technology Vol. 165 (2004) 168-175.
5. Podgornik, B., Jacobson, S., and Hogmark, S. (2003). "Influence of oil additives on the performance of DLC coatings." *Materiali in Tehnologije*, 37(1-2) (2004) 9–12.
6. B. Podgornik, S. Hogmark, J. Pezdirnik, "Comparison between different test methods for evaluation of galling properties of surface engineered tool surfaces", Wear 257 (2004) 843-851
7. B. Podgornik, S.Jacobson, S.Hogmark, "Influence of EP additive concentration on the tribological behaviour of DLC-coated steel surfaces", Surface and Coatings Technology, 191 (2005) 357-366
8. M. Carlsson, U. Wiklund, "A comparative evaluation method for low friction coatings in dry sliding thrust bearings", Tribologia, 23 (2004) 27.
9. D. Nilsson, U. Wiklund, "A flexible laboratory-scale approach to alloying and tailoring of thin films by single-magnetron co-sputtering", Thin Solid Films, 467 (2004) 10.
10. N. Stavlid, E. Coronel, U. Wiklund, "Extreme pressure tribofilm formation-compatibility between Me-DLC coatings and lubricant containing sulphur additive", Submitted to Tribology Letters.
11. N. Stavlid, U. Wiklund, Tribolytic phenomena in boundary lubricated WC/C – steel contacts, submitted to Tribology International..

International conferences: (8)

1. S. Hogmark, F. Svahn, N. Stavlid, U: Wiklund and S. Jacobson, Possibilities for optimisation of low friction coatings", Presented at the ITC Kobe May 2005
2. S. Jacobson, S. Hogmark, Design of low-friction coatings for boundary lubricated components, Presented at the ITC Kobe May 2005
3. U. Wiklund, F. Svahn, N. Stavlid, S. Jacobson and S. Hogmark, Running in of low-friction coatings – Possibilities for optimisation, First Balzers Surface Technology Forum in Asia, Kakigawa, Japan, 27-29 March, 2005
4. S. Hogmark, D. Nilsson, F. Svahn, "Interactive Tribological Coatings", Proceedings of the COST 532 Conference in Ghent, October 18-19, 2004 pp 68-75
5. S. Hogmark, Friction Mechanisms of Coated Tribological Components, Proceedings of the VTI conference Challenges in Surface Engineering, Ghent, Belgium, October10, 2004
6. S. Hogmark, Surface engineering - Which are the gains? Invited talk at of the VTI conference Challenges in Surface Engineering, Ghent, Belgium, October10, 2004
7. S. Jacobson, S. Hogmark, Coating materials Optimised for lubricated contacts, Proceedings of the COST 532 Working Group meeting at Dubrovnik April 20-21, 2006
8. S. Jacobson, S. Hogmark, Strategies for tribofilm assessment, ASIATRIB2006 in Kanazawa, Japan, Symposium No. 6, Advanced characterization of tribosurfaces and thin tribofilms, October 16-19, 2006

PhD thesis: (4)

1. D. Nilsson, *Synthesis and Evaluation of TaC:C Low-Friction Coatings*, Acta Universitatis Upsaliensis, Uppsala 2004, ISBN 91-554-6034-8.
2. F. Svahn, *Tribology of Carbon Based Coatings for Machine Element Applications*, Acta Universitatis Upsaliensis, Uppsala 2004, ISBN 91-554-6116-6.
3. E. Coronel, *Solving Problems in Surface Engineering and Tribology by Means of Analytical Electron Microscopy*, Acta Universitatis Upsaliensis, Uppsala 2005, ISBN 91-554-6148-4
4. Nils Stavlid, *On the Formation of Low Friction Tribofilms in Me-DLC-Steel Sliding Contacts*, PhD thesis, Acta Universitatis Upsaliensis Uppsala 2006, ISBN 91-554-6743-1

Planned or achieved industrial improvements in commercial use

The aim is to obtain practical recommendations on the selection and application of coatings and lubrication additives for critical engine components. One of the supporting companies has developed an hydraulic oil with a modified additive formulation that reduces a specific wear problem, based on results gained within the project.

The aim is also to be able to reduce or avoid completely toxic lubricants or lubricant additives by using the developed coatings

CH8 - CORRELATION BETWEEN OXIDATION AND TRIBOLOGICAL PROPERTIES OF THERMALLY SPRAYED HARDMETAL COATINGS

Co-ordinator and partners

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Project status and schedule

Part of the project was realised by founding directly from industry (in 2003) and by founding of the private Foundation of Industrial Research (Stiftung Industrieforschung), Cologne, Germany for the period 01.05.2003-30.04.2005.

Project aims

Thermal spray processes represent an important and rapidly growing group of surface technologies to produce hardmetal coatings for protection against wear and corrosion, but not always satisfactory tribological properties for applications, in particular in engines and transmissions. The understanding of the oxidation mechanism is the key for the preparation of hardmetal coatings with tailored tribological properties. In the financed part of the total COST-project, founded by the Foundation for Industrial Research, an application-related comparative study of the oxidation of hardmetals (WC-Co(Cr), WC-Ni(Cr), Cr_3C_2-NiCr, TiC-basis-Ni(Co)) and their tribological behaviour in different conditions is carried out.

Project results

The results of the starting experimental series (direct industrial founding) are given in [1,7].
The experimental work of the finished financed project was devided into five series:

1) static oxidation of HVOF-sprayed hardmetal coatings in air at elevated temperatures
2) unlubrictaed sliding wear against sintered alumina
3) unlubricated sliding wear of self-mated pairs
4) lubricated sliding wear of self-mated pairs
5) unlubrictaed sliding wear of pre-oxidized coatings against sintered alumina

In the first of these series, the oxidation of hardmetal coatings (WC-12%Co, WC-17%Co, WC-10%Co4%Cr, WC-20%“CrC”-7%Ni, Cr_3C_2-25%NiCr, (Ti,Mo)(C,N)-29%Ni and (Ti,Mo)(C,N)-29%Co) in the temperature range 350-900°C was studied for test durations ranging from 2 h to 128 h. The formation of oxide scales was investigated by X-ray diffraction, as well as by optical microscopy and SEM (including EDX) of coating cross sections. The results of this systematic study on the oxidation of hardmetal coatings in air mentioned above showed both common characteristics and peculiarities for the composites. For coatings obtained by spraying with DJH 2700 and TopGun HVOF systems, the phase composition had only a moderate influence on high-temperature oxidation behavior in atmospheric conditions. The first oxides detectable by X-ray diffraction appeared on the coating surfaces after oxidation at 350°C for 128 h for all coatings. Oxidation experiments at 400°C and 500°C with test durations of more than 8 h lead partially to the formation of oxide scales of more than 10 µm in thickness. For relatively short test durations (2 h), pronounced oxidation (formation of oxide scales with thicknesses of greater than 10 µm) started at 600°C. Oxide scale growth differed significantly above this temperature among the hardmetal compositions studied here.

WC-Co coatings formed oxide scales consisting of WO_3 and $CoWO_4$ and having thicknesses of at least 50 µm at 700°C. The composition WC-10%Co-4%Cr exhibited only a slightly better oxidation resistance. WC-20%"CrC"-7%Ni and Cr_3C_2-NiCr had the highest oxidation resistance, with the oxide scale thicknesses lying below 10 µm after oxidation at 800°C and 900°C for the two materials, respectively. Cr_2O_3 was the only detected phase formed as a result of high-temperature oxidation of Cr_3C_2-NiCr coatings in air. The composition of the oxide scale formed on WC-20%"CrC"-7%Ni coatings was more complex. The oxidation resistance was higher for (Ti,Mo)(C,N)-Ni than for (Ti,Mo)(C,N)-Co coatings. In the temperature region of 700°C and above, comparable oxide scale thicknesses for the two coating types were found when the oxidation temperature for the composition with a nickel binder was approximately 100°C higher than that for the composition with a cobalt binder. However, the formation of three subscales was observed for both systems.

This study also confirmed that the oxidation process for WC-Co (involving carbon loss and oxygen uptake) is different during spraying than in air.

As long as the thickness of the oxide scale is low, microstructural changes in the coating, e.g., changes in the binder phase, can be observed by X-ray diffraction as well. Due to difficulties in metallographic preparation, determination of the oxide scale thickness by microscopy is difficult for some hardmetal coatings. X-ray diffraction can deliver supplemental information on oxide scale thickness. It should be taken into account that the results in this series were obtained with free access of oxygen to the coating surface, which is often not the case in many practical applications. On the other hand, besides resisting high-temperature oxidation, coatings must also be able to withstand several types of mechanical loads, e.g., abrasion, erosion and others, simultaneously. Details of this series are reported in [2].

In the second series selected hardmetal coatings (WC-12%Co, WC-10%Co4%Cr, WC-20%"CrC"-7%Ni, Cr_3C_2-25%NiCr, (Ti,Mo)(C,N)-29%Ni, (Ti,Mo) (C,N)-29% Co) were investigated in an unlubricated dry sliding wear test (0.1-3 m/s) in the temperature range from room temperature up to 800°C at BAM. The sliding distance was of 5000 m and a normal force of 10 N was used. Hard chromium and air plasma-sprayed Mo-NiCrBSi coatings were studied in the same conditions for comparison. Under certain conditions, for HVOF-sprayed hardmetal coatings (WC-Co and WC-CoCr up to 400°C, (Ti,Mo)(C,N)-Co and (Ti,Mo)(C,N)-Ni partially up to 800°C) total (and coating) wear rates below 10^{-6} mm^3/Nm, comparable to those measured under mixed/boundary lubrication, were observed. Coating materials which form “lubricious oxides”, such as WC-based and (Ti,Mo)(C,N)-based hardmetals, as well as Mo-NiCrBSi give pxV values up to 100 MPa*m/s. Oxidation of the coatings outside the wear track gives similar results as found for oxidation experiments in a laboratory furnace, described in [2]. The properties of Cr_3C_2-NiCr coatings seem to be improved by the formation of Cr_2O_3. Details for this series are described in [3].

In the third series, the tribological properties of self-mated hardmetal coatings with nominal compositions WC-10%Co4%Cr, WC-20%"CrC"-7%Ni, Cr_3C_2-25%NiCr, (Ti,Mo)(C,N)-29%Ni, (Ti,Mo)(C,N)-29% Co were compared in an unlubricated dry sliding wear test at room temperature, 400°C and 600°C. Electrolytic hard chromium coatings were studied for comparison. Sliding velocities were varied in the range 0.1-1 m/s with a wear distance of 5,000 m and a normal force of 10 N. The results are linked with the results of unlubricated dry sliding wear tests against sintered alumina, described above and in [3]. WC- and (Ti,Mo)(C,N)-based coating couples showed in several conditions total wear rates below 10^{-6} mm^3/Nm, but especially at 400°C the wear rates are higher, as when mated with alumina. Coefficients of friction above 0.4 were found for all test conditions for self-mated couples, while for couples of (Ti,Mo)(C,N)-based coatings with alumina in some test conditions coefficients of friction of approximately 0.2 were measured. The formation of Cr_2O_3 at high temperatures on the surface of Cr_3C_2-NiCr and EHC coatings (in self-mated conditions as well as mated with alumina) seems to decrease the coefficient of friction but high total wear rates are characteristic for both coatings. Details for the results of these series are given in [5,8].

In the fourth series self-mated hardmetal coatings with nominal compositions WC-10%Co4%Cr, WC-20%"CrC"-7%Ni, Cr_3C_2-25%NiCr, (Ti,Mo)(C,N)-29%Ni, (Ti,Mo)(C,N)-29% Co were compared in an lubricated dry sliding wear test using two hydraulic oils (AVIA Syntofluid PE-B 50 and Panolin HLP Synth 46). Test conditions: 100°C, sliding speed 0,3 m/s APS-sprayed Mo-NiCrBSi and the hardchroium coatings were tested for comparison. The hard chromium coating has shown in this test better total volumetric wear rates, than all thermal spray coatings. Details from this series are planned to be published in periodical literature 2007.

In the fifth series a variety of preoxidized hardmetal coatings (WC-10%Co4%Cr, WC-20%"CrC"-7%Ni, Cr_3C_2-25%NiCr, (Ti,Mo)(C,N)-29%Ni, (Ti,Mo)(C,N)-29% Co) was tested against sintered alumina in the same conditions in an unlubricated dry sliding wear test as the samples in series two (sliding velocities were varied in the range 0.1-3 m/s with a wear distance of 5000 m and a normal force of 10 N). Previously to testing the finished coatings were oxidized at temperatures selected from results from series one at conditions that a full developed oxide scale was formed. Full developed means e.g. the formation of the three subscales in the (Ti,Mo)(C,N)-based coatings, preoxidation temperatures were in the range 600-800°C. Testing was performed at room temperature, 600°C and 800°C. Hard chromium and APS sprayed Mo-NiCrBSi and Cr_2O_3 coatings were studied in the same conditions for comparison.

In general, the existence of full developed oxide scales in beginning of the test lead to a decrease of wear resistance and did not show a positive effect on the coefficient of friction. Depending from the sliding speed and temperature the dry wear rates of several coatings were comparable to those typically measured under mixed/boundary conditions. Under certain conditions, for HVOF-sprayed hardmetal coatings (WC-Co and WC-CoCr up to 400°C, (Ti,Mo)(C,N)-Co and (Ti,Mo)(C,N)-Ni partially up to 800°C) total (and coating) wear rates below 10^{-6} mm^3/Nm, comparable to those measured under mixed/boundary lubrication, were observed. The Cr_2O_3 coating has shown excellent properties in this test. Details for the results are published in [6].

Results of all test series are also available in German language in [7] and from the final report.

Project co-operation

Cooperation work was performed with projects M10 and TS1 (M2).

Publications were project results are reported

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2. Berger L.-M., Zieris R., Saaro S. , Oxidation of HVOF-Sprayed Hardmetal Coatings, Proceedings of the International Thermal Spray Conference & Exhibition ITSC 2005, 2-4 May 2005, Basel, Switzerland, Düsseldorf: Verlag für Schweißen und Verwandte Verfahren, DVS-Verlag GmbH, 2005. – CD (ISBN 3-87155-793-5), 8 p.
3. Berger L.-M., Woydt M., Zieris R., Comparative Study of HVOF-Sprayed Hardmetal Coatings under High Temperature Dry Sliding Conditions, Proceedings of the 16th International Plansee Seminar, May 30- June 3, 2005, Reutte/Tirol, Austria. Eds. G. Kneringer, P. Rödhammer and H. Wildner, Reutte: Plansee Holding AG, 2005. - Vol. 2, p. 878-892.
4. Berger L.-M., Saaro S., Zieris R., Woydt M., Oxidation und ungeschmierter Hochtemperatur-Gleitverschleiß von thermisch gespritzten Hartmetallschichten, Tagungsband zum 8. Werkstofftechnischen Kolloquium in Chemnitz, 29.-30.09.2005, Schriftenreihe "Werkstoffe und werkstofftechnische Anwendungen", Band 22, Herausgeber: B. Wielage, Chemnitz: TU Chemnitz, 2005. – p. 207-216 (ISBN 3-00-016841-9, ISSN 1439-1597).
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CH9 - COMPOSITE MATERIALS FOR REGENERATION OF THE FRICTION MACHINE ELEMENTS

Co-ordinator and partners

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Project status and schedule

Running with partial funding
Starting and ending dates: 01.02.2004 – 31.10.2006 (33 months)

Project aims

The project is aimed at development of a *sliding* composite based on a *chemo-setting epoxide resin*, characterised by good anti-wear sliding properties useful in the course of regeneration or production of working machines elements at speeds about 0.3 m/s and bigger, working in temperatures to 150° C. The scientific objective of the carried out experiments will be finding correlation of properties of the chemo-setting polymer matrix and basic components of the composite and features characteristic for the developed sliding metal-resin composite.

Project results

Introduction

The development in the area of physicochemical foundations of manufacturing of polymer mixtures and composites enabled multicomponent plastics to compete with other engineering materials (ceramics, metals).

Apart from chemical and physical modification, a very important factor is the manufacturing processes for polymer blends and for polymer based composites. In both cases we usually achieve products with various mechanical, optical, electrical and chemical properties. These products can be transformed using well known manufacturing methods, and simultaneously allow for fulfilling increasing user demands.

Today, the interesting group among of composites is the so called *in situ* composites. They are also called second generation composites. In comparison with *ex situ* composites, also called *in vitro*, where the reinforce phase is introduced mechanically as an external body, in *in situ* composites the reinforce phase is created as a result of various reactions conducted in the liquid phase. The undeniable advantages of the *in situ* methods are: thermal stability, no chemical reactions at interfaces and the elimination of problems connected with wettability.

Currently there is no industry branch where the composites could not be applied. These materials have a lot of properties that surpass or are equivalent to typical, but sometimes shortage, materials. Furthermore, the application of plastics in sliding friction joints is increasing. The advantage of plastics is their durability. They can operate in a machine for life in the case of low loads and low sliding velocity.

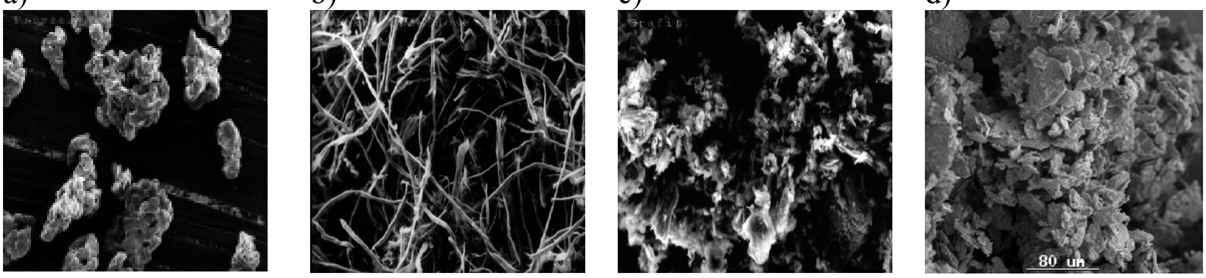
In numerous existing engineering solutions there are friction joints that fulfil technical and operational, as well as economic demands, for regeneration with the use of polymer composites. By the selective choice of the composite components, and the use of their synergetic interactions, it is possible to elaborate a new type of composite that suits requirements for sliding friction pairs. In those sliding pairs the important features are stick-slip effect and three body abrasive wear. For sliding pairs of the composite-steel it is possible to lower the wear in comparison with the classical solutions.

Practical experience indicates that the high effectiveness of the polymer composite applications (metal-resinous) results from their low manufacturing costs, simplicity of technology, and, chiefly, the possibility of regeneration of worn machine components.

Test methods and materials

The object of research was the polymer composites, intended for regeneration of sliding machine parts, with chemical-setting epoxy resin. The main composite filler was Fe powder with various grain size distributions. The composite also included aramid fibres and improving additives: graphite, molybdenum disulphide. The scanning electron images of the composite ingredients are presented in Figure 1.

a) b) c) d)



200x 200x 300x 300x

Fig. 1. Microscopic images of main components: a) Fe powder, b) aramid fibres, c) graphite, d) molybdenum disulphide.

As cross-linking agents for regeneration composites various amine compounds with active hydrogen element were used:

- aliphatic amine (Z1),
- polyaminoamide (PAC),
- the product of reaction between phenol formaldehyde and secondary amine (TFF),
- modified cycloaliphatic diamine (KT).

These compounds have various molecular weights, chain length and various number of reactive amine groups. The structure of curing agents affects the rate of the curing process and its results, mainly the degree of cross-linkage. The amine compounds were selected as cross-linking agents because of their high cross-linking rate and the possibility of conducting the curing process without elevated temperatures.

The parameters used for estimation of strength and thermal properties were:

- Brinell hardness measured using a ball, according to PN-93/C-8999030/01 Polish standard,
- impact resistance measured by Charpy pendulum machine, according to PN-81/C-89029 Polish standard,
- tear off resistance and compression strength were measured using Intron tester equipped with computer-aided recording system, according to PN-82/C-89021 Polish standard,
- thermal expansion coefficient α measured in accordance with PN-82/C-9021 Polish standard.

The tribological characteristics of the elaborated composites intended for regeneration of sliding bearings were measured using T-05 block-on-ring testing machine (Figure 2). The tester enables the conducting of tests in accordance with American standards ASTM D 2714, D 3704, D 2981 and G 77. A very wide spectrum of controlled parameters allows for simulating working conditions of sliding friction pairs.

Fig. 2. Computer aided test rig with control and measuring system.

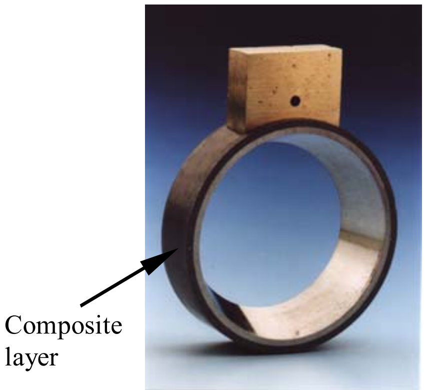


Fig. 3. Test friction pair.

The test conditions were as follow:

- contact geometry: conformal, ring diameter 35 mm, block width 6.35 mm,
- type of motion: sliding at constant velocity,
- sliding velocity: 0.25 – 0.75 m/s,
- load: 300 – 1200 N,
- sliding distance: 4500 m,
- lubrication: grease ST4S3.

Measured parameters:

- friction force,
- friction pair wear,
- rotational speed,
- block bulk temperature.

The test machine was equipped with a computer-aided measuring and control system. The test results were recorded in PC memory; and the test results were analysed by Excel software.

Results

The used cross-linking agents, because of their various chemical structures, affect the strength properties of the composite in various ways. So, it is difficult to indicate the universal cross-linking agents. The selection of a cross-linking agent depends on the application of the composite. Some of the agents i.e. polyaminoamide (PAC), positively affect the impact resistance of the composite and show some plasticity in the compression tests. The deformation of the composite is several times higher than the composite linked by the use of aliphatic amine (Figure 4 and 5).

Table 1. The strength properties of investigated composites.

	Hardness	Impact resistance	Compres-sion	Tearing off	Coefficient α
	[kJ/m^2]	[MPa]	[MPa]	[MPa]	[x10^{-6}°C^{-1}]
Aliphatic amine (Z1)	283	3.0	96	22	73
Polyaminoamide (PAC)	121	6.1	79	24	103
TFF	304	5.0	91	21	81
Modified cycloaliphatic diamine (KT)	185	2.9	80	24	112

The presented results of strength properties indirectly indicate that the most linked spatial structure with the maximum number of transversal bonds is responsible for the strength of the composite. This phenomena exists for the composites cross-linked with TFF agent and with triethylenetetramine. The higher molecular weight and more spatial structure of polyaminoamide chain (PAC) the better impact resistance and lower hardness.

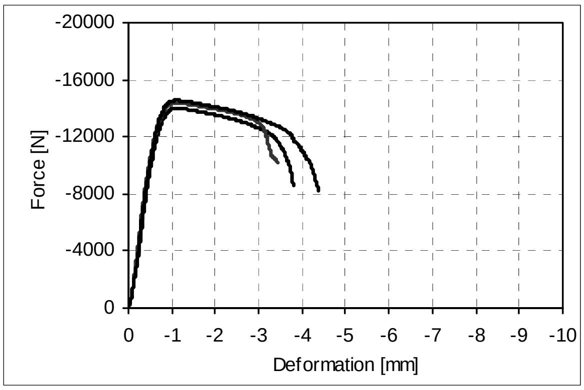


Fig. 4. Exemplary compression curve of a composite cross-linked by aliphatic amine.

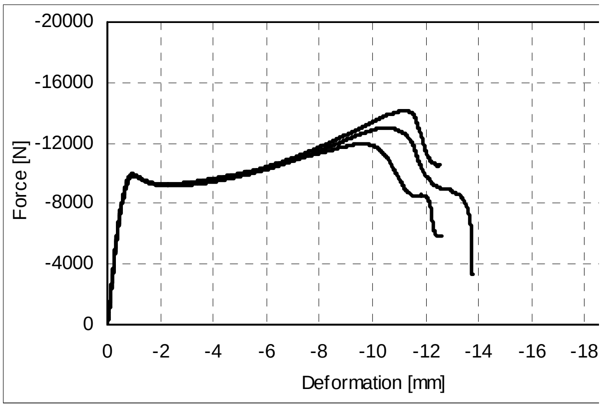


Fig. 5. Exemplary compression curve of a composite cross-linked by polyaminoamide.

Apart from the strength properties of the composites, their thermal expansion coefficients (α) were measured. Coefficient α, apart from strength parameters, affects the tribological properties of friction pairs made of various materials. Too high thermal expansion of the polymer composite, being the surface layer, in comparison with substrate material can disturb the proper operation of the sliding friction pair. The lowest changes in dimension as a function of temperature were recorded for the composites cross-linked with aliphatic amine.

Tribological tests were performed for the composite materials of the highest hardness and the best compression resistance. These parameters determine the resistance to wear of the composite at pressures existing in sliding bearings. Sample tribological characteristics of composite materials tested are shown in charts (Figures 6 and 7). They present the curves of the friction coefficient and the friction pair temperature versus sliding distance.

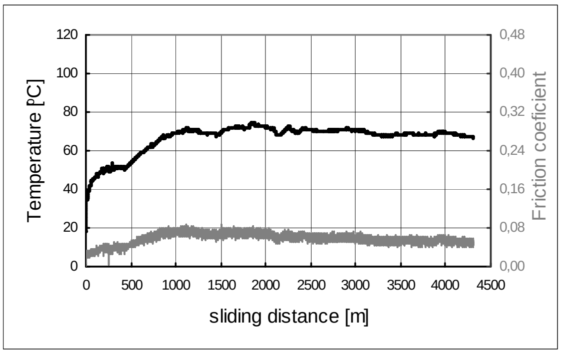


Fig. 6. The curves of temperature and friction coefficient (p = 6 MPa, v = 0.3 m/s).

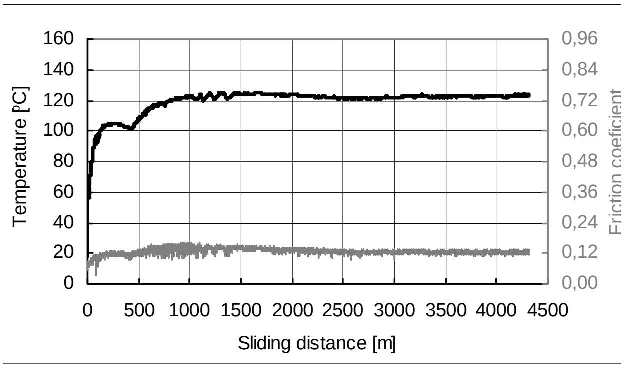


Fig. 7. The curves of temperature and friction coefficient (p = 9 MPa, v = 0.3 m/s).

Wear and friction tests of the elaborated polymer composites were performed at various unit pressures and various sliding speeds. The tribological test revealed that sliding velocity and contact pressure significantly affect the tribological characteristics. Comparing the presented curves one can state that both temperature and friction coefficient are almost constant while the increase in contact pressure causes increase in friction coefficient and friction joint temperature. The second factor affecting the contact zone is sliding velocity. The sliding velocity affects the unit friction power and tribological characteristics of the investigated composites.

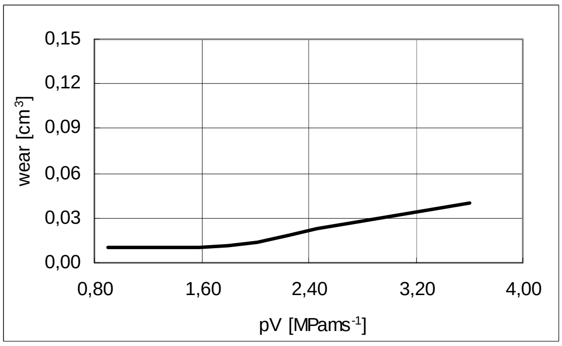


Fig. 8. Dependence of wear from friction power (pV) for variable pressures.

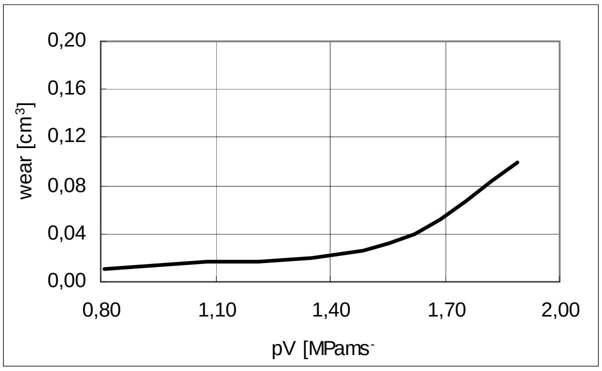


Fig. 9. Dependence of wear from friction power (pV) for variable sliding speed.

On the bases of friction and wear tests it was stated that the effect of both parameters (unit pressure and sliding velocity) is quantitatively different. The increase in friction coefficient and temperature are significantly higher for increasing sliding velocity than for increasing unit pressure. Comparing the wear curves for the investigated composite materials (Figure 8 and 9) it was observed that for increasing unit pressure this dependence is proportional and linear. In the case of increasing sliding velocity the wear of the metal-resinous composite is significantly higher, and increases rapidly after exceeding the limit value and is connected with friction joint temperature. The wear of the polymer composites based on chemical-setting resin is strongly dependent on friction pair temperature. The higher temperature accelerates the wear; this is connected with thermal resistance of the investigated composites. The thermal resistance of the composites was estimated on the basis of differential thermal analysis. Some derivatographs are depicted in Figures 10 and 11.

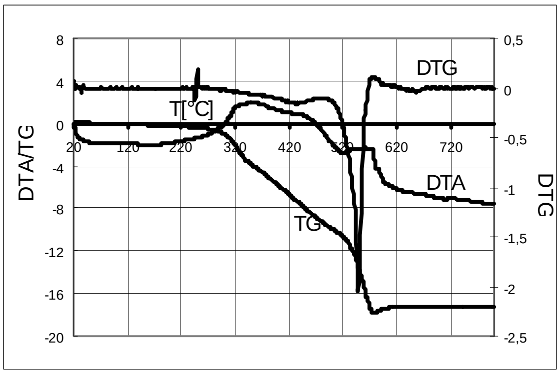


Fig. 10. Derivatograph of the composite cross-linked with polyaminoamide.

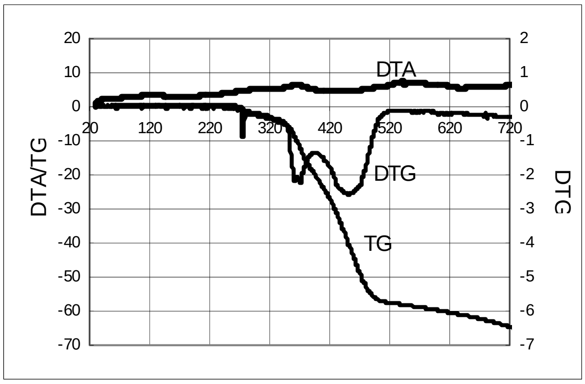


Fig. 11. Derivatograph of the composite cross-linked with aliphatic amine.

The research was performed in dynamic conditions. During measurements the curves of differential thermal analyses (DTA) were recorded (the changes in enthalpy resulting from chemical processes). Also thermogravimetry (TG) was applied. The technique involves monitoring the weight loss of the sample as well as first derivative of weight loss (DTG) in a chosen atmosphere (usually air) as a function of temperature T.

The first change in mass observed during the heating process indicates the decomposition initiation temperature. Among all tested polymer composites the highest decomposition initiation temperature was measured for aliphatic amine.

The most important filler of the polymer composite is inactive Fe powder. The grain size and specific surface of the powder affected the adhesion to polymer matrix, and through this composite strength as well as tribological properties. The powder was fractionated. The following granulation was used: grain size below 20 μm, 20÷40 μm, 40÷63 μm, 63÷80 μm and 80÷120 μm.

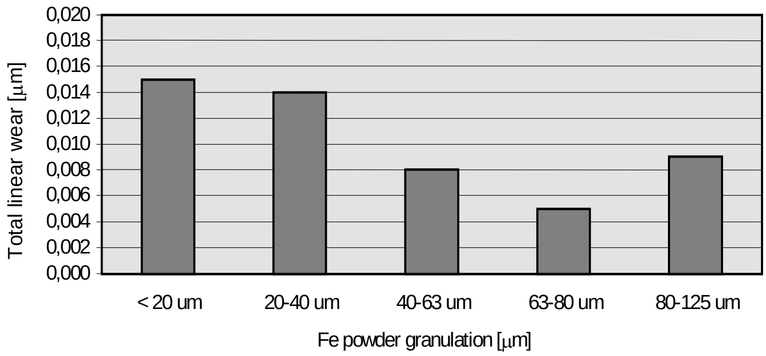


Fig. 12. Total linear wear of friction pair versus metal filler granulation.

On the basis of the wear and friction results it was observed that there is an optimum grain size. The best resistance to wear was shown by the composite based on the metal filler of grain size in the range of 63-80 μm (Figure 12). This result allows for assumption that fastening of the grains in the composite is the most rigid, and the adhesion to liquid matrix is the strongest. It affects the rise in the composite wear resistance.

Conclusions

The chemical-setting polymer composite, because of the universal properties, can fulfil the surface layer functions in various loss lubricated friction pairs. The composite exhibits good strength, thermal, and tribological properties. The application of the composite is very easy and cost-effective. The durability of regenerated parts is similar to new ones. Another factor recommending this technology is the fact that in sliding friction joints damage to the surface layer is the most frequent reason (about 80%) for their failure.

Project co-operation

Forms of co-operation will be:

- collaboration in the area of selection of composite nano-size fillers,
- exchange of experience concerning the methods of fillers surface preparation aimed at improving wettability and adhesive interaction with polymer matrix,
- collaboration in spreading of elaborated materials for industry.

Publications where project results are reported

1. Dasiewicz J., Janecki J.,: The effect of polymer matrix modifications on tribological properties of metal-resinous composite. TRIBOLOGIA 3/2004.
2. Dasiewicz J., Janecki J.,: The investigation of wear mechanisms of the thermosetting composite – steel friction pair. TRIBOLOGIA 3/2004.
3. Dasiewicz J., PawelecZ., Janecki J.,: The effect of manufacturing process parameters on properties of thermosetting polymer composites. TRIBOLOGIA 3/2005.
4. Dasiewicz J., PawelecZ., Janecki J.,: The sliding composite base on epoxide compounds modified with some polymers. TRIBOLOGIA 3/2005.
5. Dasiewicz J., PawelecZ., Janecki J.,; Badanie tarcia i zużycia kompozytów metalożywicznych dla różnych skojarzeń materiałowych. TRIBOLOGIA 2006.

Planned or achieved industrial improvements in commercial use

The project results will be applied in PONAR REMO Kępno, Poland.

CH10 - NANOSTRUCTURED COMPOSITE COATINGS OBTAINED BY ELECTRODE-POSITION TO BE USED IN TRIBOCORROSION SYSTEMS: PROCESSING AND PROPERTIES INVESTIGATION

Co-ordinator and partners

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Project status and schedule

Starting date: September 2003 Ending date: December 2008

Project aims

The present work concern the realisation and investigation of the nanostructured composite coatings obtained by codeposition of nano silicon carbide (mean diameter 20nm) dispersed particles with nickel. We study some effects of nano-sized SiC particles on the mechanism of nickel electrodeposition and how this included nanoparticles affect the nickel matrix surface morphology and structure and further the corrosion and tribocorrosion properties.

Project results

Experimental set-up

In our institution we prepared the samples with nanostructured and microstructued composite coatings Ni+SiC (20 nm diameter and 20 µm). The composite coatings were deposited on a top face of a stainless steel cylinder (high =25 mm, diameter =25mm), see Fig. 1.

The coating thickness was 50 µm, with an average volume of dispersed pahses inside nickel of 20 %.The samples were then installed in a cell, containing the electrolyte and electrodes, and mounted on a pin-on-disc tribometer, with the working surface of the specimen facing upwards. For electrochemical measurements (open-circuit potential, potentiodynamic polarization) a three-electrode set-up was used, with the sample as working electrode, a circular platinum gauze as counter electrode and a "Hg/Hg_2SO_4/saturated K_2SO_4 solution" as reference electrode (SSE = +670 mV/ NHE).

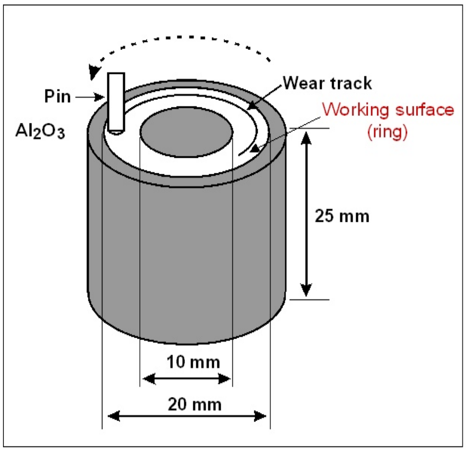

Fig. 1. Sample with nano or micro structured Ni-SiC coating on top.

The tribocorrosion properties have been studied in the following conditions:

Solution: 0.5M K_2SO_4.
Normal Force: 5N – 20N.
Rotation Speed: 30-120 tours/min.

The counterbody (pin) was a corrundum cylinder (7 mm in diameter), mounted vertically on a rotating head, above the specimen. The lower spherical end (radius = 100 mm) of the pin was then applied against the composite surface (disc) with an adjustable normal force. When rotation was applied, the end of the pin draws a circular wear track (16 mm in diameter) on the working composite surface.

Electrochemical measurements:

(a) Open circuit potential measurements
This method gives information on the electrochemical state of a material, for example active or passive state. However, open circuit potential measurements provide limited information on the kinetics of surface reactions. The open circuit potential recorded during unidirectional pin-on-disk sliding tests, in which the disk is the material under investigation, is a mixed potential reflecting the combined state of the unworn disk material and the material in the wear track. An example of the evolution of the open circuit potential before and during sliding is shown in Figure 2.

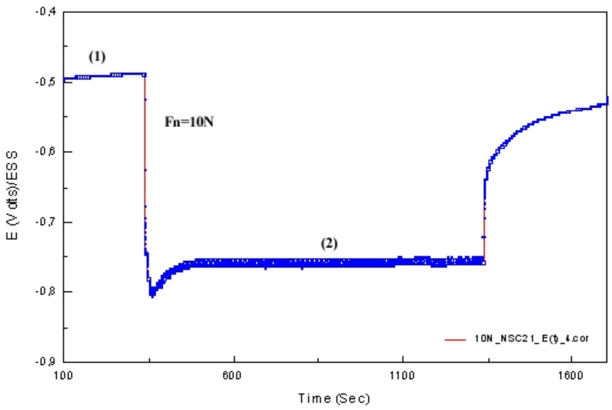

Fig. 2. Variation of the open circuit potential of Ni-SiC nanostructured coating immersed in 0.5 M K_2SO_4 before(area 1), and during sliding tests (area 2).

When friction force is applied the free potential is shutting down to active values.

(b) Polarization diagrams

More information about active and passive state can be obtained from polarisation diagrams. The polarization curves of Ni-SiC nanostructured composite coatings in 0.5 M K_2SO_4 were recorded under continuous friction (applied load 10N and 15N; 120 rpm), and without applied friction, by direct potentiodynamic scan from the hydrogen evolution potential domain up to the beginning of transpassive dissolution domain. These curves are presented in Figure 3.

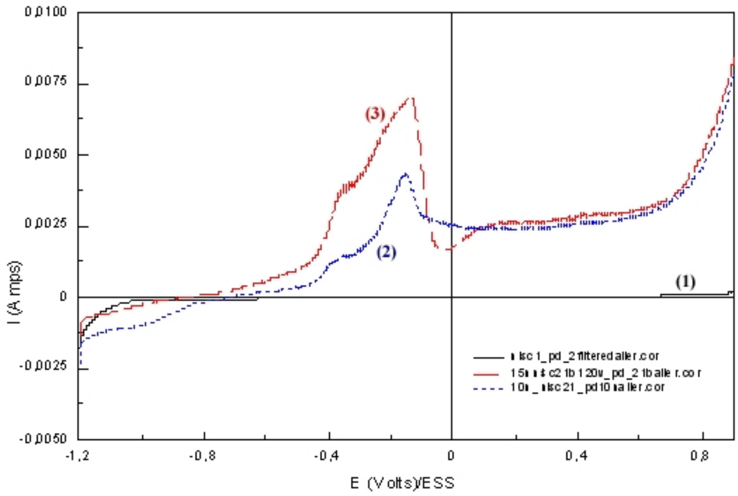

Fig. 3. Potentiodynamic polarization curves of Ni-SiC nanostructured composite coating immersed in 0.5 M K_2SO_4 recorded by direct potential scan at 0.1 V per minute. Black Curve(1): no friction applied; Blue Curve (2): continuous friction (10 N; 120 rpm);Red Curve(3): Continuous friction (15N, 120 rpm).

When friction is applied (red and blue curves), the shape of the polarization diagram changes: hydrogen evolution on composite surface is not modified, but an anodic current appears in the potential range from [-0.8 ; -0.0] V/SSE, indicating a dissolution of the coating. A first approach for interpreting the polarization curves under friction can be developed on the following considerations, based on a concept of "*active wear track*".

Under friction the measured current, I can be considered as the sum of two partial currents: I_t and I_p

$$(I=I_t+I_p)$$

I_t is the current originated from the wear track areas where the passive film is destroyed and metal is active, and
I_p the current linked to the surface not subjected to friction and that remains in passive state. We have to consider also the passive current do to the particles surfaces.

The current during sliding change from cathodic (without sliding) to an anodic one, and show a slow variation versus applied load.

(c) Current evolution during sliding at different potentials
The current during sliding change from cathodic (without sliding) to an anodic one, and slow variation versus applied load. In Figure 4 it is shown the evolution of current during sliding (Red diagram at 15 N applied force, black diagram at 10 N applied force) at imposed potential of E=-0.710V/ESS.

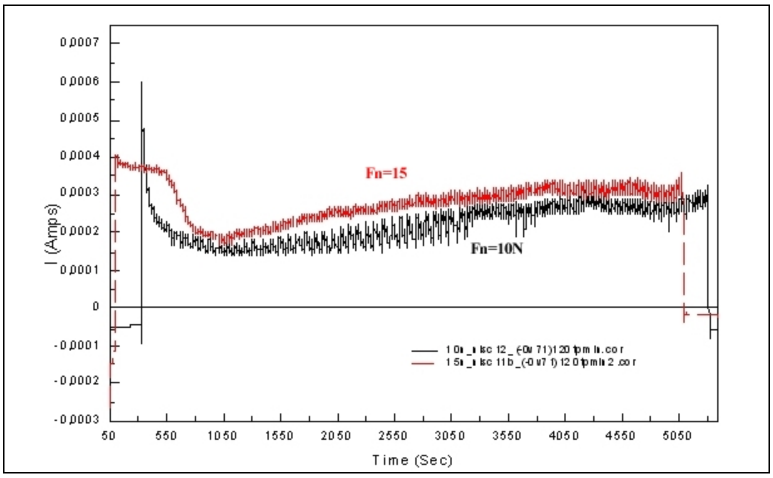

Fig. 4. Current evolution diagrams under sliding for Ni-SiC nanostructured composite coating immersed in 0.5 M K_2SO_4 recorded under sliding: Red Curve (1): continuous friction (15 N; 120 rpm); Black Curve (2): Continuous friction (10N, 120 rpm).

Structural aspects

The SEM images of nano and micro composite surfaces are shouwn in Figs 5 and 6.

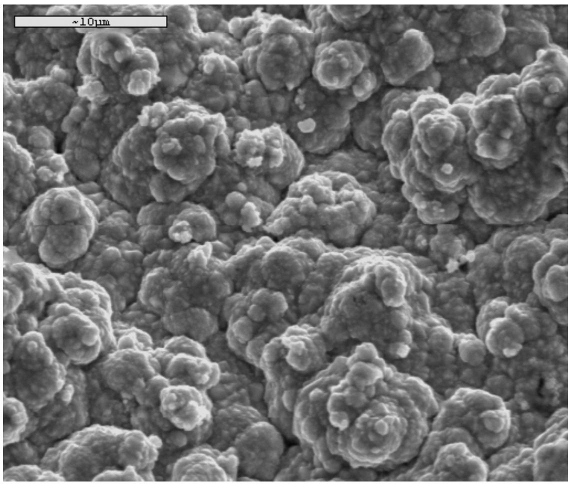

Fig. 5. Nano structured Ni-SiC (20 nm) coating before tribocorrosion tests.

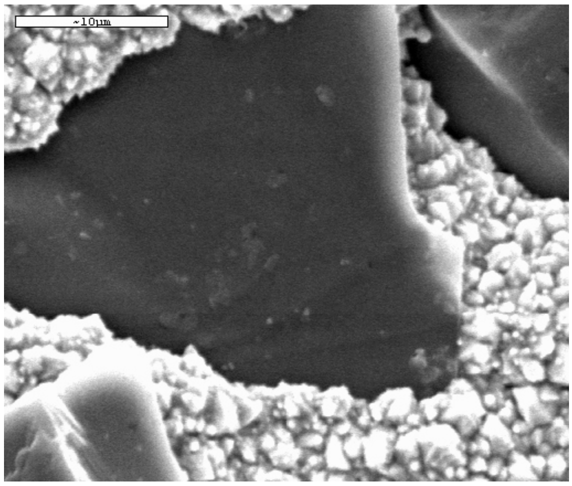

Fig. 6. Micro structured Ni-SiC (20 μm) coating before tribocorrosion tests.

After tribocorrosion tests the samples were investigated with a SEM. Few images are presented in Figs. 7-9.

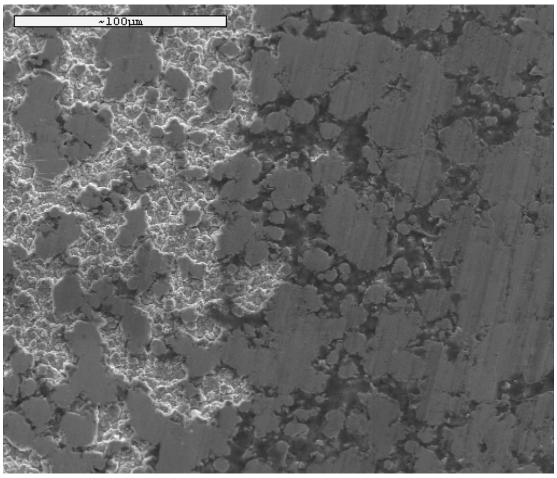

Fig. 7. SEM image of wear track on Ni-SiC (20 nm) nano composite surface (10 N and 120 tours/min, 10000 tours of friction).

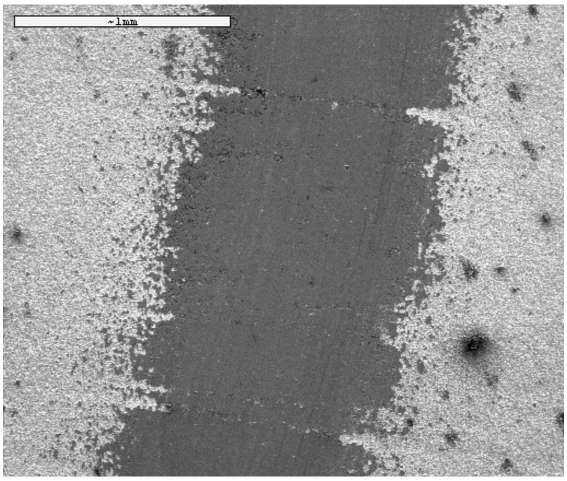

Fig. 8. SEM image of wear track on Ni-SiC (20 μm) micro composite surface (10 N and 120 tours/min, 10000 tours of friction).

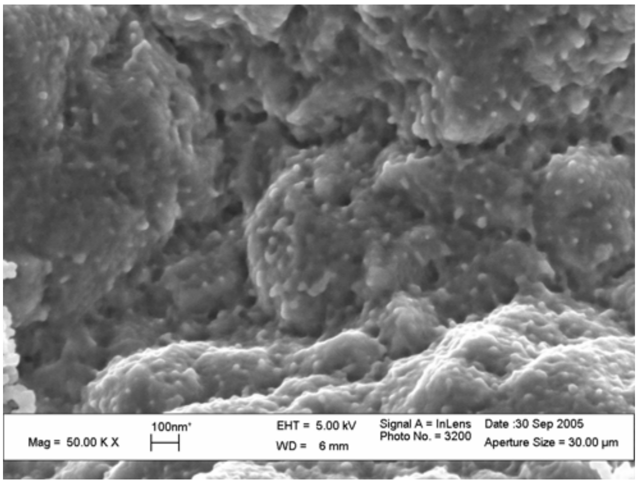

Fig. 9. Nano composite Ni-SiC (20nm) coating surface far from wear track: 10 N and 30 tours/min, 10000 tours of friction

In the near area along the wear track and far from the wear track no visible corrosion effects were observed. Comparing the behaviour of nano and microstructured coatings with a previous work on Co-Cr alloy (Stellite6) published (*L. Benea, P. Ponthiaux1, F. Wenger, J. Galland, D. Hertz, J. Y. Malo; Wear, Special Issue Wear Modelling, 256, Issues 9-10, p. 948-953, (2004)*) we could observe that the composite coatings are better that satellite 6 hard facing coating. On Stellite 6 we could observe the localised corrosion in the near area along the track for the same tribocorrosion tests. The compared SEM images for nano structured Ni-SiC composite coating and Stellite 6 hard coating are presented in Figs 10 snd11.

Detailed SEM images on nanostructured Ni-SiC (20nm) in the near area along the track surface after tribocorrosion tests confirmed that there are not localised corrosion effects, see Figs. 12 a nd b.

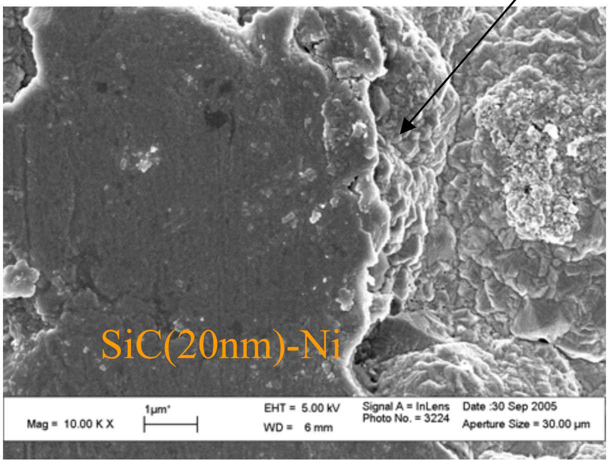

Fig. 10. SEM image of near area along the track of nano structured Ni-SiC (20nm) composite surface after tribocorrosion test: 10 N and 30 tours/min, 10000 tours of friction.

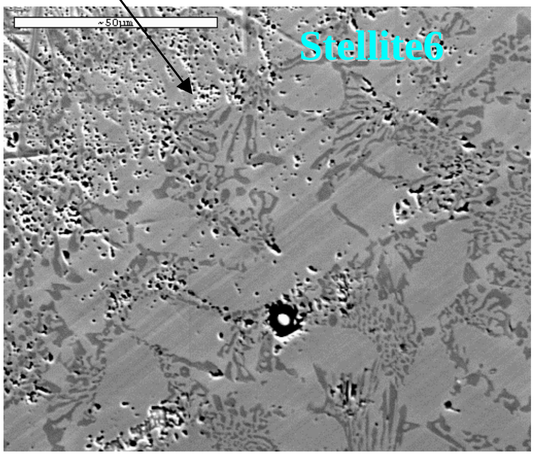

Fig. 11. SEM image near area along the track of Stellite6 hard face coating after tribocorrosion test: 10 N and 30 tours/min, 10000 tours of friction.

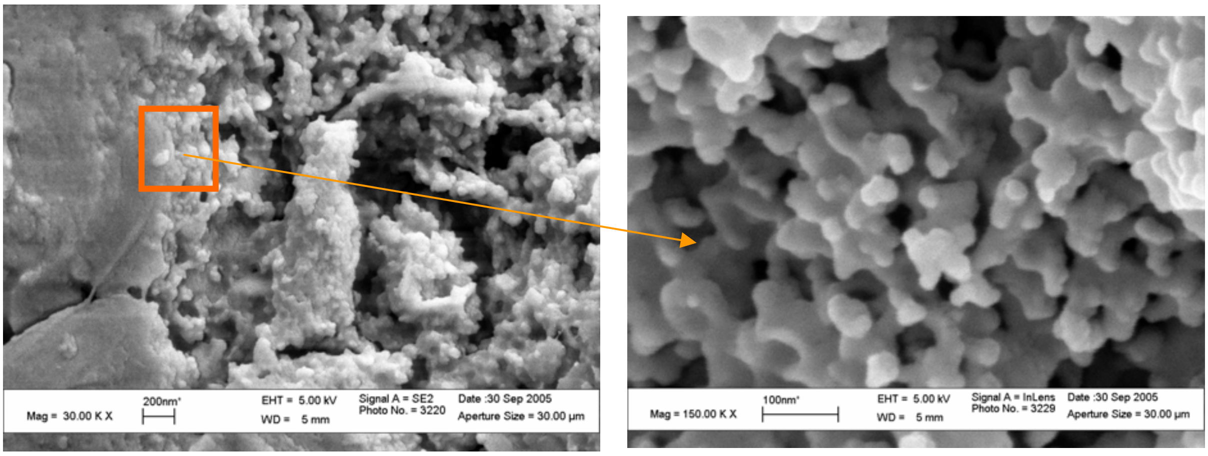

Fig. 12 a. Detailed SEM image of near area along the track of nano structured Ni-SiC (20nm) composite surface after tribocorrosion test: 10 N and 120 tours/min, 10000 tours of friction. 12 b. Zoom on marked surface from Fig 6.a.

Analysing the wear track for all sliding speeds we could not observe localised corrosion in the tracks.

As a first conclusion is that we could avoid the tribocorrosion process on nano and micro structured composite surfaces. The effects of nano and microstructure on localised corrosion have to be proved from more experimental work.

Microtopographic survey of the worn surface

Local wear in the wear track was also measured. It was deduced from surveys of the wear track recorded with an optical high resolution microtopograph, with a lateral resolution of 1 µm and a vertical resolution of 30 nm: the volume of the wear track was measured and the corresponding weight loss was calculated. On Figures 13 are presented a wear track optic image surface and 3D microtopographic surface measured after intermittent sliding test on Ni-SiC (20nm) nanostructured composite coating, with 10N sliding force and 120 rpm, after 10000 tours.

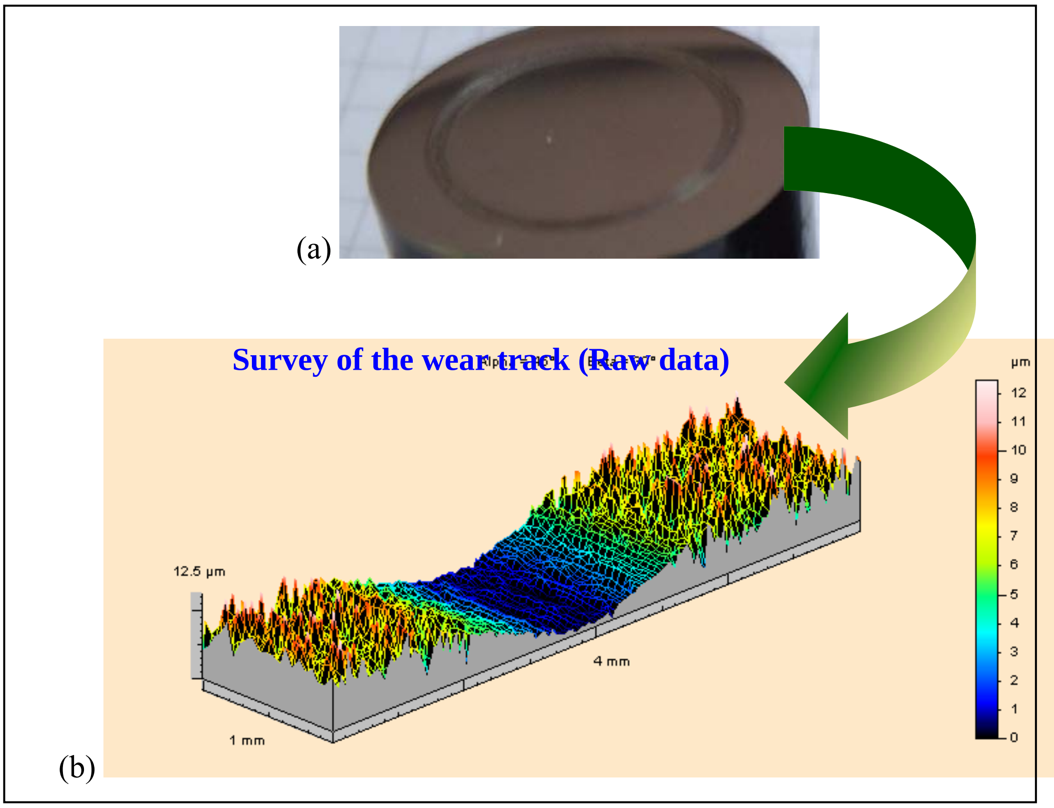

Fig. 13. (a) Optic image of wear track; (b) 3D Microtopograph image of wear track area after continuous sliding of Ni-SiC nanostructured composite coating (Fn=10N, 120 rpm, 10 000 tours).

After data processing to eliminate roughness we could calculate the wear loss and transformed after in wight loss function of tribocorrosion parameters.

At higher sliding speed of 120 t/min and smaller applied friction force (5N) the wear track was non measurable (Only flattening of roughness could be observed).
Tribocorrosion rate were calculated and compared with previous work of nickel pure coatings. In Fig. 14 are presented the summary results obtained.

The introduction of a harder reinforcing phase in the ductile matrix by a certain volume fraction can reduce ductility of the matrix material in the contact region and wear of the matrix can be reduced as a result.

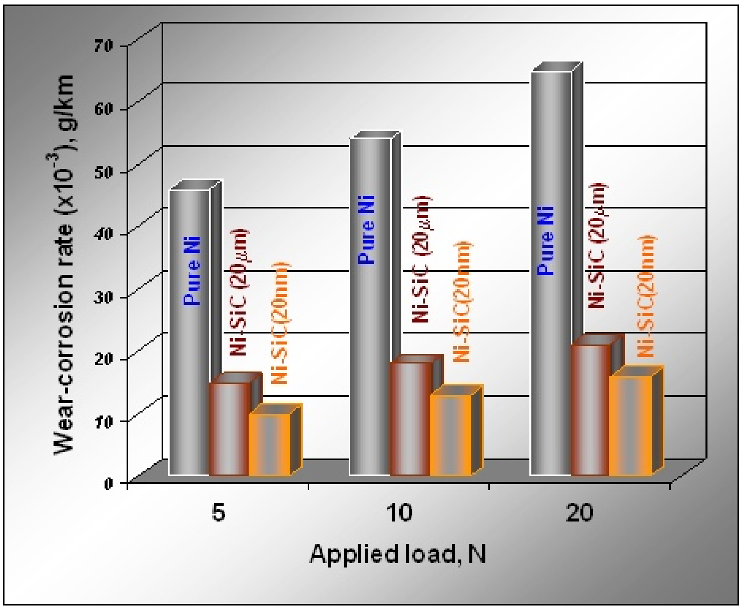

Fig. 14. Wear – corrosion rate of nano (Ni-SiC 20nm) and micro(Ni-SiC 20 μm) composite deposits in 0.5M K_2SO_4 solution at different applied sliding loads compared with pure nickel coating.

Conclusions

Nano and micro SiC could be codeposited with nickel to obtain composite coatings:

*nanostructured
*microstructured

The particles perturb the nickel crystal growth resulting in a random than preferred orientation of nickel matrix. Higher perturbation was observed in the case of nanoparticles than that of microsized particles. Good uniformity of dispersed phase inside of coating is related to a good omogenisation of electrolyte. Easier for nano particles to be omogenous suspended in the electrolyte. The tribocorrosion behaviour of nano and micro sized dispersed Ni-SiC (20nm and 20 µm) composite coatings in a pin on disk sliding system in 0.5 M K_2SO_4 solution was investigated combined with *in-situ* electrochemical (potential and polarization diagrams) measurements and *ex-situ* SEM –EDS and microtopographic surveys. A localised corrosion process when subjected to friction in 0.5 M K_2SO_4 was not observed on nano and micro structured Ni-SiC composite coatings. The mechanical destruction of the passive film occurs in the wear track by friction, and subsequent restoration of the film (repassivation) when friction stops. The wear volume loss increases with sliding forces.

Project co-operation

The forms of co-operation used in our project:
e-mail contacts, STSM – COST Short Term Scientific Missions, Bilateral Research Project Cooperation, meetings, seminars, researchers visits, joint publications, joint presentations at international conferences.

Industrial improvements in commercial use

Industrial improvements are planned at the end of laboratory testing.

Publications were project results are reported

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6. Lidia Benea, Geta Carac; 2006; *Dispersed Nano and Micro Structured Composite Coatings Obtained by Codeposition of Ceramic Particles with Nickel*. Proceeding Volume of *6th International Symposium on Electrochemical Micro & Nano System Technologies, EMNT 2006,* organizat de Max-Planck-Institut für Eisenforschung, Düsseldorf si tinut la Bonn, Germany in perioada 22 august – 25 august 2006, p.33.
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8. Lidia Benea; 2005, Interfaces, Corrosion and Electrochemical Systems – research in nano and micro materials. *Micro and Nanotechnologies Bulletin*. Vol 6/ No.4, December 2005, pp. 8-9. Edited by: IMT Bucharest and Ministry of Education and Research, Romania.
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10. G. Cârâc; L. Benea; C. Iticescu; T. Lampke; S. Steinhäuser; B. Wielage; 2004, *Codeposition of Cerium Oxide With Nickel and Cobalt: Correlation Between Microstructure and Microhardness*; Surface Engineering, vol. 20, no. 5, pp. 353-359.
11. F. Wenger, P. Ponthiaux, L. Benea, J. Peybernès; 2004, *Tribocorrosion of Stellite 6 alloy: mechanism of the electrochemical reactions.;* CD ROM Proceeding EUROCORR 2004 – Long term prediction & Modeling of Corrosion, Nice, Franta, 12-16 septembrie 2004.
12. A. Berradja, F. Bratu, L. Benea, G. Willems, J.P. Celis; 2004; *Effect of sliding wear on tribocorrosion behavior of stainless steel materials in a Ringer's solution*.; CD ROM Proceeding EUROCORR 2004 – Long term prediction & Modeling of Corrosion, Nice, Franta, 12-16 septembrie 2004.
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CH11 - INFLUENCE OF MOLECULAR STRUCTURE ON LUBRICANT PROPERTIES AND PERFORMANCE

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Project status and schedule

The project has been run successfully and ended by September 2006
Project start date: January 1, 2001, accepted as a COST project in 2005.

Project aims

To increase the understanding about how molecular parameters are related to the physical behaviour of lubricants. Study the additive response mechanisms for environmentally adapted base fluids.

From such knowledge it will be possible to make "tailor-made" lubricants, i.e. to develop lubricants with optimum properties for certain application.

Project results

12 different base oils are selected together with the project partners, some of the tested fluids are shown I table 1. All of the tested fluids are synthetic esters except some reference fluids. All esters are environmentally adapted and partly made of renewable base stocks.

Table 1. Some of the tested base fluids.

#	Fluid	Trade name	κ_{40} [cSt]	Molecular formula
G	TMP oleate	P 2089	43.78	$C_{60}H_{110}O_6$
H	Improved TMP oleate	DP 5146	48.16	N/A
I	PE oleate	P 1445	71.64	$C_{77}H_{140}O_8$
J	NPG ISO C18	P 1973	45.38	$C_{41}H_{80}O_4$
K	NPG C16-C18	P 1923	42.00	$C_{39}H_{76}O_4$
L	Complex ester	DP 5148	44.05	N/A
M	Mineral oil reference	SN 215	46.79	N/A

The base fluids are characterized and the results are put into a database. The fluid characteristics that were determined included, viscosity-temperature-pressure-effects, $\eta(p,T)$ known as alpha and beta(VI). Thermal conductivity $\lambda(p,T)$, heat capacity per unit volume, $\rho C_p(p,T)$, for an example of thermal properties see figure1 and table 2.

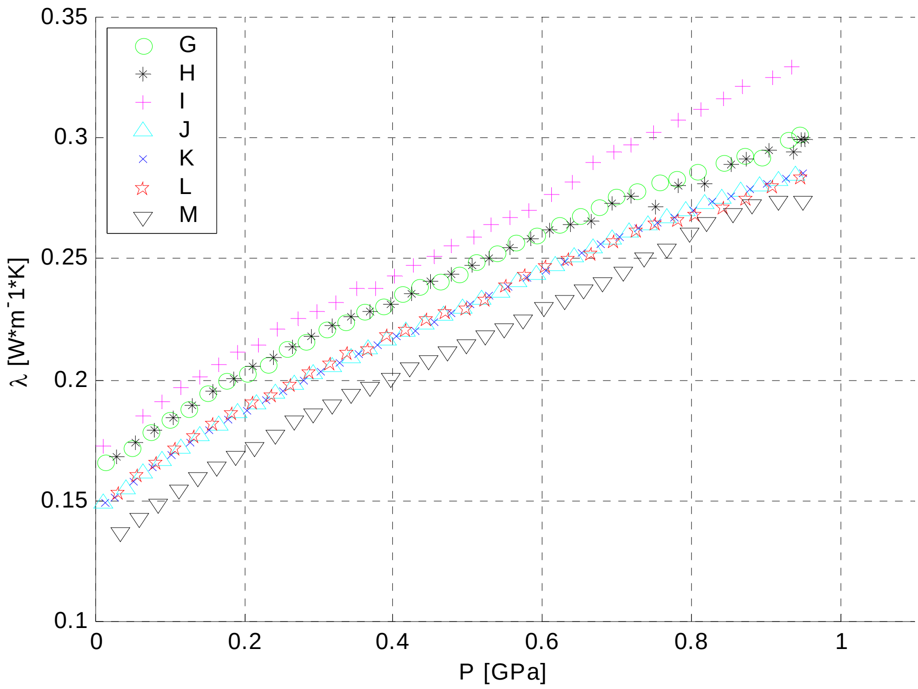

Fig. 1. Thermal conductivity for some of the tested fluids.

Table 2. Thermal properties for some of the tested fluids.

#	λ_0@20°C [W/m °C]	λ_0@80°C [W/m °C]	ρC_{p0}@20°C [MJ/m^3 °C]	ρC_{p0}@80°C [MJ/m^3 °C]
G	0.16	0.16	1.78	1.78
H	0.162	0.162	1.80	1.80
I	0.17	0.16	1.83	1.90
J	0.142	0.135	1.79	1.88
K	0.143	0.14	1.79	1.85
L	0.142	0.14	1.85	1.92
M	0.13	0.125	1.73	1.80

Density, different molecular parameters and a number of environmental properties where also measured. The film forming capability for the fluids are investigated by the use of optical interferometry in a ball and disc apparatus. The result from that study was correlated against the base fluid properties. It was found that synthetic esters are better to maintain a lubricating film under severe sliding than mineral oil, because of better thermal properties.

The running-in properties of a hydraulic rotator of vane type is studied. The contact between the vane nose and the stator ring are studied in detail. A pin on disc configuration tribometer was used for the tribotests. The pin was made out of a slice from a real vane and the disc was manufactured of same material and with the same process such the real stator ring.

The collected data was friction, wear and electric contact resistance. A new method where used to be able to measure the changes in surface topography at a specific location during the test. The results shows that the relocation method are useful for monitoring small changes in surface topography under running-in, but the most significant parameter for detection running-in for this application are electric contact resistance. The results show that the plane cut disc has better running-in properties than the turned.

The effects of some special additives where investigated during a visit to Iwate University in Japan and the formed surface film are analysed with XPS technology. The analysis of the experiments is finished and will be presented during the autumn 2006.

Project co-operation

E-mail contacts, meetings, seminars, researchers visits, joint publications.

Planned or achieved industrial improvements in commercial use

Statoil Lubricants, new guidelines for selection and additivation of environmentally adapted base fluids.

Indexator AB, new guidelines for fine tuning of machined surfaces properties.

Publications were project results are reported

1) Running-in studies of a hydraulic rotator. Pettersson A., Carlevi J., Kassfeldt E. and Larsson R. 2006. Conference paper. Pressented at Tribology and Lubrication Engineering, Esslingen, January 2006.

2) Film formation capability of environmentally adapted base fluids. Pettersson, Anders., Lord, John., Kassfeldt, Elisabet. 2004. Conference paper. Presented at IJTC -04, Long Beach, 24-27 Oct, USA, 2004.
3) High performance base fluids for environmentally adapted lubricants. Pettersson, Anders. 2004. Conference paper. Presented at the 11th Nordic Synposium on Tribology, NORDTRIB. June 01-04, Norway.
4) Properties and Performance of Environmentally Adapted Lubricants. Pettersson, Anders. 2004. Licentiate Thesis.
5) Tribological characterization of environmentally adapted ester based fluids. Pettersson, Anders. 2003. Journal paper. Tribology International, Vol 36, Issue 11, 2003, pp. 815-820.
6) Properties of Base fluids for Environmentally Adapted Lubricants. Pettersson, Anders, Larsson, Roland, Norrby, Thomas, Andersson, Ove. 2002. pp. 52-55, Handbook of Tribology and Lubrication, vol. 10, Wilfreid J. Bartz, Expert Werlag, ISBN:3-8169-2107-8.
7) Environmentally adapted ester based fluids. Pettersson, Anders. 2002. Conference paper. Presented at the 10th Nordic Synposium on Tribology. NORDTRIB 2002, June 9-12, 2002.
8) Properties of Base fluids for Environmentally Adapted Lubricants. Pettersson, Anders. 2001. Master Thesis. ISSN:1402-1617.
9) Properties of base fluids for environmentally adapted lubricants. Pettersson, Anders, Larsson, Roland, Norrby, Thomas, Andersson, O. 2001. Conference paper. Proc of 2nd World Tribology Congress, Vienna, September 3-7 2001.

CH12 - THE INFLUENCE ON FRICTION AND WEAR OF AGED ENVIRONMENTALLY ADAPTED LUBRICANTS

Co-ordinator and partners

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Project status and schedule

Finished
Start date: January 1st 2004
End date: December 31st 2005 – Experiments are complete but final articles are to be published shortly. Some additional material analysis is also being performed in an attempt to obtain even more useful information.

Project aims

The principal aim of this project was to investigate the feasibility of replacing currently employed mineral oils with environmentally adapted lubricants through an investigation of their impact on components in tribological contacts in terms of friction and wear. An understanding of the chemical effects is also paramount to this investigation

Project results

Tests are performed using a tin-bronze on steel contact. A tin-bronze pin is loaded against a rotating medium carbon steel disc. This is intended to simulate the sliding contact between a tin-bronze bushing and a steel shaft e.g. as found in a Kaplan hydro-turbine blade mounting.

The oils investigated in this study are all fully formulated lubricants containing (in their fresh state) antioxidant and corrosion inhibiting additives. The specific fluids are

- Oil A - a commercially available unsaturated synthetic ester based hydraulic fluid (ISOVG32)
- Oil B - a mineral based turbine oil (ISOVG68)
- Oil C - a saturated synthetic ester based lubricating fluid (ISOVG46).

The tribological performance of the (unaged) fully formulated saturated ester in an oscillatory bronze pin on steel plate test at 15 MPa loading was found to be superior to that for the other fluids due to low friction and wear. This can be an effect of the formation of a soft, ductile outermost copper layer in the contact and a slight hardening below the surface. This was not seen with the mineral oil lubricant.

As the tin-depleted layer thickens at higher load, wear increases and the principal surface wear mechanism changes correspondingly from abrasive to adhesive. Adhesive contact mechanisms cause fluctuating friction and higher wear, seen primarily at higher load. Some differences in wear mechanism were seen between the tested lubricants at the different load settings.

The three turbine oils were then subjected to an oxidation process encompassing a modified dry-TOST method (ASTM D 943), performed at 120°C with oxygen and iron-copper catalysts.

After the ageing process, the oils were analysed and studied using several different means of physical and chemical analysis to determine how their characteristics and properties had changed. As expected, the saturated ester showed excellent ageing behaviour, clearly out-performing the mineral based turbine fluid. Table 1 shows data corresponding to the aged fluids.

Table 1. Oil Data - aged oils.

Test fluid	**Viscosity 40°C** (mm^2/s)	**Viscosity 100°C** (mm^2/s)	**Density 15°C** (kg/m^3)	**Acid number** (mgKOH/g)
A_1	41.8	8.6	924.8	2.8
A_2	45.5	8.8	926.3	3.9
A_3	46.5	9.0	927.8	4.0
B	83.0	9.4	891.0	2.4
C	49.3	8.5	927.3	2.6

Experiments to measure friction and wear were carried out using a standard pin-on-disc configuration with the bronze pin and steel disc at a loading of 15 MPa and sliding speed of 1 cm/s.

Table 2 shows typical values for the peak coefficient of friction (at run-in) as well as values after 60 and 130 hours respectively. Where a range of values is shown, more than one test has been carried out.

Table 2. Coefficient of friction during tests.

Test fluid	**Coefficient of Friction**		
	Peak	**60 hours**	**130 hours**
Oil A			
Fresh	0.13	0.09 - 0.11	0.10
Aged (1)	0.13	0.08	0.05
Aged (2)	0.12	0.10	0.07
Aged (3)	0.13	0.07	0.04
Oil B			
Fresh	0.13	0.06 - 0.07	0.07
Aged	0.12	0.04 - 0.06	0.04
Oil C			
Fresh	0.18	0.11 - 0.12	0.11
Aged	0.14	0.08 - 0.11	0.07 - 0.09

It is clearly seen that friction is reduced for the aged samples of all three oils in comparison to results for the fresh fluids.

Figure 1 shows the relative wear rates in terms of sliding distance for the various test fluids.

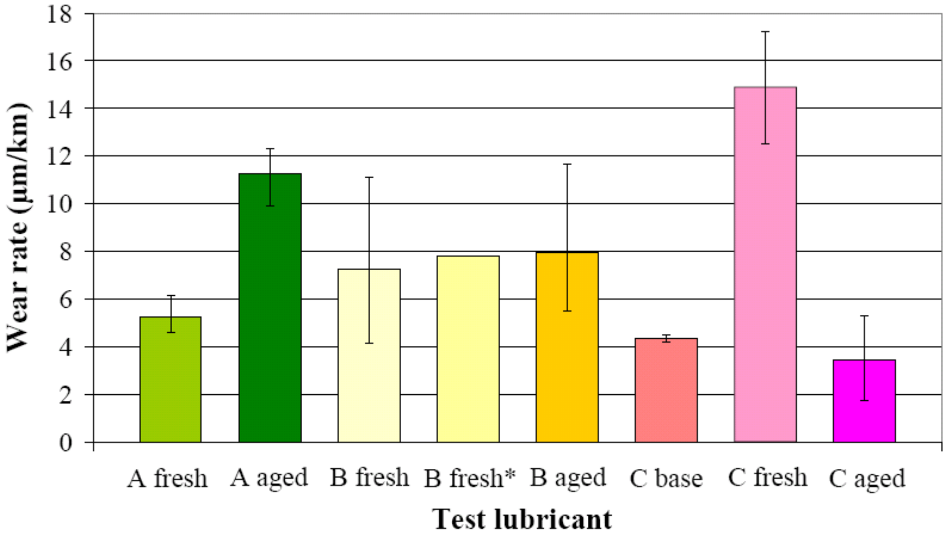

Fig. 1. Wear rates in terms of sliding distance for tests performed with fresh and aged samples of the three oils. Data for fresh oil B from a separate study (B fresh) is also shown in this diagram to assist comparison of test methods.*

It is clear from results obtained for friction and wear, most notably for the saturated ester, that ageing of the fluid does not catastrophically reduce the performance of the lubricants. Indeed, it actually improves performance for the saturated ester.

- All three fluids continue to show acceptable performance even at high acid number. This precludes the occurrence of catastrophic failure of the lubricant during normal operational use.
- Coefficient of friction appears to reduce with fluid age (thicker, more viscous fluids).
- The formation of agglomerated wear particle "sludge" occurs to varying extents with the "fresh" fluids and for aged oil B but is not seen after ageing for the esters.

These conclusions show that, for the specific application and materials examined, the ester lubricants (in particular, the saturated ester) provide suitable replacements for the incumbent mineral oil.

Project co-operation

Substantial co-operation has been received from Statoil Lubricants AB, Nynäshamn (Sweden). This has involved regular contacts in regard to discussing the lubricant properties and test results as well as the writing of joint publications (presented at the 15th International Colloquium Tribology, Esslingen in January 2006).

Planned or achieved industrial improvements in commercial use

The aim of this work was to assess whether or not an existing commercially available product will function over an extended period of time in a given application. This has been shown to be so. In this sense, an industrial improvement has been achieved in an already commercially employed product.

Publications where project results are reported

1. J. Ukonsaari, D.M.C. McCarthy, B. Prakash and P. Hedström, "Tribological studies on bearing bronze-steel pair lubricated with EALs under reciprocating sliding conditions". Published in the

doctoral thesis of Jan Ukonsaari, "Tribology of Journal Bearings under Environmentally Adapted Lubrication with Shaft Oscillation", Luleå University of Technology, 2004:22 (2004), ISSN 1402-1544. This paper is currently being reviewed for journal publication.
2. M. Pach, Å. Byheden, T. Norrby, D.M.C. McCarthy, S.B. Glavatskih and E. Kassfeldt, "Aged Environmentally Adapted Lubricants – Part I: Procedures, Techniques and Affected Properties for Aged Oils". Presented at the *15th International Colloquium on Tribology*, Esslingen, January 2006.
3. D.M.C. McCarthy, S.B. Glavatskih, E. Kassfeldt, M. Pach, Å. Byheden and T. Norrby, "Aged Environmentally Adapted Lubricants – Part II: Performance Evaluation in Boundary Lubricated Contacts". Presented at the *15th International Colloquium on Tribology*, Esslingen, January 2006.

CH13 - PROCESSING OF SELF-LUBRICATED MOS_2 DOPED TIALCN NANO-COMPOSITE COATINGS BY REACTIVE UM MAGNETRON CO-SPUTTERING AND TRIBOLOGICAL PERFORMANCE OPTIMISATION BY CONTROLLED PREPARATION CONDITIONS

Co-ordinator and partners

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Project status and schedule

Starting and ending dates: November 2005 – December 2007.

Project aims

- implementation of the adaptive process control applied for reactive co-sputtering with multi-magnetron UM system;
- controlled synthesis of self-lubricated compound coatings (MoS_2 doped Ti-Al-C-N) for deposition of nano-structured multiphase composite coatings;

- determination of the parameters playing key role in the microstructure evolution and definition of the best conditions for the tribologically optimised self-lubricated hard coatings developed on the mechanical components of sewing machine.

Project results:

Synthesis of multi-component compound coatings developed by reactive magnetron sputtering of alloyed/compound targets or by co-sputtering in reactive gas mixture of the elemental targets, raised several problems in *coating optimisation*. The incorporation of a minor amount of *impurity atoms* and/or *additive elements* into the co-deposited films provide fundamental changes in microstructure, and therefore in performance of compound coatings. The main phenomena in controlling the formation of nano-composite structure, beside the nucleation, crystal growth and grain growth, are the chemical interactions of depositing species on the top-growing surface of the coating. This phenomenon contributes to the nucleation and growth of phases related to the composition of the condensing vapor beam. An important process of this phenomenon is the segregation of the components-species not incorporated by the growing majority phase. Species in excess are segregated to the growth surface and develop new phases, like minority phases. If these phases are forming a tissue phase as a bi-dimensional layers on the surface, the crystal growth and grain growth are strongly modified, inhibited. This phenomenon can be applied for controlling the grain size by refining, the texture and the nature of the grain boundary phase.

Many of industrial equipments used in deposition of thin film coatings suffer from insufficiently control of process parameters, and therefore of process reliability. That makes unlikely reproducible results in coating properties, especially in composition range associated to the hysteresis loop behavior of the reactive process. The goal of this research project was to get an *optimised controllability* of the highly unstable reactive magnetron sputtering process applied in surface engineering of mechanical components. Reactive magnetron co-sputtering technique was used to demonstrate the opportunity of adaptive control system applied in deposition of nano-composite multi-component material systems.

A completly new *DC* reactive magnetron co-sputtering system was developed in order to synthesis multi-component self-lubricated compound coatings. Owing to the strong interdependence of the process- and plasma parameters a fast signal processing and a closed loop automatic feed-back control system was implemented in the process control system for deposition of self-lubricated *MoS_2 doped Ti-Al-C/N coatings* performed in graded composition.

By technical participation of the *Dürkopp-Adler Ltd.* industrial *SME,* as a key partner of the project, dedicated model experiments for deposition of self-lubricated *TiAlCN* coatings have been performed in strictly controlled conditions. New informations were obtained on the structure evolution of the multi-elemental nano-composite coatings, which offered knowledge for *tailoring of advanced material structures in view of superior friction and wear control* of textile machine components, as needed by the industrial end-user. Software and hardware developments for automatic control of reactive co-sputtering process have been performed in accordance with enquiry of the industrial *SME* end-user. These developments provided a real time process data *PC* acquisition and process control based on the optical monitoring of glow discharge performed in correlation with in-situ plasma parameters.

Model experiments for deposition of nano-composite multilayer coatings based on *Ti-Al-C-N* components have been performed on *Si* substrate in view of *XTEM microstructure investigation*. In order to optimise the *tribological performance of dry sliding contacts of the designed MoS_2 doped* *self-lubricated Ti-Al-C-N coatings* model experiments were also performed by sample preparation both on *Co* cemented *WC* hard metal inserts and *HSS* substrates. Coatings performed on sewing machine components emerged from the production of the industrial end-user, will be evaluated in the field-test experiments.

Based on our on-going research new information are available on the:

- nucleation kinetics of possible phases at the beginning of deposition process for given materials systems;
- possible phase transformations during the growth of nucleated phases according to the composition of the vapor beam;
- phases forming by delayed nucleation as a result of the segregation of component species not incorporating into the growing majority phase(s), which phases will form the *GB* phase;
- -detailed information on the nature and performance of the closed feed-back control system and its applicability to the reproducible deposition of designed materials structures.

By *multidimensional optimisation of the process parameters* applied in process modelling and experimental design for a short control of the *PVD* technological process, the influence of deposition parameters on the resulting compound coating system with desired composition was tested also in confirmatory experiments for long-term repeatability of the process.

Project co-operation

Long term common research activities in the host laboratories of the co-operating partners, researchers meetings, joint publications and joint presentations have been performed in frame of this project.

Industrial improvements in commercial use

A versatile semi-industrial batch coating multi-cathode *UM* magnetron sputtering system was designed and constructed in co-operation with the *SME* industrial end-user partner. The newly constructed state of the art *UM* magnetron sputtering system housed in an octagonal vacuum chamber is evacuated to a base vacuum of $p = 2 \cdot 10^{-4}\ Pa$. Mass flow gas controllers are used for gas admission, which are operated in conjunction with a dynamic controlled pressure adjusting unit and plasma emission monitoring of the process parameters.

The substrates are rotated in planetary motion by the external driven supporting table and they are *IR* radiation heated. The mounted components can be biased to a highly negative voltage during of surface cleaning by inert gas ion etching, respectively for deposition of the adhesive seed-layer. Process parameters are continuously saved to a *PC* buffer and are used in forward estimation of the reactive gas partial pressure. Optical emission spectral intensity of sputtered target atoms are excited in plasma while the characteristic radiation served as plasma state parameter. Discharge current intensity and reactive gas flow rate were selected as control parameters of the process. A sophisticate fuzzy-logic controlling software has been developed for adaptive process control of the reactive gas mass flow and of discharge power intensity.

The performance of the developed system was tested in dedicated experiments performed for sample preparation of compound phases of *TiAlN*C/MoS_2, and the results indicated a very efficient means in controlling of microstructure evolution of the multi-component multilayer coatings (Fig.1 and Fig. 2).

The research activity was extended also for architecture design of *MoS_2* doped *TiAlCrN* coatings. Processing and investigation of TiAlN/CrN/MoS_2 multilayer system prepared by unbalanced magnetron reactive co-sputtering from alloyed Ti/Al: 50/50 at.%, pure chromium and MoS_2 sputter sources were performed too. The sputter sources were arranged side by side on an arc segment, therfore a broad interface of the processed multilayer thin film structures was produced. By this technique the morphology and structure of interfaces could enhance the hardness of multilayer thin films and release the strain energy due to the lattice mismatch. The thickness of the layers could be changed both by the oscillation frequency and by the discharge power applied for the targets. The deposition was performed in Ar-N_2 mixture atmosphere of 0.22 Pa working pressure.

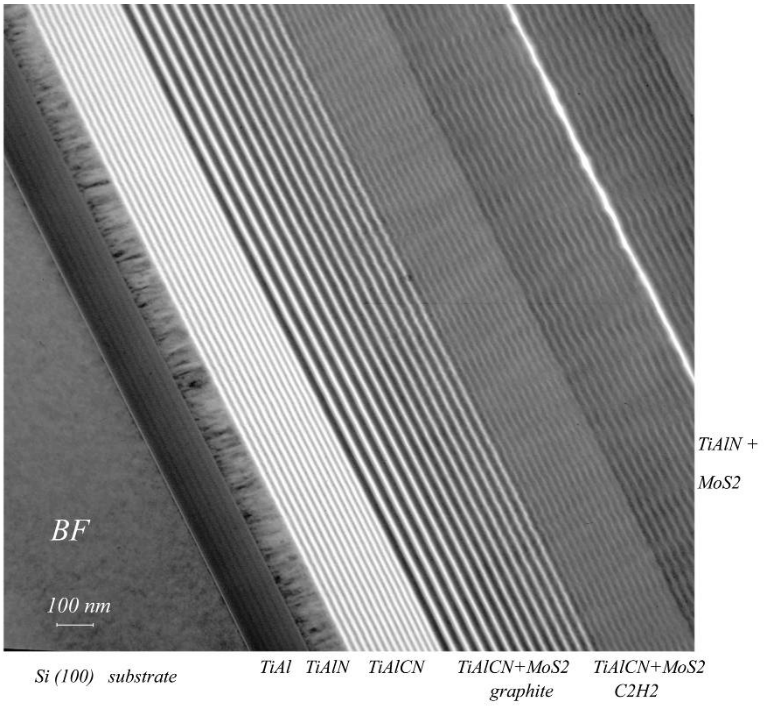

Fig. 1. Bright-field transmission electron micrograph showing the cross section image of self-lubricated MoS_2 doped TiAlCN coating developed in nano-scale multi-layer structure.

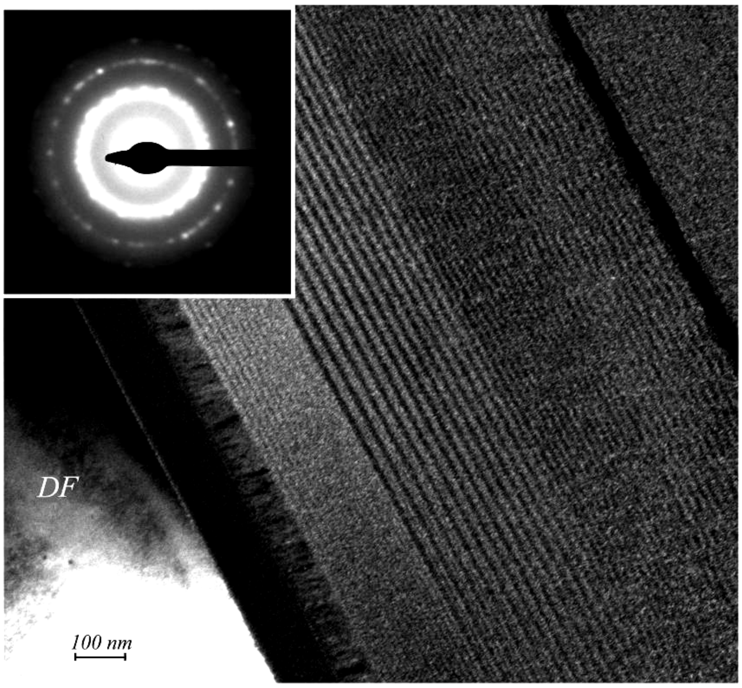

Fig. 2. Dark-field transmission electron micrograph with SAED electron diffraction pattern of the MoS_2 doped TiAlCN self-lubricating coating. The XTEM cross-section image of the as-deposited film shows a nano-grain structure (transmission electron microscope image was performed by prof. P.B. Barna in MFA-Budapest, using a 200 kV CM 20 Philips TEM microscope).

The sputtering power of TiAl source was feed-back adjusted in fuzzy-logic mode in order to avoid the fluctuation of the TiAl target sputter rate due to the poisoning of the target surface. The 4-5 *μm* thick multilayer films were deposited on high speed steel substrates for tribological measurements. The structure characterization was performed on films deposited on <100> Si wafers covered by thermally grown SiO_2. Cross sectional transmission electron microscopy and XRD were used for structure characterization. A 200 *nm* thick Cr seed-layer was deposited at first on the substrate to improve the adhesion, which was followed by a CrN transition layer. The CrN transition layer was followed by a 200 *nm* thick TiAlN/CrN multilayer system. The TiAlN/CrN/MoS_2 multilayer system was deposited on the surface of this underlayer system. The Cr, the CrN and TiAlN/CrN underlayer system was crystalline with columnar structure according to the morphology of Zone T of the structure zone models. The column boundaries contained segregated phase showing up in the underfocussed TEM images. The surface of the underlayer system was wavy due to the dome-shaped columns. The nanometer scaled TiAlN/CrN/MoS_2 multilayer system followed this waviness (Fig. 3).

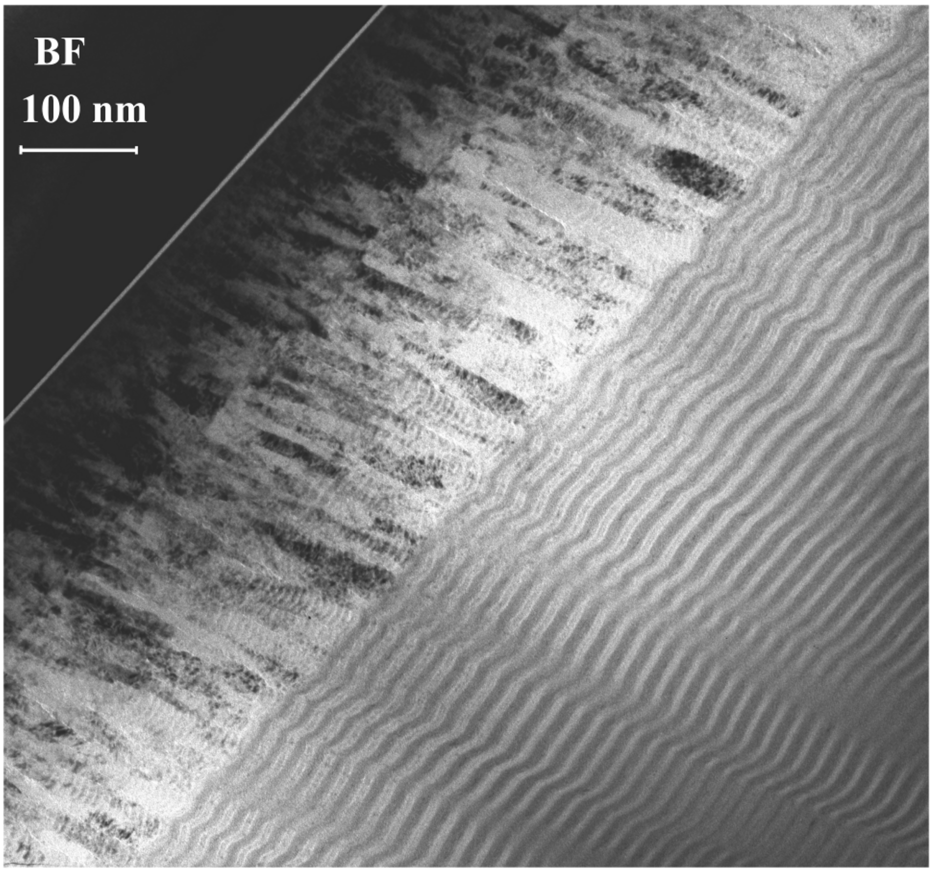

Fig. 3. The nano-scale multilayer structure of TiAlN/CrN/MoS_2 coating shown on BF XTEM-image.

The crystallinity of the TiAlN and CrN layers in the multilayer system decreased with increasing thickness of the MoS_2 layer. Conditions of the sputtering process, the influence of the plasma and process parameters on the structure and tribological properties of the films were studied. The self-lubricated multilayers were characterized in 50 % humid air atmosphere for sliding friction coefficients ranged from 0.08 to 0.12 and micro-Vickers hardness values evaluated from $HV_{0.025}$=850 to $HV_{0.025}$=2500, which were sensitive influenced by the MoS_2 crystalline phase amount and its distribution in the nanostructured coatings.

Publications where project results were reported

1. D. Biro, P.B. Barna, J. Meneve, L. Szekely, A. Devenyi, (2007), Self-lubricating nanocomposite tribological coatings of MoS_2 doped multilayered TiAlCrN films with composition-modulated interfaces, paper submitted to ECOTRIB 2007 Joint European Conference on Tribology and Final Conference of COST 532 Action: Triboscience and Tribotechnology, June 12-15, 2007, Ljubljana, Slovenia.
2. D. Biro, P. B. Barna, T. Hattori, A. Devenyi, (2007), Preparation of MoS_2 added TiAlN/CrN multilayered nanocrystalline thin films with composition-modulated interfaces, oral lecture presented on National Seminar “Nanoscience-Nanotechnology”, 26 March 2007, Bucharest, to be published in Series Micro and Nanoengineering by the Romanian Academy of Sciences, Bucharest, Romania.
3. D. Biro, P.B. Barna, L. Szekely, O. Geszti, Gy. Safran, A. Devenyi, (2007), Preparation and properties of TiAlN, CrN and MoS_2 multilayered nanocrystalline thin films with composition-

modulated interfaces, NanoSMat 2007, Algarve, Portugal, 9-11 July 2007, International Conference on Surfaces, Coatings and Nanostructured Materials (oral lecture, to be presented).

4. Strnad G., Biro D., Vida Simiti I., (2007), Researches regarding Ti-Al-N nanocomposite coatings, developed by UM reactive sputtering, International Conference on Materials Science and Engineering, BRAMAT 2007, 22-24 February, 2007, Braşov, Romania (to be published in Conference Proceedings).
5. D. Biro, A. Kovacs, L. Szekely, A. Devenyi, P.B. Barna, (2006), Microstructures in co-sputtered Al-C thin films developing at elevated substrate temperatures, in Surface and Coatings Technology 200, 6263-6266.
6. D. Biro, (2006), Relevance of process control in preparation of single layer and nano-scale multi-layer compound coatings synthesized by DC reactive UM sputtering, invited lecture, 12 October 2006, Osaka University, Japan, The Insitute of Scientific and Industrial Research Sanken, Department of Structural Characterization and Design Division of Nanocharacterization.
7. D. Biro, P.B. Barna, L. Szekely, O. Geszti, T. Hattori, A. Devenyi, (2006), Preparation of multilayered nanocrystalline thin films with composition-modulated interfaces, paper presented in Tsukuba on The 23rd World Conference of the INTDS, 16-20 October 2006, Japan (submitted to be published in Nuclear Instruments and Methods in Physics Research Section A).
8. A. Kovacs, D. Biro, P.B. Barna, (2006), Phase formation and growth in metal-composite layers (Fázisok képződése és növekedése fém-kompozit rétegekben), Workshop of IUVSTA and ELFT Vákuumfizikai Csoport, Budapest, 14 February 2006, (lecture).
9. G. Strnad, D. Biro, I. Vida-Simiti, (2006), Reactive UM magnetron sputtering of nanostructured wear resistant coatings, COMEFIM'8 The 8th International Conference on Mechanical and Precision Engineering, Acta Technica Napocensis, Series Applied Mathematics and Mechanics, 49, Vol. III. 2006, p. 787-794, ISSN 1221-5872, Technical University of Cluj-Napoca.
10. Strnad G., Biro D., Vida Simiti I., (2006), Aspects regarding the model of grain growth and structure evolution in Ti-Al-N multilayer nanocomposite coatings, 1st International Conference ″Advanced Composite Materials Engineering″ COMAT 2006, pag. 160-165, 19 – 22 October 2006, Braşov, ISBN 973-635-821-8, ISBN 978-973-635-821-0, Transylvania University of Brasov, Romania.
11. D. Biro, (2006), Processing of selflubricating MoS_2 doped TiAlCN nano-composite coatings by reactive UM magnteron co-sputtering and tribological performance optimization of controlled preparation conditions, COST 532 WG Meeting, 20-21 April 2006, Dubrovnik, Croatia (lecture).
12. D. Biro, (2006), Magnetron sputtering source-performance optimization, ISBN 973-7794-41-9, Editura Universitatii Petru Maior, p. 267-277.
13. G. Strnad, D. Biro, I. Vida-Simiti, (2006), Reactive sputtering system for self-lubricated, multiphase, wear resistant coatings, ISBN 973-7794-41-9, 2006, Editura Universitatii Petru Maior, p. 155-160.
14. G. Strnad, D. Biro, I. Vida-Simiti, (2006), Study of process parameters for reactive sputtering of self-lubricated nanocomposite, wear resistant coatings, ISBN 973-7794-41-9, 2006, Editura Universitatii Petru Maior, p. 161-166.
15. Strnad G., Biro D., Vida Simiti I., (2006), Contributions to processing of self-lubricated, nanocomposite wear resistant coatings by reactive UM magnetron co-sputtering, Matehn06, Fourth international Conference on Materials and Manufacturing Technologies, 21-23 September 2006, Cluj-Napoca (lecture).
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17. B. Barna, D. Biro, A. Kovacs, (2005), Fundamentals of the structure evolution in co-deposited multicomponent polycrystalline thin films, 2nd HIPIMS-ABS Days Advances in Industrial PVD Technologies, Workshop organized by Sheffield Hallam University, Sheffield 12-13 July 2005, (lecture).
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CH14 - SYNTHESIS AND CHARACTERISATION OF NANOSTRUCTURED MATERIALS WITH POSSIBLE TRIBOLOGICAL APPLICATIONS

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Project status and schedule

The project has finished (2003-2006)

Project aims

The main aim of the project is the synthesis of nanostructured systems for tribological applications. An improvement in the tribological behaviour (hardness, friction coefficient and wear resistance) of the new deposits, associated with the nanostructure, was expected. Different vapour phase methods (CVD and PVD) have been developed for depositing nanostructured carbon based materials.

Project results

As we proposed, our objective was the synthesis of nanostructured systems for tribological applications, because of the expected improvement in the tribological behaviour of the coatings due to the formation of the nanostructures. Then, we investigated the synthesis of BC_xN and carbon coatings, with better tribological properties using IBAD (Ion Beam Assisted Deposition) and ECR-CVD (Electron Cyclotron Resonance assisted Chemical Vapor Deposition) respectively. In the following we described the main results obtained along the study:

A) AMORPHOUS *BC_4N* COATINGS

Amorphous BC_4N thin films with a thickness of ~2 μm have been deposited by Ion Beam Assisted Deposition (*IBAD*) on hard steels substrates, in order to study the wear behavior under high loads and the applicability as protective coatings. The bonding structure of the a-BC_4N film was assessed by X-ray Absorption Near Edge Spectroscopy (XANES) and Infrared Spectroscopy, indicating atomic mixing of B, C and N atoms, with a proportion of ~70% sp^2 hybrids and ~30% sp^3 hybrids. Nanoindentation shows a hardness of ~18 GPa and an elastic modulus of ~170 GPa. A detailed tribological study is performed by pin-on-disk tests, combined with spectro-microscopy of the wear track at the coating and wear scar at pin. The tests were performed at ambient conditions, against WC/Co counterface balls under loads up to 30 N, with the sample rotating at 375 rpm. The coatings suffer a continuous wear, at a constant rate of $2x10^{-7}$ mm^3/Nm, without catastrophic failure due to film spallation, and show a coefficient of friction of ~0.2.

A-EXPERIMENTAL

Coating deposition

As substrates for the mechanical tests we used high speed steel pieces (AISI-M1) with hardness 64 HRC (~8 GPa Berkovich hardness), dimensions 45x30x5 mm^3 and polished to an rms roughness of 10 nm. Additional characterization was performed on coatings grown on two-faced polished Si(100) wafers. Prior to insertion in the vacuum chamber, the steel substrates were chemically cleaned in acetone and ethanol ultrasonic baths. Once under vacuum and before coating deposition, the substrates were annealed at 200ºC for 6 hours followed by ion bombardment cleaning for 2 minutes using a 0.02mA/cm^2 flux of 300eV Ar^+ ions. The Si substrates were chemically cleaned *ex situ*, followed by *in situ* Ar bombardment.

The BC_4N coatings were deposited at room temperature by Ion Beam Assisted Deposition (IBAD), by using two electron gun evaporators as sources of B and C atoms (AP&T CARRERA, mod. EVM-5 and EV1-8,) and a Kauffman ion gun (Commonwealth Scientific, mod IBS) for assistance with N_2 gas, installed in a High Vacuum Chamber with $1x10^{-6}$mbar base pressure. To achieve the BC_4N stoichiometry we used simultaneous impinging fluxes of $4x10^{15}$ at/cm^2·s, $4x10^{15}$ at/cm^2·s and $1x10^{15}$ ions/cm^2·s for B,C and N, respectively, in accordance to previous results. The evaporators were run at a power of 700W for B and 1500W for C. Assistance was performed at 50º incident angle with a N_2^+ ion current of 0.16 mA/cm^2 at 500eV. The working pressure was kept constant at $1x10^{-4}$ mbar.

The adhesion between substrate and coating was improved by the use of a Ti(N) interlayer, because the direct growth of the BCN coating on the precleaned steel resulted in film delamination during the mechanical tests, due to insufficient adhesion. This is a common problem for boron coatings on steel, because brittle Fe_xB compounds are formed at the interface, as occurs in the boriding of steel surfaces [1,2]. To overcome this difficulty we tried several interlayer formulations, finding out that a Ti(N) ramp layer about 0.5 µm thick composed of Ti at the interface with the substrate and TiN at the interface with the coating provides enough adhesion to permit the tribological studies with loads as high as 30 N. The Ti(N) ramp layer was formed on the M1 steel substrate by Ti evaporation with nitrogen ion assistance at increasing ion current. Our results are in agreement with previous studies that have shown that the use of pure Ti and TiN interfaces enhance the adhesion of TiN , DLC and c-BN coatings.[3,4,5]

Film characterization

Energy Dispersive X-Ray (EDX) analysis were performed to determine the composition of the coatings at different points of the wear scar and of the ball after the pin-on-disk tests. The bonding structure of the BC_4N coating was studied by X-Ray Absorption Near Edge Spectroscopy (XANES) at the beamline SA72 of LURE synchrotron in Orsay, France, and at the PM3 beamline of BESSY-II in Berlin, Germany.

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[5] C.C. Chen, A. Erdemir, G.R. Fenske, Surf. Coat. Technol. 39/40 1989 365.

The tribological properties of the BC_4N / Ti(N) / M2 steel system were tested with a TPD/10 Microtest® pin-on-disk apparatus, which provides a continuous measurement of the coefficient of friction. All the measurements were performed by sliding a 3mm diameter ball of WC/Co-6% on a flat plate rotating at 375 rpm angular speed supporting the coating/substrate, with a fixed radius of 1 mm. Normal loads of 3N, [1]3N, 20N and 30N were used. The apparatus was enclosed on an isolated cage to control the atmosphere. The tests were performed in air with a humidity of 22±2% and a temperature of 24±2 ºC. The wear experienced by the flat substrate was determined through the measurement of the wear track profile by using a Dektat 3030 profilemeter, with a resolution of ~10 nm. The wear experienced by the ball was estimated through optical and SEM microscopy of the ball contact area. Nanoindentation of the samples was carried out in the continuous stiffness measurement (CSM) mode with a Nanoindenter® II system to determine the hardness and elastic modulus.

A-RESULTS AND DISCUSSION

Type of bonding.

We used X-ray Absorption Near-Edge Spectroscopy (XANES) for studying the bonding structure of the deposits. B(1s), C(1s) and N(1s) XANES spectra of the BC_4N coatings considered here are shown in Figure 1, together with reference spectra from diamond, graphite, h-BN and c-BN, as characteristic materials with sp^2 and sp^3 bonding structures. In the studied BC_4N compound, the XANES spectra at the three edges show a significant proportion of π^* states, indicating that the bonding structure is based mainly on sp2 hybrids, although the shift to high energies as well as their broadening reflects a complex bonding structure. Finally our XANES results indicate that a true ternary is formed, although a unique coordination between B, C and N is not taking place.

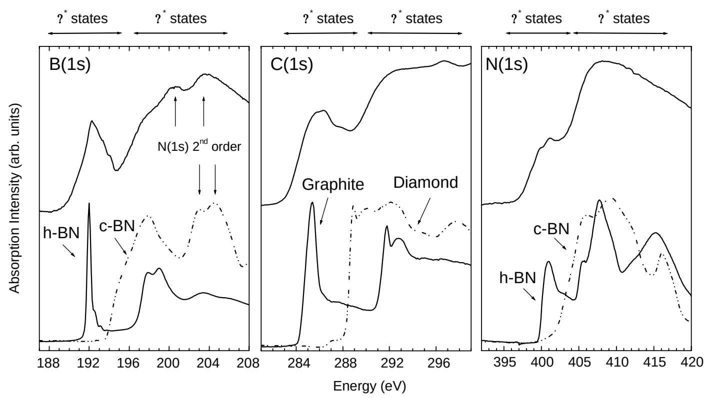

Fig. 1. XANES spectra from amorphous BC_4N films at the C(1s), B(1s) and N(1s) edges, together with references from crystalline graphite, diamond, h-BN and c-BN.

An estimate of the sp^3 fraction in this coating, obtained from the π^* over σ^* ratio at each edge, and by using the quantification method employed by J.Kulik *et al* for amorphous carbon,[6] gives an sp^3 content in the BC_4N film of ~30%.

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[6] J. Kulik, G.D. Lempert, E. Grossman, D. Marton, J.W. Rabalais, Y.Lifshitz, Phys. Rev. B 52 (1995) 15812.

Nanoindentation

Nanoindentation was performed on the continuous stiffness mode, providing hardness and elastic modulus values as a function of the indentation depth. The results are summarized in Figure 2, showing in the upper panel the Berkovich hardness as a function of the indentation depth in a 2 μm thick coating, in the lower panel the elastic modulus, and in the insert the overall load-unload curve. According to the results of Fig. 2, the coating hardness is around 18 GPa, the elastic modulus around 170 GPa, and the BC_4N samples exhibit a plastic response to the applied load, with an elastic recovery of approximately 45%.

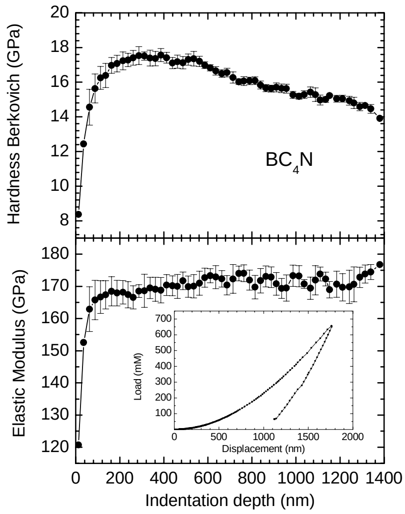

Fig. 2. Nanoindentation results showing the hardness and elastic modulus as a function of the indentation depth in continuous stiffness measurements. The insert shows the global load-unload curve.

Friction and wear

Pin-on-disk tribological tests have been carried out with normal loads of 3 N, 13 N, 20 N and 30 N, using as pin a WC ball of 1.5 mm radius. The Hertzian contact pressure for those loads is 1.25 GPa, 2.05 GPa, 2.35 GPa and 2.70 GPa, respectively. Figure 3 shows the coefficient of friction (COF) for tribology tests with applied normal loads of 13N, 20N and 30N as a function of the number of cycles and the sliding distance. In the pin-on-disk test, we are studying the wear and friction between two materials: the rotating flat specimen and the counterface ball. The relevant variable regarding the wear experienced by the coated flat substrate is the number of cycles, since each point of the rotating flat piece only experiences the ball contact once per cycle. However, from the ball standpoint, the relevant variable is the sliding distance, since the ball end is always in contact with the flat substrate.

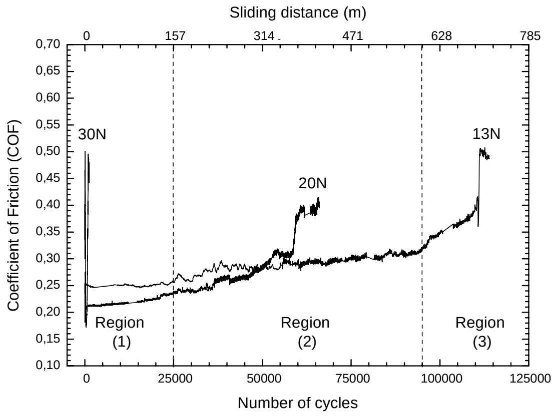

Fig. 3. Plot of the coefficient of friction vs number of cycles in pin-on-disk tests with different loads.

The three curves displayed in Fig. 3 show a similar behavior, which is described in detail for the 13 N test. We have distinguished three different regions of qualitative behaviors of friction and wear, that are shown in Fig. 3 in connection to the test with 13 N load. For the tests with loads (L) other than 13 N, the same three qualitative regions are distinguished, with their limits appearing at a different number of running cycles or sliding distance (D), but at approximately the same value of the product LxD.

Regarding the regions distinguished for the 13 N test displayed in Fig. 3, region (1) corresponds to the first 25 kcycles, and shows a COF of ~0.25 nearly constant and with a small dispersion. Wear in this first region consists in homogeneous smoothing and polishing of the surface. There is an initial stage during the first 200-400 cycles, normally denoted as the running-in period, during which the rotating plate is accelerating and the COF reaches a maximum value corresponding to the change from static to kinetic friction, and formation of the transfer layer.[7] The running-in region is not displayed in the figure, because it is hardly noticeable compared to duration of the whole test. The wear during the running-in test was below our detection limits.

Region (2) goes from 25 to 90 kcycles, shows a COF that increases very slowly with the running time and with a signal noisier than in the previous region. Wear is governed by the formation of the first microscopic holes and cracks at the surface of the BC_4N coating producing superficial delaminated areas, which increase gradually with the number of cycles. The holes in the wear track produced by the partial delamination of the coating is the cause of the jumps in the COF that gives the noisy appearance to the curve.

The final stage of the test contained in region (3) shows a gradual increase of the COF, corresponding to the complete delamination of the BC_4N coating at 95 kcycles and the wearing-out of the Ti(N) adhesive layer at 110 kycles, followed by a sharp increase of the COF to 0.4-0.5 when the steel substrate is reached. From then on (not shown), a random behavior occurs due to severe wear and large production of wear debris. The same description can be made for the 20 N curve, although the limits between regions will appear at a different number of cycles. In the description of the tribotest on coatings, other authors distinguish three periods: a running-in stage, the steady stage, and the film failure.[7, 8] Our regions (1) and (2) correspond both to the steady stage. However

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[8] Y. Özmen, A. Tanaka, T. Sumiya, Surf. Coat. Technol 133-134 (2000) 455.

due to the long duration of our wear test, a qualitative distinction can be made between these two regions.

The failure limit depends on the applied load (L), appearing at about 110000, 60000 and 500 cycles for loads of 13N, 20N and 30N, respectively. For the lower load of 3N, the coating failure did not occur within the time scale of 8 hours used in our tests. For the higher load of 30N, the film failure occurs in the running-in period and is not due to the same wear mechanism as for the lower loads. In the tests with 13N and 20N, the film failure appears at about the same value of the product of load times sliding distance (LxD), indicating similar wear mechanisms. The dependency of wear and friction with the LxD product is due to fact that the COF remains almost constant during our tribotest. Therefore, the friction force $F_{friction} = (COF) \cdot L$ can be considered as constant, and the friction work can be written simply as $W_{friction} = (COF) \cdot L \cdot D$. In a test with strong changes in COF, the dependency with the LxD product is lost, and the correlation should be done with the friction work that will take into account the changes in the COF throughout the test. Here, we must stress that tribological tests are quite reproducible when the wear mechanism is taking place continuously at a near constant rate, but have a strong random component when they are dominated by catastrophic mechanisms like film cracking. The 30 N load induces a fast degradation of the coating, either by adhesion failure or by coating cracking, establishing a high load limit for the applicability of this coating.

A-CONCLUSIONS

Amorphous BC_4N thin films synthesised by IBAD can be used as hard protective coatings of thickness exceeding 2 μm without stress build-up problems. Application of the coating to steel substrates requires the addition of a gradual buffer layer of Ti(N) to enhance adhesion and avoid formation of brittle iron borides.

The a-BC_4N material exhibits a hardness of ~18 GPa and an elastic modulus of ~170 GPa. In tribological tests against a WC/Co conterface ball, the coefficient of friction is ~0.2, and the wear rate ~$2 \cdot 10^{-7} mm^3/N \cdot m$, for tests at room temperatures in air with 22% relative humidity, rotating speed of 375 rmp, applied load below 30 N and Hertzian pressures below 2.70 GPa.

B) HYDROGENATED AMORPHOUS *CARBON* (a-C:H)COATINGS.

Hydrogenated amorphous carbon, a-C:H, films have been deposited by Electron Cyclotron Resonance Chemical Vapour Deposition (*ECR-CVD*) from argon/methane gas mixtures. The effect of the application of a dc bias on the structural, morphological and mechanical properties of the films has been explored by multiple analysis techniques such as infrared and micro-Raman spectroscopy, atomic force microscopy, nanoindentation and pin-on-disk wear testing. In the studied range of applied substrate bias (i.e. from –300 V up to +100 V) we have observed a strong correlation between all measured properties of the a-C:H films and the ion energy. From the obtained results we can conclude that the properties of the coatings can differ greatly depending on the energy of the ions arriving at the growing surface. We have detected a threshold energy in the order of 90 eV for the production of hard, low-friction coatings.

B-EXPERIMENTAL

a-C:H films have been grown in an ECR-CVD reactor operating with a 2.45 GHz microwave plasma source at 205-210 W input power. Gas mixtures of methane/argon (15/35 sccm) were applied keeping the operating pressure at $1.1\cdot10^{-2}$ Torr. A dc bias varying from –300 to +100 V was applied to the p-type silicon substrates while no intentional heating was employed. A maximum substrate temperature of only about 120 °C was found for 1-hour deposition at maximum applied substrate bias (i.e. –300 V), so any substrate temperature effect on the a-C:H film properties has been excluded. Infrared (IR) and micro-Raman spectra were taken with a 270-50 Hitachi IR spectrophotometer and a Renishaw 1001 system with 514.5 nm Ar laser light, respectively. Atomic force microscopy (AFM) characterization was performed with a Nanoscope IIIa (Veeco) equipment operating in tapping mode with silicon cantilevers. Nano-indentation tests were performed with a Nanotest (MicroMaterials, Ltd.) at loads up to 3 mN with a Berkovich diamond indenter at atmospheric conditions. Pin-on-disk wear tests were performed on MicroTest equipment using 3 mm sized WC-Co balls applying loads of 3 N and linear velocities of 0.01 m/s at atmospheric conditions.

B-RESULTS AND DISCUSSION

In Fig. 4, the a-C:H film thickness as a function of the applied dc bias is displayed for a fixed deposition time of 1 hour. In the range of bias values going from +100 V towards –150 V, the thickness increases, while for bias values more negative than –200 V, a slightly lower thickness was observed. A maximum thickness of about 1130 nm is obtained for substrate biases of –200 V and –150 V. The difference in film thickness as a function of the applied bias can be related to the operating film growth and (sub-) surface processes initiated by the incoming hydrocarbon and argon ions. At highly positive substrate biases, only radicals, neutrals and electrons will reach the growing film surface. Hence, a-C:H film growth is determined by the physisorption, chemisorption and incorporation of the hydrocarbon growth precursors only. For increasing negative substrate bias, the increasing number of impinging positive ions will increase the sticking of the radical growth precursors through the creation of dangling bonds. This will ultimately lead to enhanced film growth. However, at ion energies larger than the threshold energy required for physical sputtering[9,10], the sputtering of bounded carbon atoms will negatively influence the overall growth rate and results in a optimum growth rate at about –200 V.

[9] Weiler M., Sattel S., Giessen T., Jung K., Ehrhardt H., Veerasamy V.S., Robertson J. Phys. Rev. B 1996;53:1594-1608

[10] Yamashita Y., Katayose K., Toyoda H., Sugai H. J. Appl. Phys. 1990;68:3735-3737.

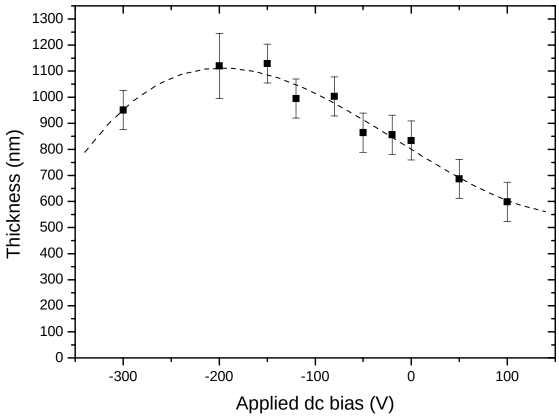
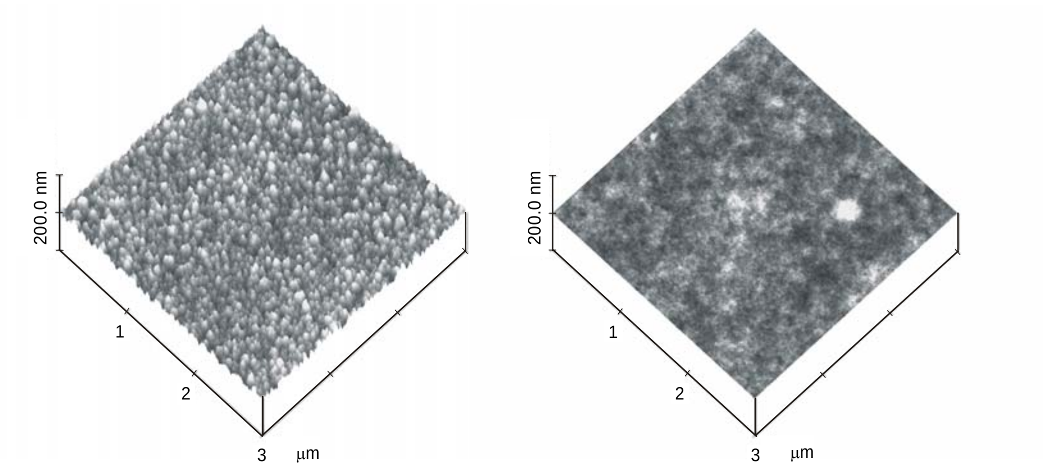


Fig. 4. a-C:H film thickness after 1 hour of deposition as a function of the applied dc bias. A third order polynomial fit is added as a guide to the eye.

3×3 μm^2 AFM images of the surface morphology of the a-C:H films deposited at 0 and –200 V are displayed in Fig. 5. For all films grown in the range of +100 to –80 V applied bias, the surface is relatively rough (root mean square roughness, σ, in the 4.5-6 nm range) and is cauliflower-like (Fig. 5a). In contrast, for large negative biases the film surface becomes very smooth (σ ~ 0.1-0.2 nm, Fig. 5b). Thus, a levelling of the surface morphology has taken place due to the relative high energy of the incoming ions[11,12]. The transition from cauliflower-like to smooth surfaces is quite sharp and is observed at about –90 V applied bias. Note that this transition coincides with the threshold energy of about 80-90 eV for physical sputtering of a-C:H films by argon ions[9,10].



(a) (b)

Fig. 5. 3×3 μm AFM images of the a-C:H films deposited for 1 hour at 0 V (left) and –200 V (right) applied bias, respectively. The vertical scale bar is 200 nm for both images.

[11] Buijnsters J.G., Camero M., Vazquez L. Phys. Rev. B, 74 (2006) 155417-7
[12] Moseler M., Gumbsch P., Casiraghi C., Ferrari A.C., Robertson J. Science 2005;309:1545-1548.

IR absorption spectra of the a-C:H films deposited at varying substrate bias are shown in Fig. 6. As it can be deduced from the presented spectra, the films grown in the range of +100 V to about –100 V applied bias are polymeric-like. On the contrary, within the high ion energy regime, i.e. for biases more negative than about –100 V, the 2900 cm^{-1} band becomes less intensive and no individual contributions could be detected. The decreasing intensity of the IR absorption band indicates a decreasing hydrogen content. This is also confirmed by micro-Raman spectroscopy analysis of these a-C:H films. In Fig. 7a, the micro-Raman spectra of the films obtained at 0 V and –200 V applied bias are shown. Neglecting the silicon substrate peak at 520 cm^{-1}, the Raman spectrum of the a-C:H film deposited at 0 V applied bias is nearly featureless. Only a strong photoluminescence (PL) background related to the presence of bonded hydrogen is observed[13,14]. No Raman signals are observed for all a-C:H films deposited at substrate bias values more positive than about –80 V. For H contents over 40-45%, the PL background overshadows the Raman signal completely[13] and, therefore, the hydrogen content of these films will be larger than about 45%. On the contrary, the D-, G- and hydrogen bands, which are typical for a-C:H films with lesser H content[15], are observed in the Raman spectra of the a-C:H films grown at substrate biases more negative than about –80 V. For example, the Raman spectrum of the a-C:H film grown at –200 V applied bias is shown in Fig. B4a (lower spectrum). The PL background is reduced significantly and two features centred at about 1500 cm^{-1} and 3000 cm^{-1} are observed. In Fig. B4b, the peak fitting of these Raman bands is displayed. The D-, G- and hydrogen bands at about 1370, 1556 and 3000 cm^{-1}, respectively, have been fitted adequately by Gaussian line shapes. Based on the ratio between the slope of the fitted linear PL background and the intensity of the G-band[13], the value of 1.7 µm for the film obtained at –200 V bias indicates a hydrogen content of 26%.

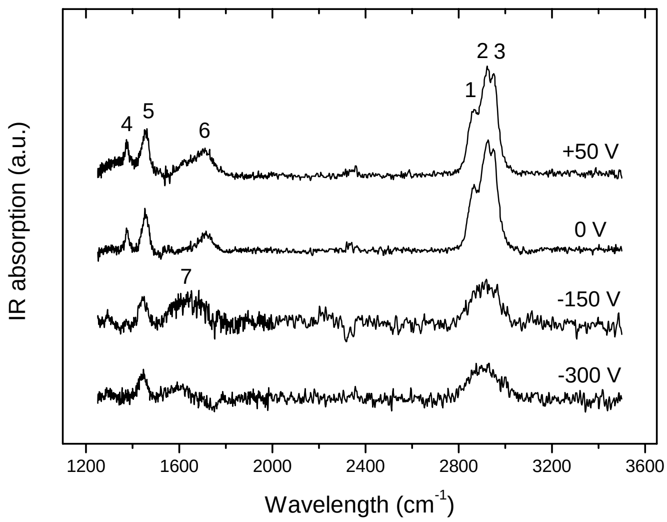
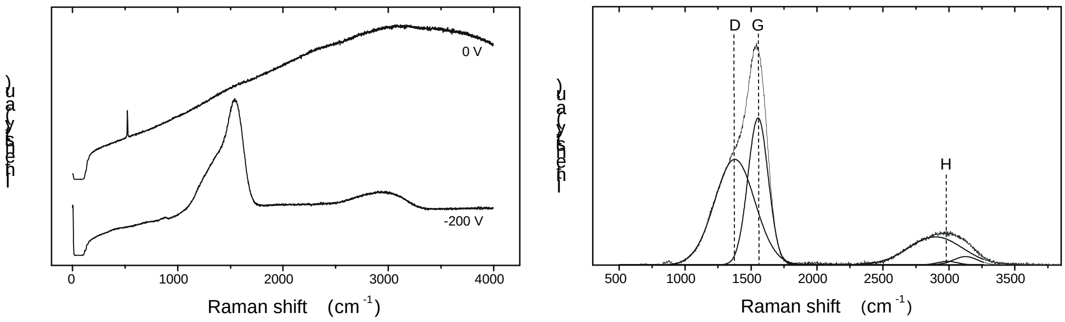


Fig. 6. IR absorption spectra of a-C:H films deposited at +50, 0, -150 and –300 V applied bias, respectively. The contributions of the various -CH_x, C=C and C=O bonds are indicated by numbers (see text).

[13] Robertson J. Phys Rev. B 1996;53:16302-16305.
[14] Casiraghi C., Piazza F., Ferrari A.C., Grambole D., Robertson J. Diamond Relat Mater. 2005;14:1098-1102
[15] Casiraghi C., Ferrari A.C., Robertson J. Phys. Rev. B 2005;72:(085401)1-14.



(a) (b)

Fig. 7. (a) Micro-Raman spectra of the a-C:H films grown at 0 V and –200 V applied bias, respectively. (b) Gaussian peak fitting of the D-, G- and hydrogen bands of the Raman spectrum of the film obtained at –200 V after background correction.

Table 1. Nanohardness, Young's modulus, friction coefficient and wear rate of the a-C:H films deposited at +50 V and –300 V applied bias. The data have been derived from nanoindentation and pin-on-disk tribotest measurements, respectively.

DC Bias (V)	Nanohardness (GPa)	Young's Modulus (GPa)	Friction Coefficient	Wear Rate (mm^3/Nm)
+50	2.4 ± 0.3	34 ± 2	0.36 ± 0.04	8.1×10^{-5}
-300	15.7 ± 1.0	134 ± 10	0.097 ± 0.015	7.9×10^{-8}

In table I, the data of the nanoindentation tests and pin-on-disk tribotest measurements derived for the a-C:H films deposited at +50 V and –300 V applied bias, respectively, are given. The film obtained at +50 V applied bias is relatively soft and displays a low Young's modulus. This results in a relatively poor performance in the pin-on-disk tribotest too. After about 300 cycles the film is already fully penetrated resulting in a high wear rate. Also, the friction coefficient (i.e. 0.36) obtained for the WC-Co ball contact during this test is relatively high. On the contrary, the film obtained at –300 V applied bias is about 7 times harder and shows a 4-fold Young's modulus as compared to that at +50 V substrate bias. This is directly exposed in the superior tribological behaviour. The film supports more than 50000 cycles and during the entire trajectory a nearly stable friction coefficient of 0.097 is recorded. The resulting wear rate is about 3 orders of magnitude smaller than that of the a-C:H film grown at +50 V bias. Likewise, two regimes with highly varying mechanical and tribological properties can be distinguished with a sharp transition at about -90 V applied substrate bias. The a-C:H films grown at high negative bias are hard and wear resistant, whereas the coatings obtained at more positive bias are soft and exhibit an inferior wear resistance.

B-CONCLUSIONS

This study shows that the bombarding high energy ions simultaneously affect the roughness, composition, structure, hardness and bulk tribological properties of the a-C:H films. Two bias regimes separated by a sharp transition at about -90 V substrate bias are observed. The first regime, running from -80 V up to +100 V, is characterized by a relatively large film roughness. For the second regime, i.e. for high negative bias, it is extremely low (~0.1-0.2 nm). These ultrasmooth films, which display a hydrogen content of about 26 at.%, did prove to be hard and wear resistant. In contrast, the films grown with more positive bias have a hydrogen content of more than 45 at.% and the presence of terminal $-CH_3$ groups indicates a polymeric-like structure, which leads to poor tribological properties.

C) HYDROGENATED AMORPHOUS *CARBON NITRIDE* (a-CN_x :H) COATINGS.

Finally, we have been studying the synthesis by *ECR-CVD* of hydrogenated carbon nitride films using as precursor gases argon, methane and nitrogen. In particular, composition and bonding structure of a-CNx:H films were determined using Rutherford backscattering (RBS) and elastic recoil detection analysis (ERDA) for the composition analysis and infrared (IR) spectroscopy and X-ray absorption near edge spectroscopy (XANES) for establishing the bonding structure. By varying the nitrogen to methane ratio in the applied gas mixture, polymeric a-CNx:H films with N/C contents varying from 0.06 to 0.49 were obtained. Remarkably, the H content of the films (~ 40 at.%) was rather unaffected by the nitrogenation process. The different bonding states as detected in the measured XANES C(1s) and N(1s) spectra have been correlated to those of a large number of reference samples. The XANES and IR spectroscopy results indicate that N atoms are efficiently incorporated into the amorphous carbon network and can be found in different bonding environments, such as pyridinelike, graphitelike, nitrilelike and amino groups. The nitrogenation of the films results in the formation of N-H bonding environments at the cost of C-H structures. Also, the insertion of N induces a higher fraction of double bonds in the structure at the expense of the linear polymerlike chains, hence resulting in a more cross-linked solid. The formation of double bonds takes place through complex C=N structures and not by formation of graphitic aromatic rings. Also, the mechanical and tribological properties (hardness, friction and wear) of the films have been studied as a function of the nitrogen content. Despite the major modifications in the bonding structure with nitrogen uptake, no significant changes in these properties are observed.

Lately, we detected the improvement in the tribological properties (harder and lower friction coefficient) of carbon nitride films as a highly negative bias (more negative than -90 volts) is applied to the silicon substrate during the deposition process. The results are now being analyzed in detail for processes with a high methane concentration. The final aim is the production at large deposition rates of hard and low friction carbon nitride coatings for industrial purposes.

Project co-operation

Our work consists basically in the study of the synthesis of carbon based materials by CVD and PVD processes. Then, our collaboration goes directed mainly to other groups with experience in vacuum techniques as well as in Electron Microscopy Analysis, these last used for the characterization of the deposited nanostructured materials. Regarding the tribological behaviour of the nanostructured coatings, an improvement in the hardness and friction coefficient in dry atmospheres has been already detected in the deposited nanostructured carbon materials. Therefore, the mechanical properties should be compared to other systems in order to estimate the utility of them as autolubricant coatings.

Publications were project results are reported

1. M. CAMERO, R. GAGO, C. GÓMEZ-ALEIXANDRE and J. M ALBELLA. "Hydrogen Incorporation in CN_x Films Deposited by ECR Chemical Vapor Deposition". *Diamond & Related Materials* **12** (2003) 632-635
2. I. JIMÉNEZ, R. GAGO, J. M. ALBELLA. "Fine Structure at the X-ray absorption p* and s* bands of amorphous carbon". *Diamond and Related Materials*, **12** (2003) 110-115.

3. I. CARETTI, I.JIMENEZ , R.GAGO , D.CACERES , B.ABENDROTH , J.M.ALBELLA. "Tribological properties of ternary BCN films with controlled composition and bonding structure". *Diamond and Related Materials* **13** (2004) 1532–1537

4. M. CAMERO, R. GAGO, C. GÓMEZ-ALEIXANDRE AND J. M ALBELLA. "Efecto del Argon en Películas CNxHy Depositadas mediante ECR-CVD". *Bol.Soc.Esp.Ceram.Vidr.* , **43** (2004) 491-493.
5. CAMERO M.; GORDILLO F.J.; ORTIZ J.; GÓMEZ-ALEIXANDRE C. "Influence of the power on the processes controlling the formation of ECR-CVD carbon nitride films from CH4/Ar/N2 plasmas". *Plasma Sources Sci. Technol* **13**, (2004)121-126
6. R. GAGO,* I. JIMÉNEZ, J. NEIDHARDT, B. ABENDROTH, I. CARETTI, L. HULTMAN, AND W. MÖLLER. **"**Correlation between bonding structure and microstructure in fullerenelike carbon nitride thin films" *Phys.Rev. B* **71**, (2005) 125414
7. GORDILLO-VAZQUEZ F.J.; CAMERO M.; GÓMEZ-ALEIXANDRE C. "Spectroscopic measurements of the electron temperature in low pressure radiofrequency Ar/H2/C2H2 and Ar/H2/CH4 plasmas used for the synthesis of nanocarbon structures". *Plasma Sources Sci. Technol*, 15 (2006) 42-51
8. I. CARETTI, J. M. ALBELLA, AND I. JIMÉNEZ. "Tribological study of amorphous BC_4N coatings." *Diamond &Related Materials* **16** *(*2007) 63-73
9. M.CAMERO, J.G.BUIJNSTERS, R.GAGO, I.CARETTI, C.GÓMEZ-ALEIXANDRE, I. JIMÉNEZ. "The effect of nitrogen incorporation on the bonding structure of hydrogenated carbon nitride films" (accepted *Journal of Applied Physics* (ref 131705JAP)
10. J. M. ALBELLA, I. JIMÉNEZ, C. GÓMEZ-ALEIXANDRE, A. ALBERDI. "Materials and vapour-phase techniques for the synthesis of ceramic coatings". 2006 (accepted *Boletín Sociedad Española de Cerámica y Vidrio)*
11. M. CAMERO , F.J.GORDILLO-VÁZQUEZ AND C.GÓMEZ-ALEIXANDRE. "Low pressure PECVD of nanoparticles in carbon thin films from Ar/H2/C2H2 plasmas: Synthesis of films and analysis of the electron energy distribution function" accepted *Advanced Materials CVD*(ref: F554PECVD)
12. J.G. BUIJNSTERS, M. CAMERO, L. VÁZQUEZ, F. AGULLÓ-RUEDA, C. GÓMEZ-ALEIXANDRE AND J.M. ALBELLA. "DC substrate bias effects on the physical properties of hydrogenated amorphous carbon films grown by Plasma Assisted Chemical Vapour Deposition". *Vacuum* (accepted 2007)
13. J.G.BUIJNSTERS, I.CARETTI, O. SÁNCHEZ , J.M.ALBELLA AND C.GÓMEZ-ALEIXANDRE. "Vapor phase synthesis of nanostructured carbon based materials for tribological applications" submitted to ECOTRIB 2007 Joint European Conference on Tribology and Final conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007, Ljubljana, Slovenia

<u>Planned or achieved industrial improvements in commercial use</u>

The use of carbon based materials with low friction coefficient as hard coating, suppose a significant reduction in the use of oil lubricants, with the well-known cost savings.

CHAPTER 3 ENGINE SYSTEMS, ES

3.1 Summary

By Amaya Igartua and Kristian Tönder, Coordinators of WG1

Number of projects: 11 (From Poland 2, Czech Republic 2, Finland, Ukraine, Spain, Slovakia, Israel, Sweden and Norway 1 each). 8 projects are finalized (100%), the other three are between 35 and 95% of finalization. WG 1 has resulted in 141 reports of which 25 are internationally refereed journal papers, 79 are international conference papers and 37 are national reports. They have generated 10 industrial improvements already in use.

The objective of the working group of tribology of engine systems is to reduce the wear and friction of engine components. In order to achieve this objective, different aspects are being considered:

- Basic mechanisms
- Materials and coatings
- Engine effects oriented developments

Basic Mechanisms

The focus is to study the effect of hydrogen diffusion, surface roughness pattern and solid particles in sliding components (cam shaft, piston rings, valve trains) in order to evaluate the influence of catalytic reactions at the component surface due to the effect of fuel, exhaust, lubricant and additive chemistry (ES1). In addition to the effect of roughness, surface texture patterns and lubrication on the friction and wear and film thickness of typical sliding/rolling contacts (cams, tappets and gears) have been studied using advanced high resolution CCD camera (ES10). In the study of the surface topography on lubricated contact, the maximum depth recommended was 5 µm to create the appropriate film thickness in the dimple (ES11). The effects of texturing under dry and lubricated conditions have been studied when applied to Pivot inlet devices, gas sliders and cylinder walls (ES4). The chemical factors influencing engine wear (lubricant, additive, surface roughness, contamination, fuel chemistry) when using artificial gases and fuel from diesel engines have been studied. A large engine test has been developed to study the tappet/follower contact (steel and ceramic), studying the influence of indentations in the endurance life. (ES1). Positron annihilation studies of defects in subsurface zones in Mg, Al and their alloys induced during friction and wear process have been studied. The subsurface zone in the samples of pure magnesium and its alloy Mg96Al3Zn1 and aluminium casting alloys: Al91Si6Cu3, Al87Si11Cu2 after dry sliding against tool steel have been studied using positron annihilation techniques, microhardenss tests and SEM. The new experimental technique called DISP has been established for studies in non destructive way, determining the defect distribution in the subsurface zone of light metals and alloys. The effect of the thermal treatment on the defects has been quantified (ES10). Basic work on the hydrogen embrittlement has shown that hydrogen behaves almost similarly on and inside bcc metals, Fe, Pd, Nb etc, so data available for one can be used for others. Iron can make hydride phase and alloying elements have a strong impact on the uptake of hydrogen. Cr, Mn, S, V, Zr, Al, together with O and H are not good for the structural stability of steel (ES1)

Materials and coatings

Three main topics have been considered:

- The increase of the duration of cylinder-piston groups by means of the development of high temperature resistant novel eutectic alloys on the base of AlMgSi system alloyed with transition and earth metals to apply in pistons (ES5). The maximum temperature resistance of the alloy is 530ºC and due to the Mg content, it has been optimised the strength/weight relationship. Advanced nanostructured materials based on intercalated metal cichalcogenides (MS2, MSSe), have been deposited by ultrasonic solutions in lubricants. The size of the particles were <10nm. Antiwear properties were improved 10-20%, antiwelding properties 10-15%, friction and wear reduction 10-15% was achieved.

- Development of thermal sprayed coatings to improve erosion, abrasion, corrosion and temperature resistance, correlating the microstructure and tribomechanical properties with the deposition parameters. Different type of coatings has been developed (WC, TiC, WC-Co, Cr3C2-NiCr, NiCrSiB, AISI 316L to substitute chromium coatings. The tribological studies (indentation fracture, cohesion, wear rate, scratch tests, AFM ..) have been complemented with the study of the degradation mechanism and imaging process (MATLAB), (ES7 and ES9).

- A new low-pressure magnetron coating deposition rig with Radio Frequency Electron-Cyclotron-Resonance discharge in low magnetic field is taken into use in Radom, PL. Thermo chemical treatment (gas carburizing) that was carried out on PVD coatings deposited on steel substrate. The deposition of alumina coatings was described using RF magnetron systems. Development of duplex coatings, composites on diffusion layer thin antiwear coatings (PACVD, PAPVD) to increase the durability of different type of steel materials. Different type of continuous duplex composites (diffusion layer + PVD coating) deposited in-situ has been developed. Also multilayer coatings (TiN, TiC, CrN, ZrN, Ti(CN), TiAlN combined with thermochemical treatments have been synthesised. The application of a TiN coating on a carburising steel, allows to increase the harder layer from 0,5mm to 1mm (ES3)

*Engine effects oriented development*s

- Increase of power efficiency, reduction of fuel consumption and exhaust emissions of internal combustion engines by means of the reduction of the friction and wear and the selection of optimised tribological solutions. (ES2)

- Reduction of the environmental impact and emissions from engines by means of the development of advanced surface treatments (duplex coatings, hard coatings, low evaporation lubricants in engines to avoid scuffing, abrasion, wear and corrosion. (ES6)

- LST treatment for piston rings (ES8)

- **New experimental facilities:** a large Scania engine test rig is built (ES1); an advanced cylinder/ring test rig has been taken into use by VTT to perform friction measurements with a dynamic loading ring tribometers. The gas pressure between the piston rings and behind them has also been measured, and finally the film thickness. (ES2). A new testing device has been designed by Guascor to test the cam/tappet system, and Tekniker, has develop a simulation programme to predict the behaviour. (ES6)

Alternative coatings and lubricants for engine applications

Mechanical calculations to measure the axial effort of a pump and a cam/tappet system have been performed and the calculations are being validated in a testing bench by accelerometers and strain measurement techniques. New alternatives to replace hazardous chromium plating in piston rings are investigated. The studied alternatives are High Pressure - High Velocity Oxi Fuel coated piston rings using standard and nano size powders and two different chemistries, PVD coatings (TiN-CrN, WC-C) and an electrolytic composite coating (NiPCo-Si3N4) The tribological simulated tests for selection of the coatings were carried out by TEKNIKER and engine tests by the company CIE Tarabusi and the coatings were developed by the partners (ES6)

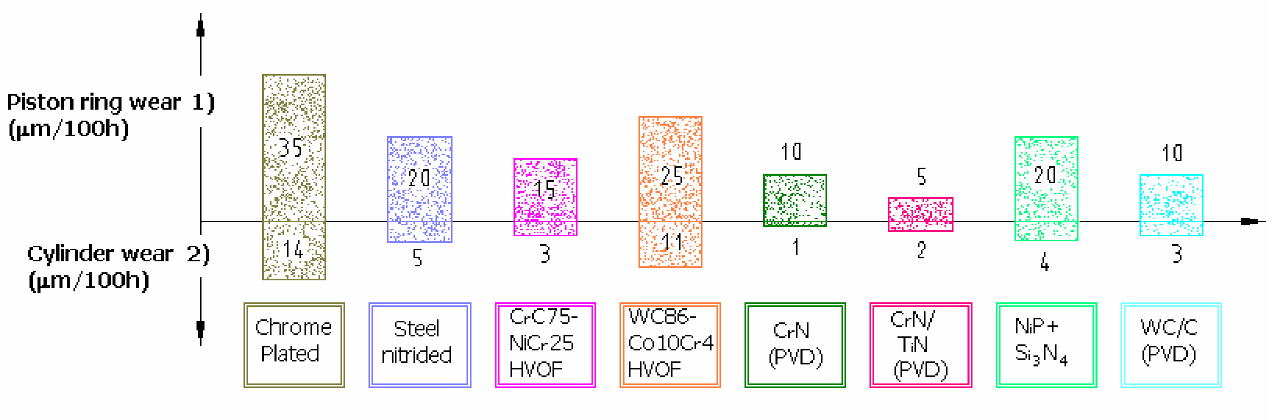


Fig. 1.- Wear behaviour after hot endurance tests.

Different biodegradable PCMO engine oils have been developed, screening the lubricants by means of cylinder liner/piston ring simulation tests. The results also were published in a book edited by TEKNIKER with the collaboration of Virtual Tribological Institute. Biodegradable lubricants for heavy duty engines were also developed in combination with triboreactive materials. A reduction of oil consumption of 45% and a maximum reduction of fuel consumption of 2% were measured when using the new lubricants developed by FUCHS and BAM. A new generation of 4 stroke low viscosity lubricants has been developed by KRAFFT for heavy duty engines. The lubricants tested by TEKNIKER, when simulating the valve/guide contact, showed excellent extreme pressure properties.(ES6).

Test Number	Lubricants	COF	COF mean
OG2179T316	Low viscosity R1	0.072	**0.072**
OG2180T316	Low viscosityR2	0.062	**0.061**± 0.002
OG2186T316		0.060	
OG2181T316	Low viscosity R3	0.067	**0.067**
OG2182T316	Low viscosity R4	0.079	**0.079**
OG2183T316	Low viscosity R5	0.067	**0.067**
OG2184T316	Low viscosity R6	0.073	**0.073**
OG1838T316	Motor oil 30_40	0.183	0.182± 0.02
OG2112T141	Motor oil M4000	0.16	0.160
OG2115T141	New developed oil EHD-25	0.14	*0.135±0.001*
OG2118T141		0.13	
OG2116T141	New developed oil EHD-26	0.15	*0.150*
OG2197T316	Motor oil BIOGAS	0.192	0.192

COF: Friction coefficient

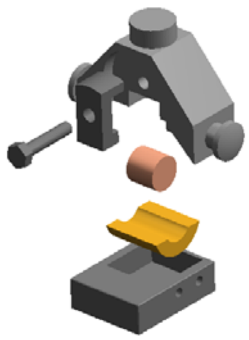


Fig. 2.- Properties of the low viscosity lubricants developed by KRAFFT and tested by TEKNIKER, ES

Surface laser texturing has been investigated both theoretically and experimentally by TECHNION, to find optimal surface parameters for the lubricating mechanism, and empirically to verify the assumptions. Excellent friction and wear reduction have been achieved both for piston rings and mechanical seals. The best results were obtained with partial texturing than with full texturing. The scuffing resistance, increase with the texturing. The comparison from untextured barrel face piston rings (serie 1), have been compared with textured rectangular shape face piston rings (chromium+LST, serie 2 and LST serie 3), showing a reduction of 1-2% of the fuel consumption with the textured rings, (ES8).

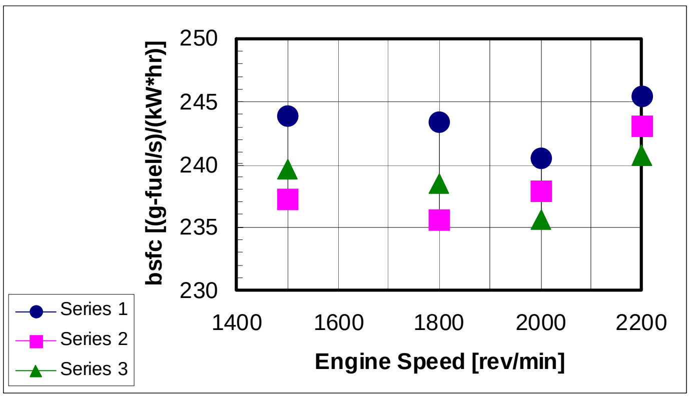


Figure 3.- Engine specific fuel consumption vs. engine speed

High temperature resistant light alloys

Work has been done to develop the scientific basis of the purposeful alloying by transition and rare earth metals of cast quasi binary eutectic alloys of the Al-Mg-Si system as a promising material for pistons. It has been shown a better temperature resistance for the new alloys in comparison with standard alloys 356.0 and 390.0, Kiev. Besides, they also have good casting properties, high wear and crack resistance and, due to a high Mg content, the weight of the alloys decreases. The advantages of the new alloy under dynamical modes are shown below (ES5).

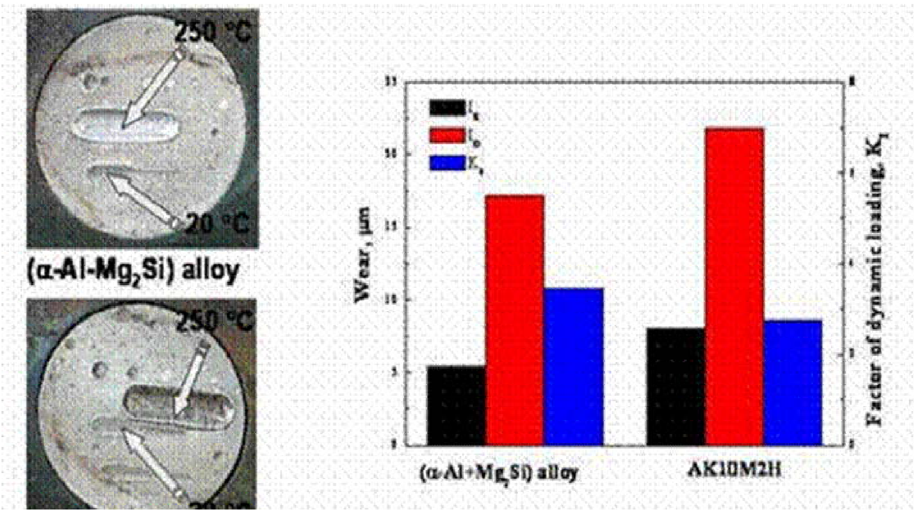


Fig. 4.- Decided superiority of α-Al-Mg2Si cast alloys tribology behaviors

Advanced Coatings

The adhesion of **duplex coatings** (nitrided layer/PAPVD coatings) is higher than the adhesion of the coating with the HSS substrate just with thermal treatment. The one step duplex treatment increases the indenter load value. Properties of duplex (carburised/PAPVD) coatings (Fig. 5) depend on PAPVD coating process temperature, presenting similar indenter load value than the TiN/HSS but with a core hardness of 45HRC, which should ensure significantly higher torsion and bending strength in comparison to the high-speed steel SW7M. The obtained alumina coatings allow improving the hardness and anti-wear properties of steel substrates, reducing friction coefficient between the substrate and the counter-part material, improving corrosion resistance of steel substrates, and creating a composite multi-layer coatings of Al-Al_2O_3, TiN-Al_2O_3 types. (ES3)

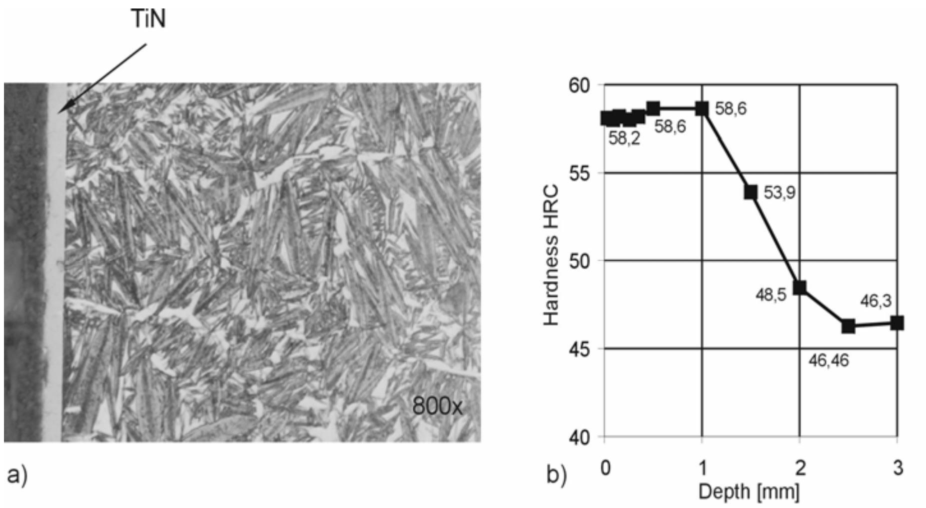


Fig. 5.- The multilayer structure "carburized case/TiN coating" created on the gear steel Ferrium C61: a) metallography, b) hardness penetration pattern

Advanced **HVOF coatings** (WC-17%Cim Cr_3C_2-20NiCr, WC-12%Co, Cr_3C_2-20NiCr, Co28Cr-4W-Si), have been deposited in order to compare the scuffing resistance, being higher for the last coating, (ES7, ES9). Skoda Research, Czech Republic, explained the influence of thermally sprayed coatings in their tribological characteristics, wear resistance and mechanisms were evaluated under different wear conditions, using four different wear tests. The superior wear results were proved for WC-based HVOF coatings. The lower friction coefficient was for the Cr_3O_2 and the highest erosion and abrasion resistance for the WC-Co-Cr, WC17Co and WC-Hasteloy.

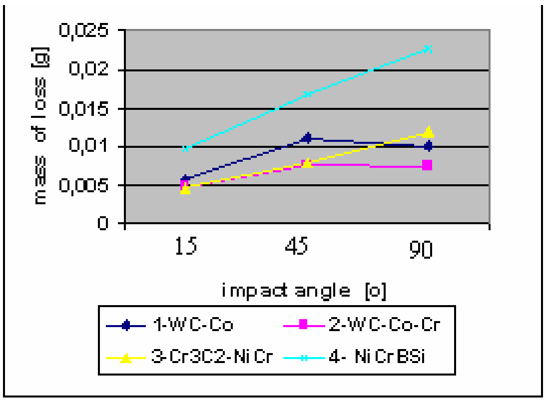


Fig. 5.- Erosion resistance of the coatings

3.2 Project result reports

ES1 – CHEMICAL FACTORS INFLUENCING ENGINE WEAR

Co-ordinator and partners

Co-ordinator:

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Partners:

Jan Flensburg, Materials Technology, Scania CV AB, Sweden, jan.flensburg@scania.com

Project status and schedule

Running with full funding
Starting and ending dates 02-2001 to 12-2006 (The project has finished 2006-12.21.)

Project aims

Find:

- Influence of lubricant and additive chemistry on cam mechanisms.
- Influence of surface roughness pattern on lubrication and wear.
- Influence of contamination on wear rate and running in.
- Influence of fuel chemistry on wear rate and runnig in.
- Most important parameters determining wear.

Project results

The building of the large Scania engine test rig is finished and the experiments with cam shafts and different followers (steel and ceramic) have been run. Influence of surface indentations on running in has ben run. The endurance life of damaged cam surfaces of different hardness have been measured, and the results follow the endurance life calculations for rolling bearings. The last experiments with cam and roller follower in different gas atmospheres have been run, and the large test rig has been dis-assembled and sent to KTH in Stockholm.

Project co-operation

The forms of co-operation used: e-mail contacts, meetings, seminars, researchers visits.

Planned or achieved industrial improvements in commercial use

The results will be implemented by Scania on their truck diesel engines.

Publications were project results are reported

The first publication was published in the NORDTRIB conference in June 2004.

The second publication was at the Leeds-Lyon conference 2005.

The third report was the PhD thesis “Diesel Engine Cam and Roller Follower Tribology”, Doctoral Thesis, Division of Machine Elements, Lund Institute of Technology, 2006, ISRN-LUTMDN/TMME-1019-SE. pp.137.

The fourth report is “Cam and Roller Follower Tribology COST532-ES1” submitted to ECOTRIB 2007 Joint European Conference on Tribology and final conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007. Ljuljana, Slovenia).

ES2 - LOW-FRICTION ENGINES

Co-ordinator and partners

Co-ordinator:

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Mr. Antti Valkonen
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Project status and schedule

Finished.
Starting and ending dates: From 1st April 2003 to 30th September 2005.

Project aims

The aim of the project was to investigate the major sources for frictional losses in internal combustion engines, to quantify the energy losses and describe the wear phenomena taking place due to the frictional work, and to propose improvements in the technical solutions in order to reduce friction.

Project results

Four meetings and the final meeting of the Steering Group of the project were arranged. The research activities have been finished.

Piston ring tests with friction measurements were done at VTT Industrial Systems, using frequencies up to 40 Hz and temperatures up to 200 ºC. Dynamic loading of the piston ring tribometer was included for demonstration. Selected results have been published.

Journal bearings were studied at Helsinki University of Technology, the Laboratory of Machine Design, by using a crankshaft bearing test rig. Isothermal curves for load and speed combinations have been made for different lubricants. The prime reporting has been completed. Detailed reporting is in progress. A Master´s Thesis has been made on thin film pressure transducers in journal bearings.

Firing engine tests at Helsinki University of Technology, the Internal Combustion Engine Laboratory for measurements on the gas pressure behind and between the piston rings were done, and results were presented at the Leeds-Lyon Symposium on Tribology in September 2005 and at the SAE Powertrain & Fluid Systems Conference in October, 2005. Simultaneously with the results of the gas pressure measurements, the results of oil film thickness measurements and computer simulations on piston rings, using software from Ricardo, were presented.

Fuel consumption tests in a diesel engine at VTT Processes showed differences between different lubricants, and differences in the exhaust emissions have been found. A Paper on the results was presented at the SAE Powertrain & Fluid Systems Conference in October, 2005.

Project co-operation

Co-operation with other COST 532 projects progressed as follows: Co-operation on computer simulations of journal bearing was done with Université de Poitiers, Laboratory of Solids Mechanics. Piston ring coatings were discussed with Dr. Berger of Fraunhofer Institute, who also has visited the research groups of the Low-friction engines project.

Planned or achieved industrial improvements in commercial use

In order to give the largest benefits of the study, the engine sub-systems chosen for the study comprised the piston-ring-cylinder system, and the crankshaft and connecting rod bearings. Future industrial improvements in commercial use are likely to be found within this field of applications, in terms in improvements in both engine and lubricant technology.

Publications where project results are reported

Conference and post-conference Papers

1. Andersson, P., Kytö, M., Murtonen, T., Valkonen, A., Tamminen, J. and Sandström, C.-E. Low-friction engines. In: Holmberg, K., De Baets, P. and Celis, J. P. (Eds.). COST 532 Conference - Triboscience and Tribotechnology - Superior Friction and Wear Control in Engines and Transmissions, 18-19 October 2004, Ghent, Belgium. Ghent, Belgium, 2004, Ghent University, pp. 113-120. ISBN 90-8091-591-2, NUGI 971.

2. Tamminen, J., Sandström, C.-E. and Andersson, P. Influence of load on the tribological conditions in piston ring and cylinder liner contacts in a medium-speed diesel engine. In: Synopses of papers presented at the 32nd Leeds-Lyon Symposium on Tribology, Lyon, France, 6th-9th September 2005. INSA de Lyon. Abstract, 1 p.
3. Tamminen, J., Sandström, C.-E. and Andersson, P. Influence of load on the tribological conditions in piston ring and cylinder liner contacts in a medium-speed diesel engine. Tribology International, 39 (2006), pp. 1643–1652.
4. Tamminen, J., Sandström, C.-E. and Nurmi, H. Influence of the Piston Inter-ring Gas Pressure on the Ring Pack Behaviour in a Medium Speed Diesel Engine. Paper presented at the SAE Powertrain & Fluid Systems Conference 2005, San Antonio, Texas, USA, 24-27.10.2005. SAE Technical Paper Series 2005-01-3847. 13 p.
5. Murtonen, T. and Sutton, M. New crankcase lubricants for heavy-duty diesel engines: effect on emissions and fuel consumption. Paper presented at the SAE Powertrain & Fluid Systems Conference 2005, San Antonio, Texas, USA, 24-27.10.2005. SAE Technical Paper Series 2005-01-3717. 7 p.
6. Andersson, P., Murtonen, T., Valkonen, A., Tamminen, J. and Sandström, C.-E. The Low-friction engines project. In: Holmberg, K., Hsu, S., A. Ferreira, L. and Seabra, J. (Eds.). COST 532 Conference: Triboscience and Tribotechnology, Superior Friction and Wear Control in Engines and Transmissions - Integrated with NIST Conference: Integrated Engineered Surface Technology to Reduce Friction and Increase Durability, 12-14 October 2005, FEUP/ISEP, Porto, Portugal. Porto, Portugal, 2005, University of Porto, ISBN 972-8953-01-1, pp. 215-222.
7. Andersson, P. Friction and wear measurements on piston ring and cylinder liner combinations for internal combustion engines. Abstract submitted to ECOTRIB 2007 Joint European Conference on Tribology and Final Conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007, Ljubljana, Slovenia. 1 p.

Papers presented at the Thematic Day on Engine Tribology, arranged by the Finnish Society for Tribology, at Helsinki University of Technology in Espoo, Finland on the 4th of November, 2005

1. Andersson, P. Piston ring tests in the project Low-friction engines. Tribologia - Finnish Journal of Tribology, 24 (2005) 3-4, pp. 3-11. ISSN 0780-2285.
2. Murtonen, T. Fuel consumption and emission measurements in the project Low-friction engines. Tribologia - Finnish Journal of Tribology, 24 (2005) 3-4, pp. 23-29. ISSN 0780-2285.
3. Valkonen, A. Bearing experiments for the comparison of engine lubricants. Tribologia - Finnish Journal of Tribology, 24 (2005) 3-4, pp. 17-22. ISSN 0780-2285.
4. Tamminen, J. and Sandström, C.-E. Piston ring area tribology in a medium speed diesel engine. Tribologia - Finnish Journal of Tribology, 24 (2005) 3-4, pp. 30-37. ISSN 0780-2285.

Master's Thesis

Martikainen, J. Ohutkalvopaineanturin kehittäminen (In Finnish / Development of a thin-film-pressure sensor). Espoo, Finland, 2005, Helsinki University of Technology, Department of Electrical and Communication Engineering, Master's Thesis.

Final report for the project Low-friction engines

Andersson, P., Murtonen, T., Valkonen, A., Tamminen, J. and Sandström, C.-E. Low-friction engines - Final Report. Espoo, Finland, 2005, VTT Industrial Systems, Research report BTUO43-051391, 47 p.

ES3 - CREATION OF MULTILAYER COMPOSITE STRUCTURES: DIFFUSION LAYER/PVD COATING WITH THE USE OF COMPLEMENTARY DUPLEX TECHNOLOGIES

Co-ordinator and partners

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Project status and schedule

Running with partial funding
Starting and ending dates: 11.06.2003 – 31.12.2006

Project aims

There are two aims in the project:

- Development of new, hybrid methods of creation of multi-layer composites "diffusion layer / thin PAPVD coating" differing in chemical composition, structure and properties, for anti-wear and anti-corrosion applications
- Identification of the influence of different duplex complementary technologies and different structures of multi-layer composites on their mechanical and anti-corrosion properties

Project results

The scope of the work consists of three parts.

- Creation of multi-layer composite structures "diffusion layer / thin anti-wear coating" by diffusion treatment of metallic PVD coatings on steel substrates
- Creation of multi-layer composite structures "diffusion layer / thin anti-wear coating" by deposition of hard PVD coatings on steel substrates, which underwent diffusion treatment
- Creation of complex composite structures "diffusion layer / thin anti-wear coating" based on high quality aluminium oxide

Creation of multi-layer composite structures "diffusion layer / thin anti-wear coating" by diffusion treatment of metallic PVD coatings on steel substrates

In the first part of the project the ability to create the multi-layer composite structures by gas nitriding of metallic PVD coatings (Ti and Cr) and heat treatment of hard PVD nitride coatings (TiN, CrN, Cr_2N) was investigated.

In both metalic coatings the gas nitriding was not an effective process. After diffusion treatment only small diffraction picks were observed but the layers of TiN and CrN were not observed by microscope. The diffusion layer into the substrate was also not created.

However the changes of the Young Modulus and the lattice parameters of the PVD nitride coatings were observed after the heat treatment. The changes of the Young Modulus in the function of heating temperature were significant for the TiN coating (Fig. 1). The values of Young Modulus of the CrN and Cr_2N coatings were stable in the changes of heating temperature in the range 350°C – 500°C. Similar situation was observed with the changes of lattice parameters of investigated nitride coatings in a function of heating temperature.

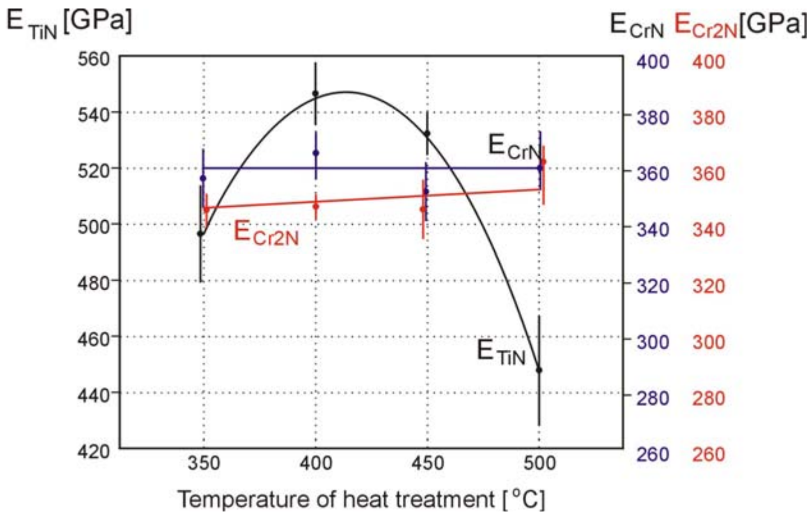


Fig. 1. The changes of the Young modulus of TiN, CrN and Cr_2N coatings after heat treatment.

Creation of multi-layer composite structures "diffusion layer / thin anti-wear coating" by deposition of hard PVD coatings on steel substrates, which underwent diffusion treatment

In the second part of the project two different types of composite structures: "nitrided layer / PAPVD coating" and "carburized case / PAPVD coating" were created.

<u>Composite structures "nitrided layer / PAPVD coating"</u>

Five different PAPVD coatings: TiN, CrN, $Ti(C,N)_{gradient}$, $TiN/Ti(C,N)_{multilayer}$, and $CrN/TiN_{multilayer}$ were used for creating the composite structure "nitrided layer / PAPVD coating" on hot working steel DIN 1.2367. The selected materials of the coatings were created by the arc evaporation method. The created composites underwent investigations aimed at defining their materials properties: morphology, phase composition, chemical composition, hardness, Young modulus and adhesion of PAPVD coating. For comparison the composite properties obtained on different substrate materials two selected types of composite structures: "nitrided layer / CrN coating" and “nitrided layer / $TiN\text{-}Ti(C,N)_{gradient}$ multilayer coating” were created on two different substrate materials: hot working steel DIN 1.2367 and HSS steel S690 produced by powder metallurgy methods. All composites were created by means of two-stage discontinuous”duplex” surface treatment. Their properties are presented in Table 1.

Table 1. Properties of created composites “nitrided layer / PAPVD coating”.

Thickness of diffusion layer	Hardness of nitrided layer	*Thickness of PAPVD coating*	Hardness of PAPVD coating	Young modulus of PAPVD coating	H^3/E^2 (GPa)	Adhesion of PAPVD coating
Substrate: HSS steel S690, Composite: Nitrided layer Feα(N) / TiN-TiCN multilayer						
0.11mm	HV10=1000	5.3µm	35 GPa	440 GPa	0.22 GPa	110 N
Substrate: HSS steel S690, Composite: Nitrided layer Feα(N) / CrN coating						
0.11mm	HV10=1000	6.2µm	24 GPa	280 GPa	0.18 GPa	160 N
Substrate: Hot working steel DIN 1.2367, Composite: Nitrided layer Feα(N) / TiN-TiCN multilayer						
0.18mm	HV10=1100	3.5µm	30 GPa	380 GPa	0.18 GPa	95 N
Substrate: Hot working steel DIN 1.2367, Composite: Nitrided layer Feα(N) / CrN coating						
0.18mm	HV10=1100	3.5µm	19 GPa	260 GPa	0.10 GPa	115 N

On the basis of the executed investigations the following conclusions can be formulated:

- The adhesion of $TiN\text{-}TiCN_{gradient}$ multilayer and CrN coatings in the composites “*nitrided layer / TiN-TiCN multilayer coating*” and “*nitrided layer / CrN coating*” created by the two-stage separable duplex technology (nitriding process and PAPVD process) on the powder-metallurgy HSS S690 steel is higher then the adhesion of coatings obtained on this substrate after heat treatment solely.
- The influence of the structure of substrate material on the structure of PAPVD coating obtained in the duplex treatment processes and consequently on their material properties, *e.g. hardness, Young modulus, adhesion* is significant.
- All investigated composites were obtained by the ”duplex” surface treatment method in two-stage separable cycles. In the earlier investigations, the authors proved that the composites “*nitrided layer / PAPVD coating*” created by means of continuous duplex treatment method are characterized by better material properties which are important in the destruction process, *i.e. adhesion, hardness, Young modulus*. The intender load value of the coating for complete removal for the composite “*nitrided layer / CrN coating*” created on the hot working DIN 1.2367 steel by the single-stage continuous technology increased in comparison to the composite obtained by two-stage separable cycles technology from Fn=115N to Fn=190N. Based on this result the development of the complementary duplex technology for HSS S690 steel seems very promising.

<u>Composite structures “carburised case / PAPVD coating”</u>

The multilayer structure “carburized case / TiN coating” was prepared by a discontinuous duplex method, using the vacuum carburizing, on the substrate made of the gear steel Ferrium C61 (Fig. 2).

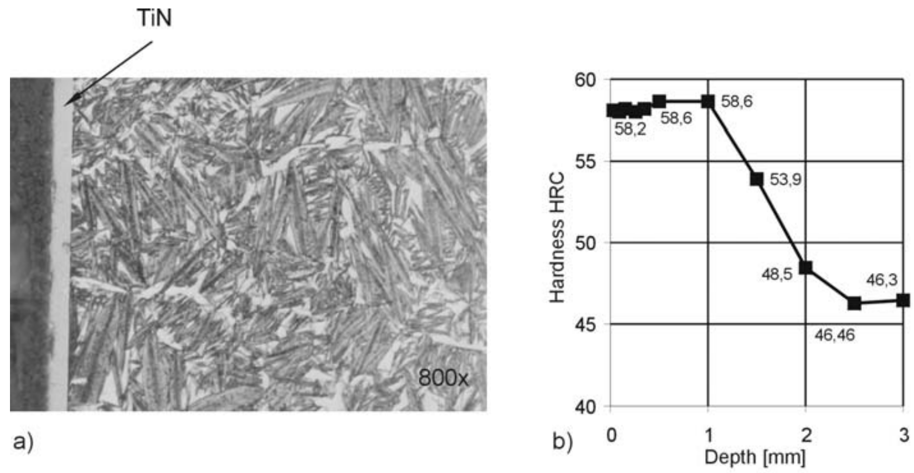


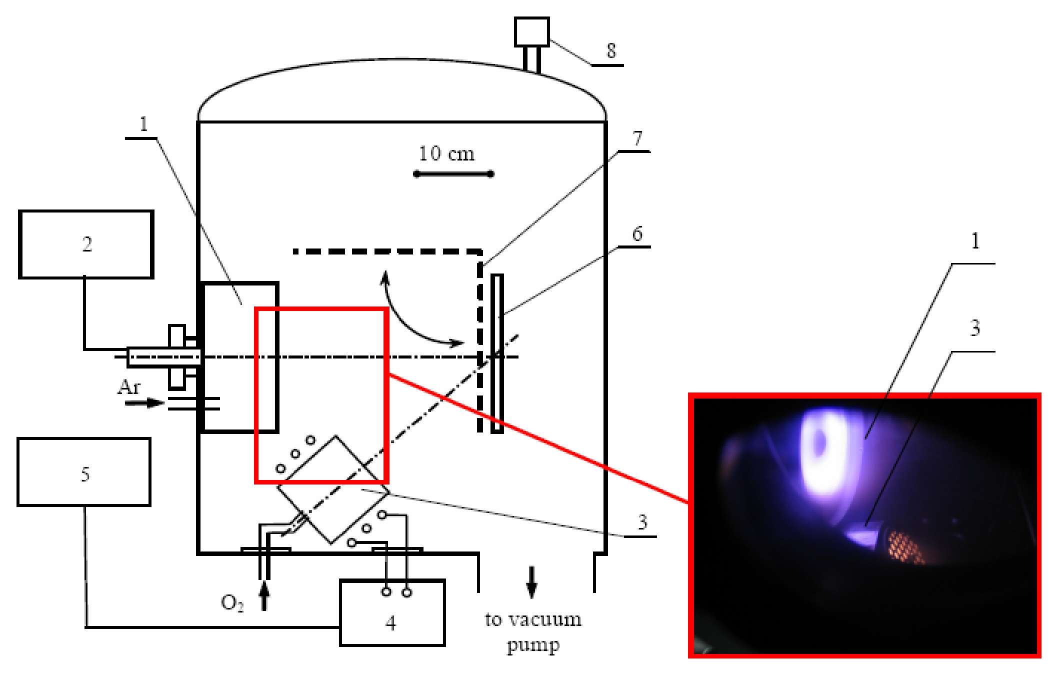
Fig. 2. The multilayer structure "carburized case / TiN coating" created on the gear steel Ferrium C61: a) metallography, b) hardness penetration pattern.

The experiment proved that it is possible to compose hybrid technologies that produce multilayer structures "carburized case / PAPVD coating". The scratch-tests indicated that obtained specific load values (Fn1 – initiation of cohesive failures, Fn2 – initiation of adhesive failures, Fn3 – removal of the coating from the scratch trace) are comparable with those determined for TiN coating deposited on the substrate made of the high-speed steel SW7M hardened to 60 HRC. At the same time the core hardness of 45 – 46 HRC should ensure significantly higher torsional and bending strength in comparison to the high-speed steel SW7M. Moreover, the analysis of the materials investigation results indicated that individual stages of hybrid technology strongly influence the properties of the created multilayer structures "carburized case / PAPVD coating". Particularly, a significant influence of the PAPVD process temperature on the creation of the final structure of the composite, by stimulation of the carbide ε precipitation processes in the carburized case, was proved.

Synthesis of alumina coatings by ICP enhanced reactive magnetron sputtering

In the third part of the project the innovative magnetron sputtering system for synthesis of high-quality aluminum oxide coatings was developed and validated. The basic idea of the system consists in separation of two main constituent processes: metal target sputtering by DC magnetron discharge in inert gas, and activation and transport of reactive gas by additional plasma source based on RF inductive discharge. The key novelty of the present system comparing to known designs is the operation pressure range $(0.7 – 3.5)\times10^{-3}$ mbar where motion of particles may be treated as free fall. It allows the distance magnetron – substrate holder to be increased up to 30 – 40 cm, which leads to significant increase in the deposition area at acceptable deposition rate.

A schematic layout of the magnetron and ICP source in the sputtering chamber is shown in Fig. 3. Properties of deposited coatings are summarized in Table 2.



a) b)

Fig. 3. Experimental setup: a) arrangement of main elements of the deposition system, b) DC magnetron and ICP source during deposition process; 1 – magnetron, 2 – DC power supply, 3 – ICP source, 4 – RF matchbox, 5 – RF power supply, 6 – substrate holder, 7 – substrate shield, 8 – vacuum gauge.

Table 2. Properties of Al_2O_3 coatings deposited by ICP enhanced reactive magnetron sputtering.

Sample No	Underlayer	Thickness [μm]	Roughness Ra/Rz [μm]	Hardness H [GPa]	Young Modulus E [GPa]
1	Al	4.3	0.017/0.199	7.8	197
2	TiN	3.5	0.120/1.477	8.1	209
3	–	2.9	0.037/0.240	7.2	184
4	TiN	2.8	0.130/1.403	8.6	216
5	Al	2.4	0.013/0.143	7.3	180
6	TiN/Al	2.5	0.153/1.653	8.6	213

According to the aim of the work the new ICP enhanced reactive magnetron sputtering technology of synthesis of complex composite high quality coatings based on aluminium oxide for application in duplex technologies have been developed.

During the project execution the following problems have been solved:

1. Original low-pressure magnetron has been developed, produced and researched;
2. Two types of ICP source for the reactive gas activation have been developed, produced and researched;
3. URM3 and Balzers BA510A installations have been modernized for reactive magnetron deposition of oxide coatings;
4. Complex study of the inductive and magnetron plasma has been performed;

5. The new method of arc suppression, suitable for the reactive magnetron sputtering, has been developed;
6. Complex investigations of reactive magnetron deposition of alumina coatings have been carried out;
7. The technology of deposition of high-quality Al_2O_3 coatings in Balzers BA510A installation has been developed.

The obtained alumina coatings allow:

- to improve the hardness and anti-wear properties of steel substrates,
- to reduce friction coefficient between the substrate and the counter-part material,
- to improve corrosion resistance of steel substrates,
- to create composite multi-layer coatings of Al-Al_2O_3, TiN-Al_2O_3 types.

The technique, explored in this study turned out to be an effective method of production of high quality aluminum oxide films by a DC reactive sputtering method with minimized effect of target poisoning. The parallel application of low pressure DC magnetron in the sputtering system has allowed to expand the parameters ranges of stable system operation: working pressure (0.7×10^{-3} mbar - 3.5×10^{-3} mbar), magnetron discharge power (1 – 8 kW), power of activated oxygen source (up to 1 kW), Al_2O_3 coating deposition rate (up to 8 microns/hour), and to improve essentially the coatings quality.

The developed technology allows to obtain, with high reproducibility, on the area up to 1000 cm^2 the highly stoichiometric Al_2O_3 coatings with hardness up to 9 GPa, adhesion up to 100 N and high corrosion resistance.

Project co-operation

E-mail contacts, meetings and researchers visits:

Meetings:
1. Working Group Meeting 12-14.10.2005, Instituto Superior de Engenharia do Porto (Portugal);
   Presentation: *"Comparative analysis of material properties of various composite diffusion layers/PAPVD coating obtained by Complementary Duplex Technologies"*.
2. Conference "SURFACE TREATMENT" 20-23.09.2005, Częstochowa-Kule, Poland
   Presentation: *"Durability of hot forging dies after duplex treatment"*.
3. Working Group Meeting 20-21.04.2006, Inter University Centre, Dubrownik (Croatia);
   Presentation: *"Structure and properties of the multilayer structure "carburized case/TiN coating" obtained by duplex treatment method on the gear steel Ferrium C61"*.
4. Technical Seminary "SURFEX" – The Poznań International Fair (2006)
   Presentation: *"Generation of composites „nitrided layer / PAPVD coating" on cold stamping tools"*.
5. Working Group Meeting 2-3.11.2006, Uppsala University, Uppsala (Sweden);
   Presentation: *"Structure and properties of the multilayer structure "carburized case/TiN coating" obtained by duplex treatment method on the gear steel Ferrium C61"*.

Researchers visits:
Working visits of researchers of Kharkov National University at ITeE aimed at execution of joint tasks within the project:

1. Date of the visit: 09-13.05.2005
   The scope of work: Development of the construction of circular flat magnetron and ICP source, and the systems of their connection to the Balzers BA-510A vacuum chamber.
2. Date of the visit: 11-15.07.2005
   The scope of work: Assembling and start-up of circular flat magnetron and ICP source at the Balzers BA-510A vacuum chamber.
3. Date of the visit: 12-16.12.2005
   The scope of work: Development of processes parameters for deposition of Al_2O_3 coatings in the Balzers BA-510A vacuum chamber equipped with circular flat magnetron and ICP source.

Joint publications:

- A.V. Zykov, S.V. Dudin, S.D. Yakovin, A.N. Dahov, J. Walkowicz, "*Investigation of ICP source with transversal magnetic field",* Physical Surface Engineering, 2005, V.3, No 3-4 (in Ukrainian).
- S.V. Dudin, V.I. Farenik, A.N Dahov, J Walkowicz, *"Development of arc suppression technique for reactive magnetron sputtering"*, Physical Surface Engineering, 2005, V.3, No 3-4 (in English).
- A.V. Zykov, S.V. Dudin, S.D. Yakovin, J. Walkowicz, R. Brudnias, *"ICP enhanced reactive magnetron sputtering system for synthesis of alumina coatings"*, Tribologia 6 (2006) 163

Other forms of international co-operation:

- Joint materials investigation of the composites "nitrided layer / PVD coating" in co-operation with Technical University of Košice, Faculty of Mechanical Engineering, Department of Materials and Technology (Slovakia).

<u>Planned or achieved industrial improvements in commercial use</u>

The following industrial applications of different multi-layer diffusion structures "diffusion layer/PVD coating" were executed:

Tools for cold stamping	FAURECIA, Poland – Car Sites Factory
Tools for hot forging	KRAŚNIK, Poland – Rolling Bearings Factory
Lock accessories – 1	GERDA, Poland – Lock Accessories Factory
Lock accessories – 2	GERDA, Poland – Lock Accessories Factory
Implants and medical tools	Institute for Orthopeady and Traumathology, Ukraine

<u>The project results are reported in following publications</u>

1. A.V. Zykov, S.V. Dudin, S.D. Yakovin, J. Walkowicz, "*Magnetron sputtering system for synthesis of dielectric coatings*", 10th International Conference and School on Plasma Physics and Controlled Fusion, Alushta, Ukraina, September 13-18, 2004.
2. S.D. Yakovin, A.V. Zykov, S.M.I. Borodin, V.I. Farenik, "*Characteristics of magnetron discharge near the pressure switch off*", 10th International Conference and School on Plasma Physics and Controlled Fusion, Alushta, Ukraine, September 13-18, 2004.

3. J. Walkowicz, J. Smolik, C. Bertrand, A. Ioncea "*Application of two stage duplex processes to surface treatment of hot forging tools*", Problemy Eksploatacji, 57 2005 83-92.
4. J. Smolik, J. Walkowicz, Z. Słomka, R. Różycki, *"Comparative analysis of material properties of various composite diffusion layers/PAPVD coating obtained by Complementary Duplex Technologies"*, Proceedings of International Conference-COST 532 Triboscience and Tribotechnology Superior Friction and Wear Control in Engines and Transmissions, Porto, Portugal, 12-14.10.2005, p.223-229.
5. A.V. Zykov, S.V. Dudin, S.D. Yakovin, A.N. Dahov, J. Walkowicz, *"Investigation of ICP source with transversal magnetic field",* Physical Surface Engineering, 2005, V.3, No 3-4 (in Ukrainian).
6. S.V. Dudin, V.I. Farenik, A.N Dahov, J Walkowicz, *"Development of arc suppression technique for reactive magnetron sputtering"*, Physical Surface Engineering, 2005, V.3, No 3-4 (in English).
7. J.Smolik, J.Walkowicz, P.Hermanowicz, Z.Słomka, „*Adhesion investigations of TiN coating in the composite structure „carburised case / TiN coating" obtained on the low-carbon steel Ferrium C61*", ZEM z.4(148) vol.41 (2006) 73
8. A.V. Zykov, S.V. Dudin, S.D. Yakovin, J. Walkowicz, R. Brudnias, *"ICP enhanced reactive magnetron sputtering system for synthesis of alumina coatings"*, Tribologia 6 (2006) 163

ES4 - EFFECTS OF TEXTURE PATTERNS ON TRIBOLOGICAL MACHINE ELEMENTS

Co-ordinator and partners

Co-ordinator:

Krisian Tønder, Norwegian University of Science and Technology (NTNU), Norway; kristian.tonder@ntnu.no

Partners:

At present none outside NTNU

Project status and schedule

Running with partial funding
Starting and ending dates: Jan 2003 – June 2006

Project aims

To study the effects of texturing under dry and lubricated conditions, at the micro and nano levels, in order to generate improved models of the associated phenomena. Further, to establish methods for optimising surface texture for improved machine performance.

Project results

The project is based on theoretical results by Kristian Tønder (hydrodynamically lubricated devices) and by Nam P. Suh (dry and boundary lubricated devices).

A certain amount of experimental data has been obtained, but the results are rather widely scattered. This seems to be caused by difficulties in manufacturing the test rigs and test pieces. In spite of this, the findings do appear to support the existing theories, at least qualitatively. However, the results are still too inconclusive to be published at present.

However, more theoretical work has been conducted. The findings seem to explain some of the odd results obtained in the experimental work. The material was presented in a paper at the International Tribology Conference, WTC2005, in Washington, DC, in Sept. 12-16. "Pivot Inlet Textured Devices".

The findings have been compared to previous results and general trends found in certain classes of differentially textured devices have been studied in a paper that was presented at the COST 532 Conference 12-14 October 2005, in Porto, Portugal, "Special Features of the Performance of Differentially Textured Tribo-Devices".

The paper, "Effects of Striated Texturing on Pivoted Gas Sliders", was presented at the Nordtrib 2006 Conference and the paper "Partial Textured Gas Sliders: Effects of Pivoting", was presented at the Austrib 2006 conference in Brisbane, Australia. Although primarily addressing gas lubrication, some of the results are directly applicable in connection with the present project. Finally, I have written a paper for the Ljubljana Eco Tribology conference in June, entitled “An alternative cylinder wall texture pattern: A first assessment”.

Project co-operation

Various forms of collaboration were hoped for – the Etsion group in Israel seemed very interesting in this context. We have been in touch and have discussed the possibilities of co-operation. No definite results have been obtained.

Planned or achieved industrial improvements in commercial use

Improved sealing properties of rings, seals etc. Better cylinder surface micro-geometry. Better stiffness and damping properties of bearing, seals, read/write heads in magnetic recording. Reduced friction and possibly reduced wear in various devices. Improved hard disk slider performance.

Publications where project results are reported

4. See above

ES5 - ELABORATION OF NOVEL EUTECTIC ALLOYS ON THE BASE OF Al-Mg-Si SYSTEM FOR TRIBOTECHNICAL APPLICATION IN CYLINDER-PISTON GROUPS AT ELEVETATED TEMPERATURES

Co-ordinator and partners

Co-ordinator:

Yuly V. Milman Professor, Corresp. Member of National Academy of Science of Ukraine, Institute for Problems of Materials Science, National Academy of Science of Ukraine (IPMS NASU), Ukraine
milman@ipms.kiev.ua

Project status and schedule

Finished
Starting and ending dates 01.01.2003-21.03.2007

Project aims

The aim of the investigation suggested is both the development of the scientific basis of the purposeful alloying by transition and rare earth metals of cast eutectic alloys of the Al-Mg-Si system as a promising material for cylinder-piston groups and the clarification of the mechanism of influence of the alloying on their tribological properties. As a result, a new material will be created in which all main mechanisms of strengthening will be realized; conditions of hardening by thermal treatment will be optimized, and its tribological behavior will be studied in the temperature range 20-300 °C.

Project results

It is well known that details of the cylinder-piston group play the most important role in the operation of engines. During the operation, a piston undergoes the action of a number of factors, which leads to a deterioration of its working characteristics (www.avtrmat.com) To such factors, we refer, first of all, the temperature and wear (crumpling) of separate sections. Therefore, a material taken for the production of pistons must be heat-resistant and wear-resistant. The next problem is the wear of different part of piston. (Fig 1) It is necessary not only to create high wear-resistant material, but to evaluate its tribotechnical properties as well. In solving the complicated problems of friction and wear, researchers pay more attention at present to the methods that allow one to get reliable information about the nature of structural and phase transformations in the contact zone that is the basis for development of the physical criteria of the forecasting of behaviour of tribosystems under given conditions.

Analysis of the conditions of operation of a cylinder-piston group including a “piston ring- piston” couple has shown that it is necessary to simulate both reversible sliding and impact (dynamical) loads in friction and wear test of this group materials. Thus also it is necessary to take into account high temperatures in a zone of a piston flute and the impoverished conditions of greasing with possible occurrence of an abrasive

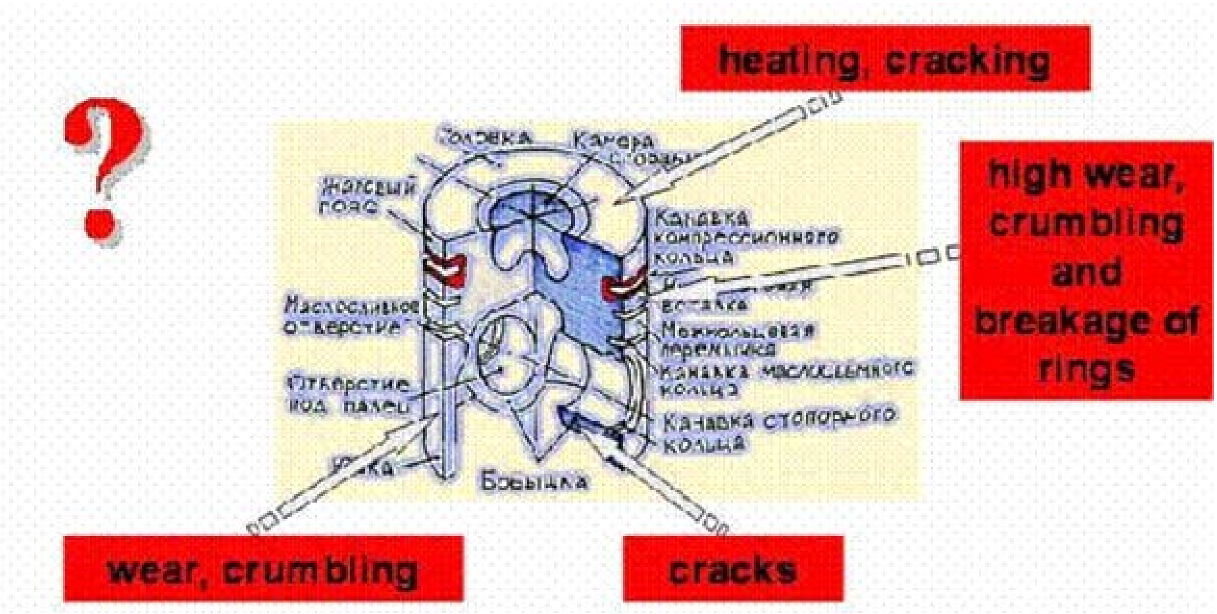


Fig. 1. Pistons, problems which demand the discussion.

The traditional cast aluminium alloys are the eutectic alloys of binary systems, whose structure and phase composition are directly formed in the process of crystallization and the subsequent thermal treatment. The presence of the eutectic and a narrow interval of crystallization ensure the good casting properties and the quality of produced ingots. But at present, the resources to improve the parameters of industrial alloys, in particular their heat resistance which is closely related to the melting temperature of alloys are practically exhausted.

To develop a basically new class of Al-base cast alloys with high melting temperature, authors have advanced the own approach that is based on the using the ternary phase diagrams that have quasi-binary eutectic type cross sections between the aluminium solid solution and the intermetallic phases. The ternary Al-Mg-Si system belongs to this type of diagrams. The (α-Al+Mg_2Si) eutectic in alloys which compositions are located on the quasi-binary cross sections crystallize at a constant temperature (~600 °C) that exceeds the melting temperatures of the eutectic of boundary binary Al-Si and Al-Mg systems fig 2. A distinctive feature of ternary system Al-Mg-Si is a shift both of the quasi-binary section and of the area of two-phase alloys to the magnesium enriched region. This creates premises to regulate in a wide range (0.2 - 6 at. %) magnesium content in matrix of the eutectic alloys, retaining simultaneously their phase composition and structure. In turn, it creates a possibility to develop a principally new system of alloying these alloys.

To ensure high level of physical and mechanical properties at room and elevated temperatures, different systems of coherent particles in matrix of eutectic (α-Al+Mg_2Si) alloys can be created in the selected system of alloys. Note that such particles should not interact with eutectic colonies. This guarantees a stability of strength of the eutectic composite at elevated temperatures. In addition, quasi-binary eutectic transformation in alloys ensures the retaining of necessary phase composition of the material directly in crystallization process.

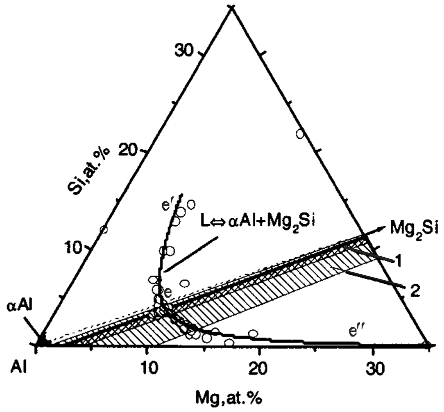
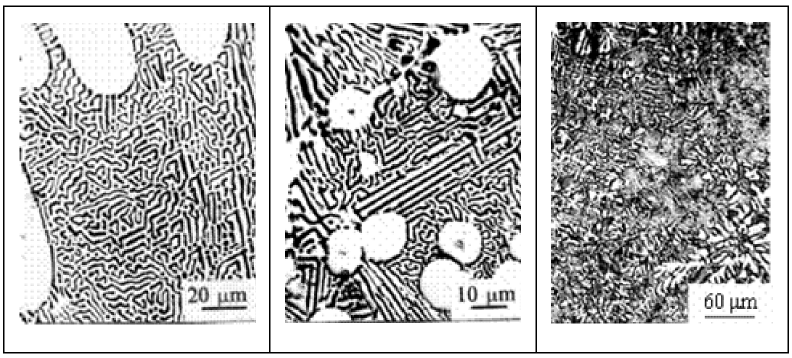


Fig. 2. Fragment of the phase diagram of the Al-Mg-Si system: experimental line e′e e″ of the monovariant eutectic transformations L⇆ α-Al+Mg_2Si (solid curve). Thick straight line represents the quasi-binary section and dash line represents the stoichiometric section. 1 is the area of (α-Al+Mg_2Si) binary after annealing alloys, and 2 is the area of (α-Al+Mg_2Si) binary at crystallization alloys.

Doing this we must follow to a number of criterions. First, the chemical nature of reinforcing particles, which don't interact with eutectic colonies, must differ from chemical composition of phases, that form eutectic. It will guarantee the stability of materials properties during exploitation for a long time. Secondly, the best dispersed particles must have the crystal structure which will be coherent to matrix of the eutectic composite.

The alloying of baseline alloy influences to its structure essentially: the anisotropy of growth rate of α-solid solution metallic dendrites diminishes the morphology and dispersivity of eutectic change (fig. 3).



a b c

Fig. 3. Microstructure of eutectic (α-Al+Mg_2Si) alloys: a) baseline alloy; b) alloy 2, alloyed with $Me^{III}Me^{IV}$; c) alloy 3, alloyed with $Me^{III}Me^{IV}BMn$.

To design new the modern cast alloys for piston group the ternary Al-Mg-Si system was select as the base system. Wide region of existence of univariant eutectic transformation L⇆α-Al+Mg_2Si in this system allow us to change a proportion of components of alloys in wide limits without changing of its phase composition. The alloys, compositions of which are situated on the quasibinary sections of the phase diagrams are the most suitable for such requirements. These alloys have a high eutectic temperature, with high volume part of reinforcing phase in eutectic and with phase composition, which will be stable under alloying. Optimization of alloying system was carried out taking into account the concentration-temperature parameters of eutectic transformation, thermal stability and phase composition of the multicomponent eutectic alloy.

Due to purposeful alloying the system of particles is created in the matrix of eutectic (α-Al+Mg_2Si) alloys, that promises the premeditated level of physical and mechanical properties As seen (fig 4), the proposed family of cast eutectic alloys possesses a high level of the strength properties in the whole temperature interval. These strength characteristics are much superior to those of hypoeutectic silumin in the «dangerous interval» for piston (260 °C).

On the whole, the course of implementation of the project oriented so that we will be able to choose the optimum variant of an alloy by the totality of its mechanical and wear-resistant properties, to estimate its workability, and to draw conclusion on the possibility to use it in the batch production of automobile pistons. At the same time, we have all the reasons to believe that the pistons made of alloys on the base of the Al-Mg-Si system will reveal a number of advantages as compared to the ordinary ones made of silumins used as piston materials.

First, authors expect a greater heat resistance of new alloys produced on the base of the Al-Mg-Si system, which is desirable under conditions of the operation of a bottom and piston grooves. Secondly, we may assume the presence of good casting properties and workability of the alloys of this system. Thirdly, the peculiarities of a structure of the new alloys allow us to expect their high wear resistance and crack resistance, which is important for the operation of piston grooves, piston bosses, and piston skirt. Fourthly, a high content of Mg will lead to a lesser weight of pistons, which is essential for modern engines. Fifthly, we may expect that the new piston material will remain in the same price range as ordinary silumins.

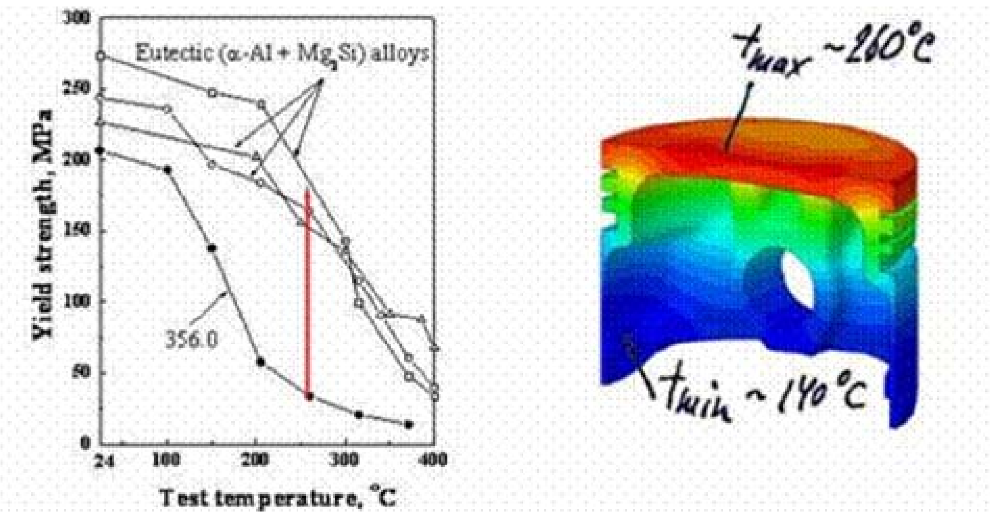


Fig. 4. Temperature dependence of yield stress in the tensile test of the multicomponent eutectic (α-Al+Mg_2Si) alloys and commercial cast alloy 356.0.*

** Information acquired from monograph "Aluminum and Aluminum Alloys" (ASM International Materials Park, USA 1993)*

It is known that the mechanical properties of alloys are defined by their phase composition and structure (the dispersion, morphology of phases, distribution of alloying elements, etc.). These factors depend to a significant extent on the production conditions and the modes of thermal treatment. The results of earlier performed studies which were given in the previous reports were obtained on the study of the structure and properties of laboratory specimens of about 200 g in weight. The last stage of the study is devoted to the influence of the scale factor under the transition to ingots of up to 20 kg in weight.

With this purpose, special equipment was manufactured, and the work aimed at the determination of the temperature-time relationships of the smelting of these ingots was started.

In Fig. 5, we give the general view of an induction furnace. The consumed power of the furnace with its capacity of 20 kg is 160 kW.

Fig. 5. Overall view of induction furnace and ingot weight ~20 kg.

The heating and melting of a charge occur at the expense of the heat produced by a secondary current induced in the charge material. A packed crucible chemically inert relative to melted aluminum was manufactured from graphite.

A crucible was placed in an inducter fed by an alternate current with a frequency of 2.4 kHz. The inductor height was significantly greater than that of a crucible, and the ratio of the diameters of the inducter and a mold ensured the homogeneity of the field.

A charge is loaded into the crucible from above by hand. A melted metal is poured in a metallic mold through a lip under tilting the furnace with the help of a hydraulic drive. After each smelting, the crucible can be easily inspected and trimmed.

In the production of alloys, we used the master alloys composed of basic and alloying elements. To provide the correspondence between the chemical composition of produced alloys and the rated data, we keep a certain sequence in the loading of charge materials. For example, we introduced the intensively burning-out elements in the last turn. The master alloys with close melting temperatures were loaded simultaneously. Experimentally, we established the order of the loadings of charge materials which led to both the acceleration of the smelting and a decrease in the temperature, at which the smelting is carried out, with the purpose to ensure the purity of a melt and, hence, to remove nonmetallic inclusions from the ingot. To create the chemically inert layer on the surface of a melt during the smelting, we used a flux consisting of a mixture of halogen salts possessing a lesser density and a lower melting temperature as compared with the alloy.

The master alloys used in the production of alloys had low melting temperatures and were homogeneous by their chemical compositions. In a number of cases, to ensure both the homogeneity of a chemical composition and the dispersion of phase components introduced into a melt, the master alloys were obtained in the form of a strip by the method of fast crystallization on the installation for production of melt-spun ribbons.

We have determined the temperature-time conditions of the realization of a smelting which include the heating rate (more than 170°/min to prevent the oxidation of a charge), temperature and duration of a smelting which are crucial for the provision of the maximum purity of a melt relative to hydrogen and nonmetallic inclusions, and casting temperature and crystallization rate which ensure the conservation of alloying elements in a solid solution. The successive thermal treatment of specimens made of the alloy promoted the separation of dispersed particles additionally strengthening the matrix of the eutectic (α-Al+Mg_2Si) composite.

The smelting of small ingots was carried out in the electric furnace of resistance from pure materials and ligatures. For creation on a surface melt chemically passive layer as a flux used a mix of salts LiF and LiCl. The order of loading of the burden materials and time-temperature parameters swimming trunks is by practical consideration determined: T_{fusion}=700-750 °C; $T_{filling}$=680-750 °C; T_{mould}=150 °C; duration of fusion – 30-40 min.

The complex investigation of physical and mechanical properties of eutectic alloys in comparison with known industrial cast 356.0 and 390.0 alloys (USA) has been carried out. Hypoeutectic cast alloy 356.0, related to silumin class, might be selected as prototype of baseline alloy. The alloy 390.0 has the best wear characteristics and coefficient of thermal expansion among cast alloys, the good high-temperature strength and, from this point of view, is interesting for comparison.

For the alloys melted in resistance furnace the dependence of strength on duration of exposure time at test temperatures of 205, 260 and 315 °C has been studied. All samples were maintained during 10 and 50 hours in a furnace under test temperature. Then the samples were transposed in heating chamber of test installation, were stabilized under test temperature and were loaded up to fracture.

The dependences of yield strength of alloys on time, presented in fig. 6, indicate about exclusive thermal resistance of eutectic (α-Al+Mg_2Si) alloys at temperatures mentioned comparing with alloy-prototype 356.0 or cast alloy 390.0. The degree of weakening of last alloys depends on duration time under test temperature and, in contrast to eutectic alloy, sharply increased with temperature rise.

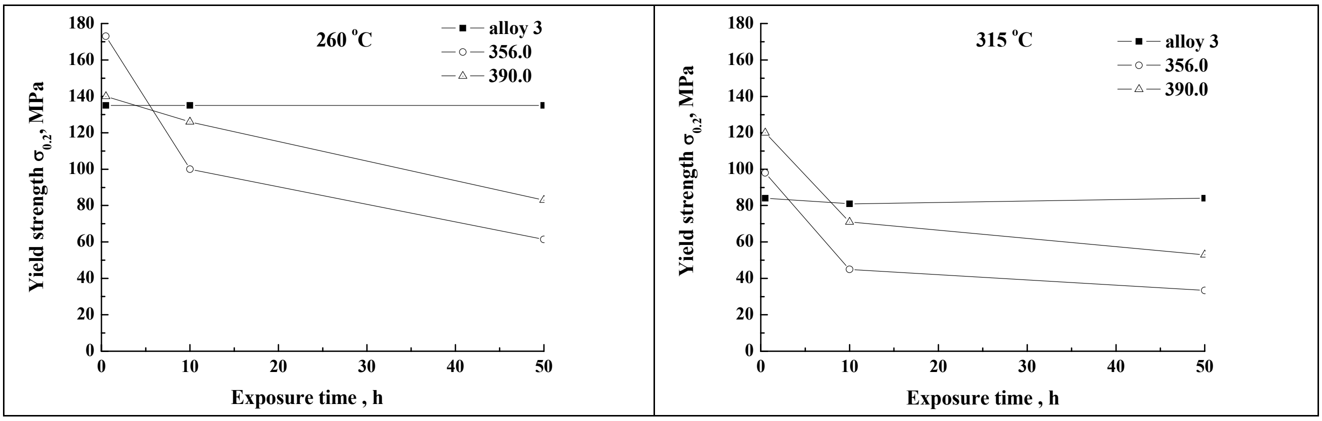


Fig. 6. Influence of exposure time at the testing temperature on yield strength of cast alloys.

Note that in all temperature interval of tests the yield strength of alloyed eutectic (α-Al+Mg_2Si) alloys is higher than prototype – cast alloy 356.0 (fig. 3), and after long-term duration in temperature interval of 200 – 400 ^oC the new alloys exceed the best cast high-temperature strong alloys.

With the help of dilatometer method the coefficient of thermal expansion (c.t.e.) of cast alloys in temperature interval of 20-300 ^oC has been determined. As it known from data obtained (table 1), the values of thermal expansion coefficient for workable alloys are found on the level of alloy-prototipe 356.0 and some rebate to 390.0 alloy.

Table 1. Values of thermal expansion coefficients of cast alloys.

Alloy (alloying)	Thermal expansion coefficient α (μm / m·K)	
	20-100^{o}C	20-300^{o}C
Al	23,9	-
	23,6*	25,5*
356.0	21,3	23,1
	21,5*	23,5*
390. 0	18,2	18,7
	18*	-
alloy 3	21,1	23,1

The procedure of studying friction and wear with inactive lubricant specimens containing different volume part of Mg_2Si realized during reversible sliding on the scheme "sphere-plane. As it is known, the additional applying of a dynamical component of normal loading, even if it makes up several percents of the steady-loading level, can give substantial nonlinear (multiple) increasing the wear intensity and even changing the type of wear. All the tests were carried out in the tribocomplex CATC (Computer Assistant Tribology Complex Wear 258 (2005) 77–82) by the ball-on-plate test with reciprocating sliding movement of the indenter. The indenter was a ceramic sphere 6 mm in diameter made from Si_3N_4. The sliding velocity was 0.013 m/s, the load on the indenter was 22 N, a lubricant of liquid paraffin was used. The presence of the lubricant increased the reproducibility of the results, eliminating the contribution of chemical interactions on the friction force. The tests in the quasistatic mode were carried out at constant load. The tests in the dynamic mode were carried out imposing an alternating component of the load with the amplitude equal to 10% of that for the static mode and with the frequency of 25 Hz. The duration of each test was 30 min. During the motion of the indenter some material is displaced from the contact zone, and lateral pile-ups of material form on both sides of the friction track. The transverse profiles of the friction tracks for areas under investigation were determined using a profilometer. Based on the experimental parameters, the set of criteria (Wear 258 (2005) 77–82) for the mechanism of friction were calculated:

K, the factor of the relative intensity of dynamical wear $K = h_d\text{-}h_s/h_s$. h_s, h_d are the depths of wear groove for quasistatic and dynamical modes of loading, respectively;
P, parameter of plastification $P = S_b/S$. S_b is the area of the piled-up material and *S* is the area of the wear groove;
D, the debris product factor (correlates with the weight wear) $D = S\text{-}S_b/S$.

Wear rate (table 2 and fig. 7) is minimum for alloy-prototype 356.0 and 390.0 by quasistationary loading. There is the 356.0 alloys wear rate sharply increases due to the dynamic loading. This alloy has not enough reliability to use in unsteady dynamic loading conditions. When criterion K is small, materials has the advantages in friction under tribotests, usually. Therefore for 390.0 alloy the magnification of wear rate are insignificant under dynamic loading. Taking into account the data presented earlier about thermal stability of the alloys investigated (fig. 6), it is possible to forecast that elevation of test temperature higher than 250 ^{o}C will lead to weakening of this alloy and, as a consequence will the wear intensification.

From standpoint of wear resistance the structures in fig. 3c are optimal, that gives essential increase of wear resistance under both regimes of loading.

Table 2. Results of tribotechnical tests for cast aluminum alloys.

Alloy	Quasistationary regime		Dynamical regime		K
	I_S (μm)	F_S (H)	I_d (μm)	F_d (H)	
Alloy 1 (baseline alloy)	6.298		15.58		1.474
Alloy 4 (Me^{III} Me^{IV})	6.322		16.097		1.546
Alloy 3 ($Me^{III}Me^{IV}$B Mn)	2.99		8.39		1.807
Alloy 5 (Me^{III} Me^{IV} Fe Ni)	6.322	1.240	14.08	0.255	1.227
Alloy 6 (Me^{III} Me^{IV} Cr Mn)	4.711	1.208	7.846	0.168	0.665
Alloy 7 (Me^{III} Me^{IV} Cu Ni)	3.612	1.005	8.445	0.174	1.338
356.0	2.204	0.8963	15.34	0.192	5.959
390.0	1.557	0.786	1.989	0.115	0.227

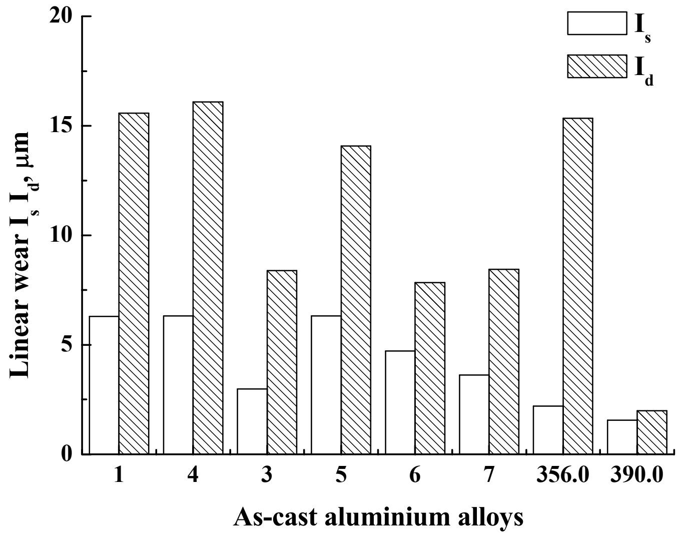


Fig. 7. Factors of wear for cast aluminum alloys (table 2) under quasistationary and dynamic regimes of loading.

In the mode of a static loading, the advantage of a new alloy becomes obvious at increasing the testing temperature. At the dynamic testing, the wear resistance of our alloys is much higher than that of hypoeutectic silumin but somewhat less than that of hypereutectic one.

However, upon the testing for wear, one analyzes usually the behavior of a friction couple such as a piston and a piston ring. In cars produced at the Volga automobile plant (VAP), piston rings are made of high-strength cast iron which is strongly worn in the couple with hypereutectic silumin. At present, the best piston alloy used at VAP is alloy AK10M2N. The comparative tests of this alloy and the new hypereutectic α-Al+Mg_2Si alloys showed the obvious advantage of the latter under both the static and dynamical testing modes. Fig 8.

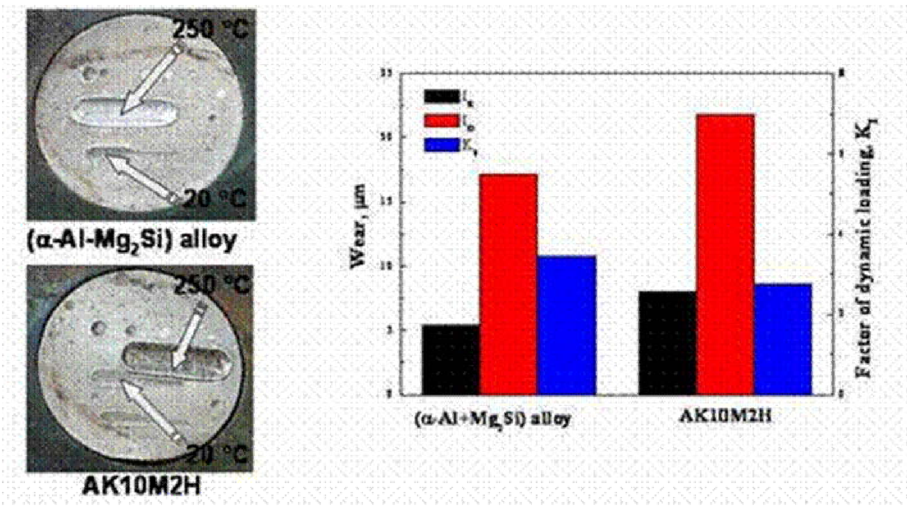


Fig. 8 Decided superiority of α-Al-Mg_2Si cast alloys tribology behaviours.

Conclusion

The new conception that is based on the using the ternary phase diagram Al-Mg-Si that have quasi-binary eutectic type cross sections between the aluminum solid solution and the intermetallic phases was proposed.

In view of the performed studies, may be concluded that the new cast □-Al-Mg_2Si alloys of Al-Mg-Si ternary system with a unique complex of physical, mechanical and tribology properties can be successfully used for the substitution of available piston hypoeutectic alloys of the binary system Al-Si.

1. It was shown a greater heat resistance of new alloys produced on the base of the Al-Mg-Si system, which is desirable under conditions of the operation of a bottom and piston grooves.
2. New alloys have good casting properties and workability.
3. The peculiarities of a structure and tribology characteristics of the new alloys allow us to expect their high wear resistance and crack resistance, which is important for the operation of piston grooves, piston bosses, and piston skirt.
4. A high content of Mg leads to the decreasing of weight of pistons, which is essential for modern engines.

Project co-operation

Mention the forms of co-operation used: e-mail contacts, meetings, seminars, researchers visits, joint publications, joint presentations, COST Short Term Scientific Missions etc

Industrial improvements in commercial use

Description of the planned industrial improvements or improvements already in commercial use. Appropriate company and product names can be mentioned but do not include confidential information

Publications were project results are reported

1. Milman Yu.V. High-strength aluminum alloys. *Metallic Materials with High Structural Efficiency. Eds.: O.Senkov, D.Miracle and S.Firstov.* Kluwer Academic Publishers, 2004, p.139.
2. Barabash O.M., Milman Yu.V., Korzhova N.P., Legkaya T.N., Podrezov Y.N., 2002, Design of new cast aluminium materials using properties of monovariant eutectic transformation L↔α-Al+Mg_2Si, Proceedings of the 8^{th} Conference ICAA8, Cambridge, UK, July 2-5, part 2, p. 729-734.
3. Barabash O.M., Milman Yu.V., Korzhova N.P., Legkaya T.N., Podrezov Y.N., Voskoboinik I.V., 2002, Principles for creation of new advanced high-strength cast eutectic aluminum alloys, Proceedings of the International Conference “Science for Materials in the frontier of centuries: Advantages and Challenges”, November 4-8, Kyiv, Ukraine, part 1, p. 473-474.
4. Patent 2224811 RU, МПК[7] C22 C 21/06. Cast aluminum alloy.
5. Patent 72560 UA, C22C21/08, 21/06, 21/00. Cast aluminum alloy.
6. Korzhova N.P., Milman J.B., Barabash O.M., Legka T.M., New piston cast alloys of the ternary system Al-Mg-Si with enhanced level od their physical and mechanical properties, POLISH - UKRAINIAN FORUM ALUMINIUM IN FUTURE, KRAKÓW, 23-24 JUNE 2005.
7. Final reports of national program state register #01030006382.

8. Yu.V. Milman, K.E. Grinkevich, N.P. Korzhova, Yu.N. Podrezov, O.M. Barabash, T.N. Legkaya New conception for creation al eutectic alloys for tribology application at elevated temperatures “COST 532 ES5” submitted to ECOTRIB 2007 Joint European Conference on Tribology and Final conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007, Ljubljana, Slovenia.

Planned or achieved industrial improvements in commercial use

Direct discussions with EADS Company (Munich’) take place.

ES6 - REDUCTION OF THE ENVIRONMENTAL IMPACT BY MEANS OF THE USE OF ADVANCED SURFACE TREATMENTS AND LUBRICANTS IN ENGINES

Co-ordinator and partners

Co-ordinator:

Dr. Amaya Igartua, Fundación TEKNIKER, Eibar, Spain

Partners:

Peru Arribalzaga, Guascor; Jesús Landa, Tarabusi; José Soler, Krafft; Ricardo Zabala, Abamotor

Project status and schedule

Project started nearly 3 years ago

Project aims

The aim of this project is to reduce the environmental impact (vibration, noise, CO_2 emissions, friction wear) in engines. For that, different approaches will be analysed by means of this project:

- The use of advanced lubricants for low fuel consumption, emissions reduction and improvements of the wear and friction to increase the life of critical components of the engine.
- The use biogas as combustible for engines. The presence of siloxanes in the oil should be avoided or their effects minimised.
- The use of advanced surface treatments, thin or thick coatings and laser surface texturing (LST) in critical engine components (cylinder liners, pistons, piston rings, guides, valves,..).
- The use of light weight materials in critical engine components (cylinders, pistons,..)

The way to increase efficiency to reduce emissions by the use of high thermal fatigue resistant materials for dry exhaust manifold, reduced friction and higher resistance materials for more severe working conditions.

Project results

- Up to know, in collaboration with ABAMOTOR, the mechanical **calculus to measure the axial effort of a pump** has been performed by TEKNIKER using strain gauges techniques. Good results for the measurements will allow improving the design.
- A new software to calculate the cam/tapped test bench from GUASCOR has been developed by TEKNIKER and validated in the testing bench from GUASCOR. The calculus are used for design improvements.
- In a third stage, in collaboration with TARABUSI the materials of the critical components of the engine (piston rings) are being modified applying **surface treatments** and the effect of the treatments evaluated using **tribological tests**. New coatings have been applied to the piston rings. The results of the evaluation has been presented in the COST Conference from Ghent and

Porto Conference. These results have been compared with the triboreactive surface treatments developed in the frame of EREBIO project, and the results have been presented in the COST 532 workshop in Dubrovnik.

On the other hand, it has been made tests to setup a new configuration developed by TEKNIKER to test cylinder liner/piston rings. TEKNIKER is contributing with VTT and BAM to setup a new standard.

A new biodegradable lubricant for 2 stroke engine oils has been developed by KRAFFT and tested by TEKNIKER. The lubricant allows reducing the oil% in the mixture from 4% to 2%.

A new lubricant for 4 stroke engines with low viscosity has been developed by KRAFFT for the application of heavy duty engines. The low viscosity oil had a better behaviour than the higher viscosity oil also under extreme pressure tests. No significative influence in the reduction of emissions has been achieved, just a small reduction of blowby. It seems that a reduction is achieved with low viscosity grades.

Project co-operation

The forms of co-operation used: e-mail contacts, meetings, seminars, researchers visits. Collaboration to other members of the COST Action are welcome, for example:

- A collaboration with Prof. Y. V. Milman, Institute for Problems and Materials Science, Acad. Sci. of Ukranie, Kiev, Ukranie, will be performed and the **new eutectic alloys** based on Al-Mg-Si could be tested in REMTRAL project as an alternative to actual used alloys in pistons. Also collaboration with **VTT, Finland** (project L9) is being defined in relation to perform **intercomparison between their (piston ring bench tests) and REMTRAL piston ring/cylinder liner bench tests**. This collaboration will take more dimensions with the elaboration of a standard for piston ring/cylinder liner simulation. A proposal for the European Commission has been prepared in collaboration with BAM.
- A collaboration can be realised with the project **M13 and M10**, the supply of the powder to deposit by **thermal spray plasma of the new alloys containing TiC,** can be performed, or on the other side, the engine components supplier of REMTRAL Project could supply components to be deposited by the projects M13 and M10 in order to be tested in the company.
- The REMTRAL consortium is interested in the results of the project M12, considering **continuous duplex coatings** a good alternative for their application in critical engine components. Malta representative would like to cooperate with Prof. Milman in the treatment of the new **eutectic aluminium alloys** with **plasma nitruration**, A. Igartua from TEKNIKER in **high pressure nitruration**, and Jan Meneve from VITO in **Laser treatment** of these alloys Eureka Umbrella ENIWEP.

In the frame of the Eureka Umbrella ENIWEP, it has been proposed the continuation of this project called EQUIMOTOR.

Publications were project results are reported

The publications performed related to this project are the following:

1. A Igartua, G. Mendoza, J. A. Picas, A. Forn, *“”**Tribological behaviour of HVOF Thermal Sprayed Nanocrystalline CrC-NiCr Coatings**”,* International Conference The Coatings,

Thessaloniki, Greece, 28-29 November 2002, 24th IRG-OECD Meeting Slovenia, 16, 17th October, Portoroz, Slovenia, 2003.

2. J. A. Picas, A. Forn, A. Igartua, X. Fernández y G. Mendoza, **"*Comportamiento tribológico de los recubrimientos de CrC-NiCr, WC-Co y WC-CoCr obtenidos por proyección térmica HVOF*",** IX Congreso Nacional de Tratamientos Térmicos y de Superficie, Tratermat 2003, San Sebastián, 28-29 Mayo 2003.
3. Igartua[1], G. Mendoza[1], X. Fernández[1], V. Bellido-González[2], S. Powell[2], M. Bolton[3], M.G. Talks[4], E. Momeñe[5] "*Replacement of hard-chrome in cylinder liners. A PVD deposition approach", 1st COST 532 Conference in Ghent*", 18-20th 2004
4. J. Landa, I. Illarramendi, J. M. Montalban, A. Igartua and G. Mendoza, *"Wear and friction in piston rings"*; 1st COST 532 Conference in Ghent, 18-20th 2004.
5. A. Igartua, O. Areitioaurtena, N. Kelling, M. Hartelt, A. Skopp, M. Woydt, C. Seyfert, R. Luther, "Tribological performance of bio-no-tox lubricants and new triboactive materials for piston ring/cylinder liner system", Green Tech 2005, 2,3 February, 2005.
6. A. Igartua, J. Barriga and A. Aranzabe "Report Biodegradable Lubricants", Virtual Tribology Institute Edition, 2005.
7. "Recubrimientos por Electro Oxidación de Plasma para aplicaciones en Pistones de Magnesio", A. Igartua , X. Fernández, J. Barriga, P. Shashkov, S. Usov, I. Illarramendi, J. Landa, **III Ibertrib**, Guimaraes, Junio 2005.
8. A. Igartua, "Emission reduction from engines and transmissions substituting harmful additives in biolubricants by triboreactive materials (EREBIO), **Thematic Network** *"Efficient and low emitting propulsion technologies* ***(PREMTECH II)"*** , Praga, 16, 17 Junio 2005.
9. Igartua, A. Marcaide, O. Areitioaurtena, A. Aranzabe & J. Terradillos " *I European Ecolabel*" "Report Biodegradable Lubricants" I1-I7, Virtual Tribology Institute Edition, 2005.
10. A. Igartua & X. Fernández from TEKNIKER, R. Luther & CH. Seyfert from FUCHS, B. Duffau from RENAULT. *"Biolubricants for automotive applications - IV Engine Oils"***.** "Report Biodegradable Lubricants" IV1-IV5, Virtual Tribology Institute Edition, 2005.
11. M. Woydt & A. Skopp from BAM, O. Areitioaurtena & A. Igartua from TEKNIKER. " *ASH-free and bionotox engine oils- IV Engine Oils*". "Report Biodegradable Lubricants" IV6-IV9, Virtual Tribology Institute Edition, 2005.
12. A. Igartua, O. Areitioaurtena, X. Fernández, R. Luther, Ch. Seyfert, B. Duffau, M. Berg, H. Schultheiss, I. Illarramendi, J. Landa, "Biolubricants for automotive applications", COST 532-NIST Conference , Proceedings pag. 171-9, 12-14 Octubre, 2005, Porto, Portugal
13. A. Igartua, X. Fernández, P. Shashkov, S. Usov, I. Illarramendi and J. Landa, "Plasma Electroxidation coatings for magnesium piston applications, COST 532-NIST Conference, Proceedings 207-215, 12-14 de Octubre 2005, Porto, Portugal. EUROMAT, 5-8 Septiembre 2005, Praga, República Checa.
14. J. Landa, A. Igartua, "Selección de materiales para disminuir el desgaste de los componentes de motor", Seminario de fricción y desgaste. Su impacto en la industria organizado por TEKNIKER, 27 de Octubre 2005, Madrid, España
15. A. Igartua, G. Mendoza, A. Forn, J.A. Picas, "Comportamiento tribológico de los recubrimientos nanocristalinos de CrC-Ni-Cr obtenidos por proyección iónica de nitrógeno", Boletín de la Sociedad Española de Cerámica y Vidrio, vol. 43, nº 2, marzo-abril **2004.**
16. A. Alberdi, S. Merino, "Microstructured Surfaces for Tribological Applications", Tribology and Lubrication Engineering, 14th International Colloquium Tribology, 13-15th January **2004.**
17. A. Igartua, J. Barriga and A. Aranzabe "Report Biodegradable Lubricants", Virtual Tribology Institute Edition, 2005.
18. R. Martins, J. Seabra, A. Brito, Ch. Seyfert, R. Luther, A. Igartua, "Friction coefficient in FZG gears lubricated with industrial gear oils: Biodegradable ester vs. mineral oil", Tribology International, 39 (2006), 512-521.

19. A. Igartua, P. Arribalzaga, L. Urdangarin “Emission reduction from engines and transmissions substituting harmful additives in biolubricants by triboreactive materials (EREBIO), **Thematic Network** *"Efficient and low emitting propulsion technologies* ***(PREMTECH III),*** *Krakow, 16-17th June 2005.* COST 532 Symposium of Tribology, 20-21st April 2006, Dubrovnik, Croatia.
20. A. Aranzabe, A. Igartua, X. Fernández, O. Areitioaurtena, R. Luther, C. H. Seyfert, L. Urdangarin, P. Arribalzaga, M. berg, H. Schultheiss, M. Woydt, “Biolubricants for heavy duty engine oil”, LUBMAT Conference, Preston, UK, 14-16 June 2006.
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22. R. Martínex, R.J. Rodríguez, J. A. García, A. Igartua, R. Bayón, X. Fernández, A. de Frutos, M. A. Arenas, J. de Damborenea, “Comportamiento frente a corrosion y desgaste de recubrimientos PVD multicapa Cr/CrN para aplicaciones de transmisiones”, Iberotrib, 21-22 Junio 2007, Bilbao, España.
23. A. Igartua, X. Fernández, O. Areitioaurtena, R. Luther, C. H. Seyfert, O. J. Rausch, I. Illarramendi, M. Berg, H. Schultheiß; B. Duffau, S. Plouseau, “Biolubricantes y Materiales Triboreactivos para automoción”; Iberotrib, 21-22 Junio 2007, Bilbao, España.
24. A. Igartua, X. Fernández, O. Areitioaurtena, R. Luther, C. H. Seyfert, O. J. Rausch, I. Illarramendi, M. Berg, H. Schultheiß; B. Duffau, S. Plouseau, “Biolubricants and triboreactive materials for automotive applications”, ECOTRIB 07, 14-15Junio, Slovenia

Planned or achieved industrial improvements in commercial use

The results will be implemented by Guascor and Abamotor in their engines and motopumps respectively. The lubricants will be selling by KRAFFT. Tarabusi will sell piston rings and pistons with new surface treatments.

ES7 - INFLUENCE OF HVOF COATINGS MICROSTRUCTURE ON THEIR TRIBOLOGICAL CHARACTERISTICS AND THE VISUALISATION OF SURFACES CHANGES

Co-ordinator and partners

Co-ordinator:

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Ing. Štefan Perháč
Technical University, Slovakia

Running and funding

Starting and ending dates 8/2002 –8/2007

Project aims

The scientific aim of the study is to determine relationship between structure of thermally sprayed coatings by HVOF method and their tribological behaviors. After analysis of thermally sprayed samples and selection of optimal parameters for spraying the abrasion, adhesion and erosion apparatus will be used for evaluating of their tribological behaviors. The SCAN, EDX analysis will applied for study of surface changes during the wear tests. The mechanisms failure of coatings will be studied by AFM.

Project results

In the first stage of the project the program for investigation the influence of morphology after erosive and abrasive wear was prepared. Czech participants were prepared the specimens by HVOF methods. The specimens thermally sprayed (cold spraying) were equiped by VUZ PI Bratislava, Slovakia. For thermally sprayed coatings the adhesive, erosive and adhesion tests were carried out.

The microstructures of thermally sprayed coatings were evaluated EDS, SEM and optical microscopy.

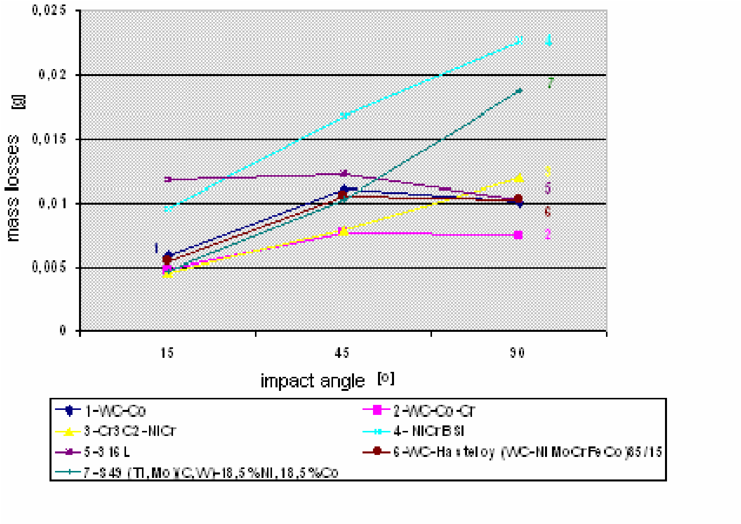


Fig. 1. Erosive wear resistance.

The results of erosive tests of HVOF coatings (for parameters: incidence speed of particles: 50 $m.s^{-1}$, impact angle of particles: 15°, 45°, 90°) showed that wear resistance of material WC-Co is little dependent on impact angle Fig. 2.

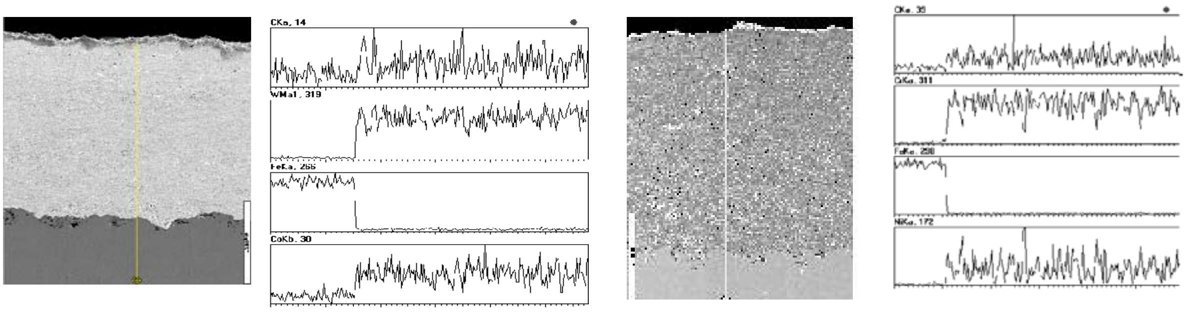
In the framework of the project the tests of the erosive wear were carried out with samples thermally sprayed (cold spraying) prepared by VUZ PI Bratislava. The results of erosive test are in Tab. 1.

WC-Co- α=15°   WC-Co- α=90°

Fig. 2. Morphology of HVOF coatings after impact angle α=15° and α=90°.

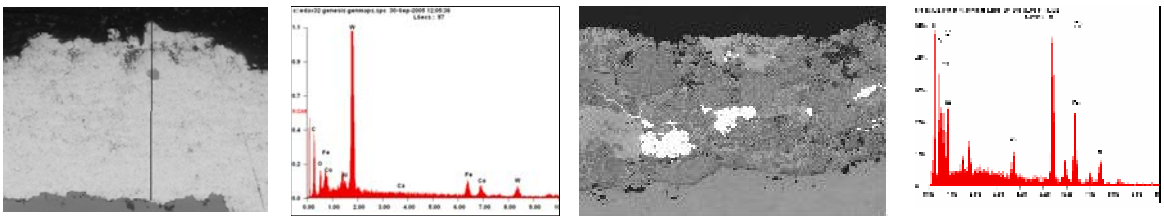
Table 1. Thermally sprayed coatings - VUZ PI- erosive wear.

Coating	Impact angle [o]	Mass losess [g]
Castolin10680 two steps-remelting	15°	0,00513
	45°	0,00647
	90°	0,00297
Castolin Xuper 5100	15°	0,00627
	45°	0,0100
	90°	0,0027
NiAl5 Cold spraying	15°	0,00593
	45°	0,0977
	90°	0,0029
NP22 two steps-remelting	15°	0,00563
	45°	0,00697
	90°	0,00297
NP22P two steps remelting	15°	0,0055
	45°	0,0064
	90°	0,0027



WC-Co – I Cr_3C_3-*NiCr- I*

Fig. 3. EDX analysis of coatings WC-Co a Cr_3C_3-NiCr – HVOF –TYPE I.



WC-Co –II Cr_3C_3-*NiCr- II*

Fig. 4 . EDX analysis of coatings WC-Co a Cr3C3-NiCr – HVOF -TYPE II.

The tribological characteristics of HVOF coatings (sprayed by two HVOF equipments) were analysed under dry friction conditions by Falex tester. The coating microstructures were studied with optical microscopy and SEM. The optimalization of deposition parameters on the structure of coatings is very important – (Fig. 3 and Fig. 4). It was concluded that the wear rates were sensitive to deposition parameters (Fig. 5).

The tribological properties of thermally sprayed coatings from Welding Research Institute, Bratislava were analyzed. The microstructure of powders from different producers of powders were shown at Figs.6 and 7. The structure of Castolin powder is non-spherically shaped. The particles of powders NP22 and NP22P are spherically shaped. Microstructures of thermally sprayed coatings were studied EDS, SEM and optical microscopy.

It was concluded that the wear rates were sensitive to both the production process and to the microstructure of the coatings. These experiments were carried out using the commercially spraying system. The influence of grain size and morphology powders on thermally sprayed coating properties were evaluated by Falex tester. For three types of powders and coatings the wear tests were performed.

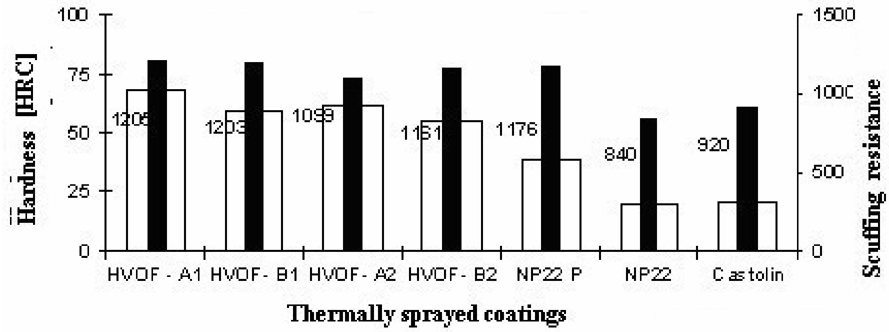


Fig. 5 Scuffing resistance of thermally sprayed coatings.

The highest scuffing resistance was obtained at coatings WC-Co and Cr_3C_2-NiCr (method HVOF).

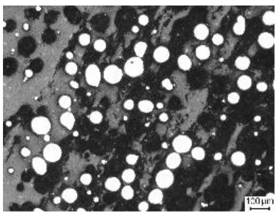
Non-homogenities and local differences in structure were observed in HVOF-2 coating, the result was the decreasing of scuffing resistance.

Coating NP22P with relative lower hardness showed comparable scuffing resistance as HVOF coatings-Fig. 5.

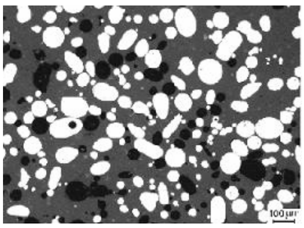
For all sprayed coatings tests on resistance against scuffing were repeated three times. There were carried out for evaluation of scuffing resistance of thermally sprayed coatings realised by cold spraying by systems Castodyn 8000.

There were determined that the wear rates were sensitive to shapes of powders but also to microstructure of coatings. The scuffing resistance of thermally sprayed coatings observed under laboratory tests was as follows : highest value for NP 22P, Castolin 10680 and NP22 respectively.

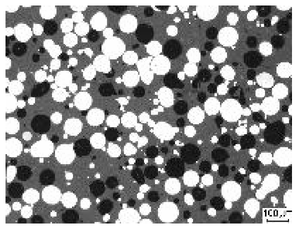
The adhesive wear tests under dry friction conditions by Falex tester were carried out for HVOF and (cold spraying) were prepared by VUZ PI Bratislava.



NP 22P

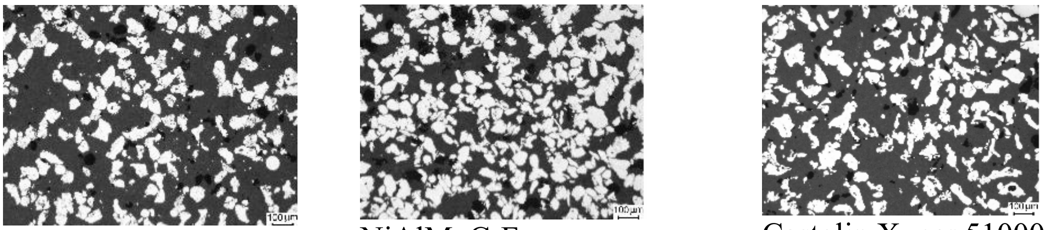


Castolin 10680



NP 22P

Fig. 6.



NiAl5 NiAlMoCrFe Castolin Xuper 51000

Fig.7.

The abrasive wear tests under dry friction conditions were carried out for HVOF coatings and coatings prepared by VUZ PI Bratislava.

The parameters of abrasive wear tests parameters

- Temperature 20 °C
- distance of sliding trajectory 50 m
- diameter of disc 480 mm
- velocity of samples 0,3 $m.s^{-1}$
- specific pressure 0,32 N.mm-2

The wear abrasive resistance were tested on the STN 01 5084 with corundum cloth A99- G.S 25 - GLOBUS 120.

Table 2. Tested coatings.

Coatings	ψabr	HRC
NP 22 P	1,241	34
Castolin 10680	1,083	19
NiAl5,5	0,898	24
Ni7Al5,5Mo9CrFe	1,216	20
Castolin 51000 Xuper	1,262	19
Ni, Cr16%, Si4%, B3,5%, Fe4%, C0,8%	2,051	53
WC –17 %Co	17,58	64

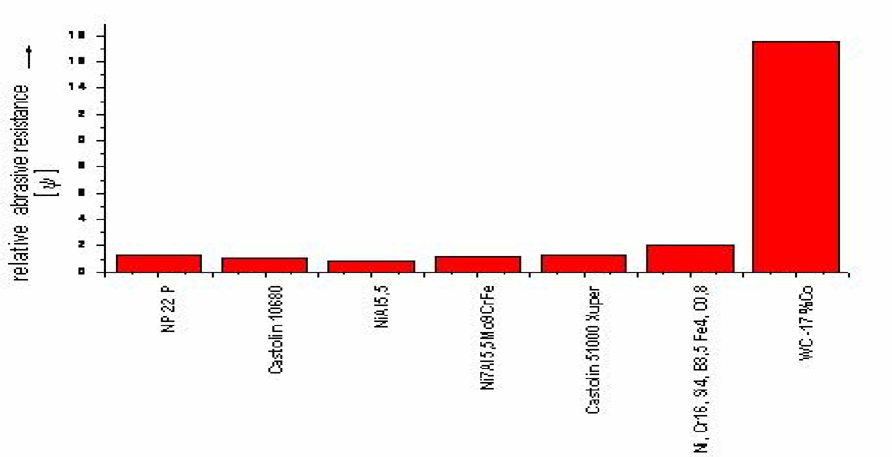


Fig. 8. Abrasive wear resistance.

Project co-operation

The co-operation with Research Welding Institute, Slovakia and Czech Republic. The thermally sprayed specimens were prepared by Welding Research Institute VUZ PI Bratislava. HVOF coatings were prepared by Czech participants.

Planned or achieved industrial improvements in commercial use -2

Publications where project results are reported

1. ZDRAVECKÁ,E.et al.: Examination of surface characteristics in tribological systems by AFM. In:Tribologia. ISSN 0208-7774Nr.6/2002 1713-1722.
2. ŽORAWSKI,W.-ZDRAVECKÁ,E.- SKRZYPEK,S.- TRPČEVSKÁ,J.:Tribological characteristics of HVOF. TRIBOLOGIJA, 3-2005, ISSN 0208-774, pp. 361-368.
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5. ZDRAVECKÁ, E.- TKÁČOVÁ,J.: Erosive wear metallic materials and HVOF coatigs. In: TRANSTRIBO 2005, Sankt Petersburg 2005, YDK 621.891, pp. 17-23.
6. ZDRAVECKA, E. - SMETANA, Š.: Tribologické aspekty žiarovo striekaných povlakov. STROJÁRSTVO, 2006
7. ZDRAVECKÁ, E.- JANČO, V.-TKÁČOVÁ,J.- PERHÁČ, Š.: Vplyv parametrov žiarového striekania na odolnosť povlakov proti zadieraniu. INTERTRIBO 2006, ISBN 80-969365-7-3. Tatranská Lomnica, 2006, p. 212-215.

ES8 - IMPROVING THE ENGINE PERFORMANCE BY LASER SURFACE TEXTURING (LST) OF PISTON RINGS AND OTHER COMPONENTS

Co-ordinator and partners

Co-ordinator:
Izhak Etsion, Technion, Israel, etsion@tx.technion.ac.il

Project status and schedule

Running with full funding
Starting 0104 and ending 1206

Project aims

The aim is to define a suitable theoretical model of micro-dimples, to texture piston rings for car, trucks, motorcycle, and agricultural and marine engines, and to perform laboratory simulation and engine tests to validate the model. Another aim is to test laser textured piston pins.

Project results

Theoretical modelling was accomplished for both full and partial laser surface texturing (LST) of piston rings. Parametric analysis was performed to optimise the texturing parameters. It was found that substantial friction reduction can be obtained with surface texturing of the face of cylindrical piston rings. A special reciprocating test rig was built and laboratory tests where performed showing good correlation with the theoretical prediction.

Fig. 1. Tested liner and piston rings holder.

All the results are presented in Refs. (1-4) and (6). The tests were performed with actual liners and rings as shown in Fig. 1 and typical results are shown in Fig. 2.

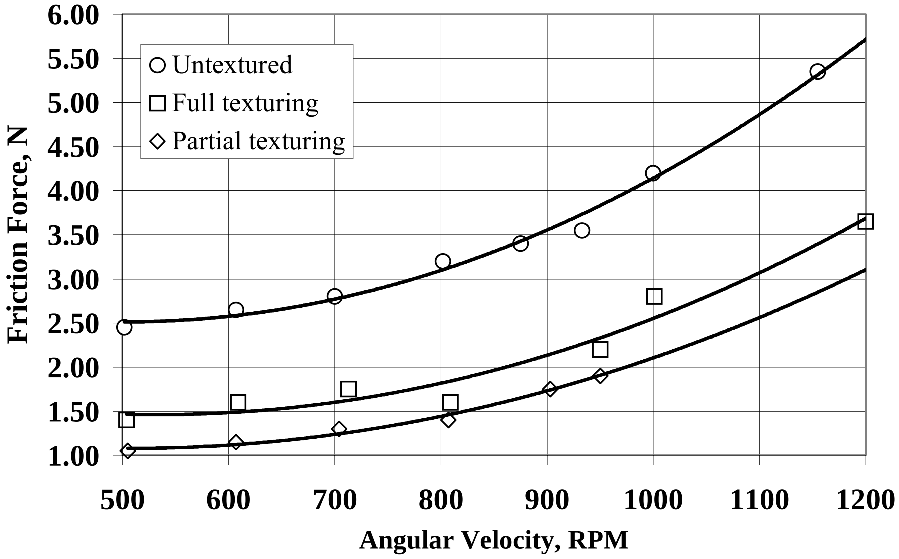

Fig. 2. Typical results of laboratory tests.

Another test rig was built to evaluate the effect of LST, in comparison with other surface engineering technologies, on scuffing resistance of piston pins. The results obtained with this test rig are presented in Ref. (5). The test rig is shown in Fig. 3, and some of the results in Fig. 4.

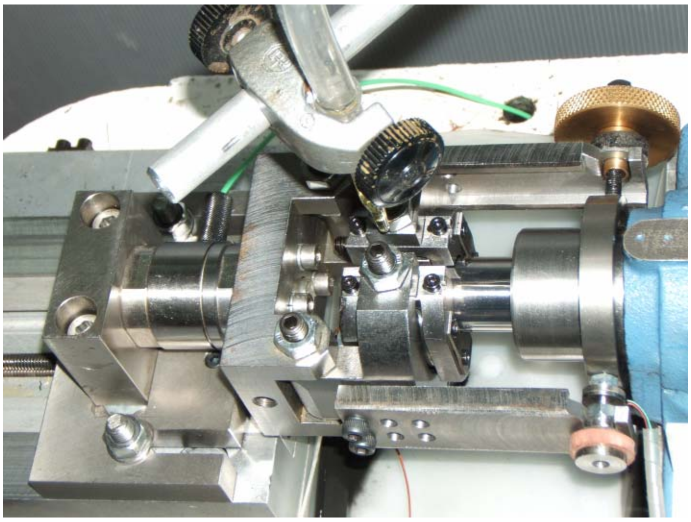

Fig. 3. A reciprocating piston pin test rig.

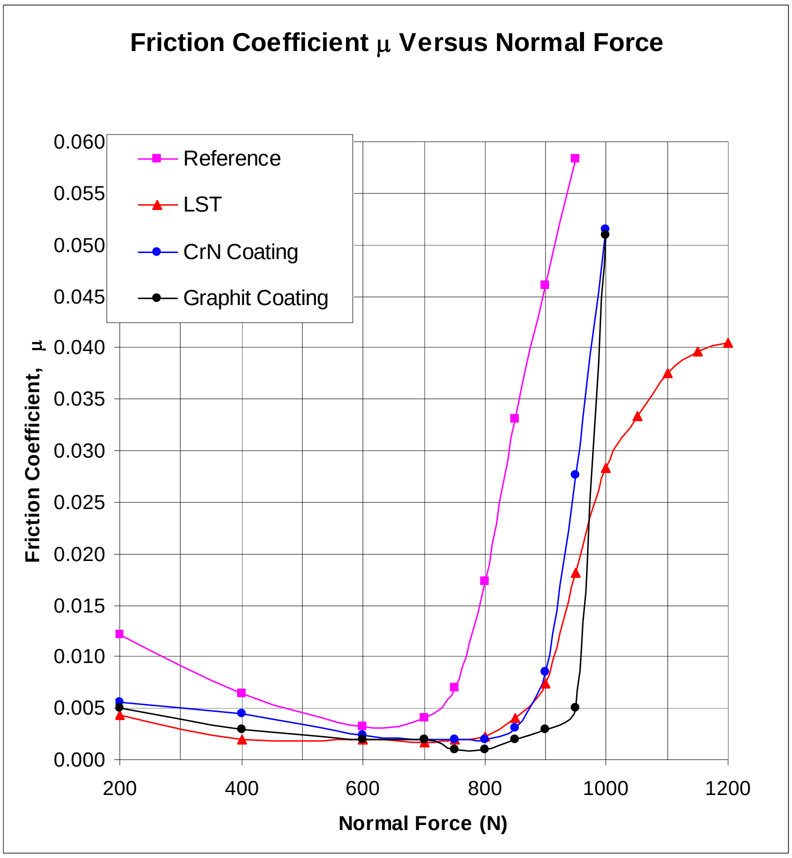

Fig. 4. Scuffing resistance results of various surface treatments of piston pins.

Finally some engine tests were recently performed to evaluate fuel efficiency of partial laser textured cylindrical face piston rings in comparison with a reference conventenional un-textured barrel shape face piston rings. The cross sections of these rings having nominal face width of 25 mm are shown in Fig. 5 with their chrome coating. Additionally a partial laser textured cylindrical face piston rings but without the chrome coating was also tested. Fig. 6 shows the results of the specific fuel consumption over a range of engine speeds for the three piston ring types where series 1, 2 and 3 correspond to the un-textured reference ring, the textured chrome coated ring and to the textured uncoated ring, respectively. A reduction of 1% to 2 % in the fuel consumption is clearly observed with the textured rings.

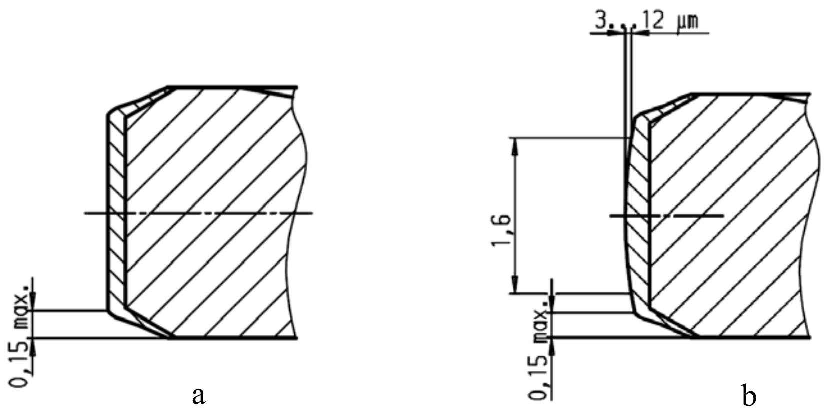

Fig. 5. Cross sections of Cylindrical (a) and barrel shape (b) piston rings.

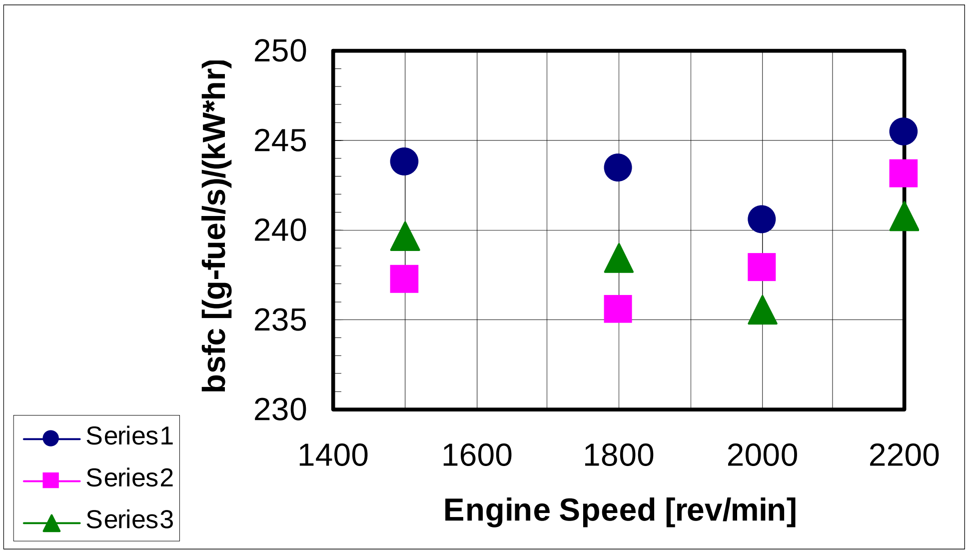

Fig. 6. Specific fuel consumption of the un-textured reference ring (Series 1), the textured chrome coated ring (Series 2) and the textured uncoated ring (Series 3).

Publications were project results are reported

1. A. Ronen, I. Etsion and Y. Kligerman: Friction-Reducing Surface Texturing in Reciprocating Automotive Components. Tribology Transactions, Vol. 44, No. 3, July 2001, pp. 359-366.
2. G. Ryk, Y. Kligerman and I. Etsion: Experimental Investigation of Laser Surface Texturing for Reciprocating Automotive Components. Tribology Transactions, Vol.45, No. 4, Oct. 2002, pp. 444-449.
3. Y. Kligerman, I. Etsion and A. Shinkarenko: Improving Tribological Performance of Piston Rings by Partial Surface Texturing. J. of Tribology, Trans. ASME, Vol. 127, 3, 2005, pp. 632-638.
4. G. Ryk, Y. Kligerman, I. Etsion, and A. Shinkarenko: Experimental Investigation of Partial Laser Surface Texturing for Piston Rings Friction Reduction. Tribology Transactions, 48 (2005), pp. 583-588.
5. I. Etsion, G. Halperin, and E. Becker: The Effect of Various Surface Treatments on Piston Pin Scuffing Resistance. Wear, 261, (2006), pp. 785-791
6. G. Ryk and I. Etsion: Testing Piston Rings with Partial Laser Surface Texturing for Friction Reduction. Wear, 261 (2006), pp. 792-796.

ES9 - THE INFLUENCE OF THERMALLY SPRAYED COATINGS ON THEIR TRIBOLOGICAL CHARACTERISTICS

Co-ordinator and partners

Co-ordinator:
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Partners: Olga Bláhová, University of West Bohemia, Czech Republic, blahova@ntc.zcu.cz
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Project status and schedule

Running with partial funding
10/2003-12/2007

Project aims

The scientific aim of the project is deeper understanding of relationship between HVOF coatings structure and their tribological behavior. New knowledge of the coatings wear mechanisms with respect to various wear conditions will be developed.

The technological aim is to optimize the spray parameters for each coating material to obtain the best coating's tribological properties. The properties of current wear-resistant coating's application will be improved and a new application will be found.

Project results

For an extensive study, 7 HVOF sprayed coatings (WC-Co, WC-CoCr, WC-Hasteloy, Cr_3C_2-NiCr, (Ti)(Mo)(C,N)-NiCo, NiCrSiB, AISI 316L and 1 plasma sprayed coating (Cr_2O_3) , suitable for wear application were chosen. In the first stage of project solution, the coatings' spraying parameters were optimized in terms of microstructure, hardness, microhardness and deposition efficiency. The set of optimal parameters were found for all the coatings and they were used for coatings sample preparation.

The optimized coatings were further analyzed. Except of standard mechanical properties, such as superficial hardness HR 15N and microhardness HV0,1, the indentation fracture toughness were measured by Vickers indentation technique. The results of mechanical properties measurements are summarized in Table 1.

The microstructure studies showed that all cermet coatings have a homogenous structure with regularly dislocated hard particles in the matrix and very low degree of porosity. The particles seem to have a good binding with the surrounding matrix. No evidence of cracks or another discontinuity can be seen. The microstructure of metal NiCrSiB coating has low size of precipitates that also exist in the powder feedstock. Porosity value is under 1%. In some cases, imperfectly unmelted particles are built-in coating and surrounding melted particle can be observed. That has a significant influence on interlaminar bonding strength and mechanical behavior at wear tests. The CrB, Cr_7C_3 and Ni_3B are ordinary most frequently phases occurring in coating after spraying.

Table 1. Coatings properties.

Coating	Thickness [μm]	Density [g.cm^{-3}]	Microhardness HV0,1	Hardness HR15N	IFT (LF) [MPa.m$^{-1/2}$]
WC-Co	442 ± 10	13,161	1240 ± 116	92,7 ± 1,2	2,41 ± 0,46
WC-CoCr	467 ± 9	13,096	1369 ± 114	92 ± 1,0	2,37 ± 0,26
WC-Hasteloy	410 ± 17	13,256	1167± 109	92,8 ± 0,7	0,68 ± 0,17
Cr_3C_2-NiCr	433 ± 9	6,646	786 ± 123	91 ± 0,8	1,45 ± 0,47
(Ti)(Mo)(C,N)-NiCo	430 ± 7	6,312	799 ± 131	91,5 ± 1,5	0,5 ± 0,05
NiCrSiB	379 ± 12	7,305	735 ± 59	89 ± 1,6	0,92 ± 0,18
AISI 316L	427 ± 12	7,800	321 ± 31	54 ± 5,4	0,33 ± 0,04
Cr_2O_3	490 ± 16	5,200	962 ± 112	93,2 ± 3,2	0,35 ± 0,03

However, its volume fraction in coating is in comparison with volume fraction of carbides in cermets substantially lower. The AISI 316L coating has a different shape of individual splat after impact during spraying process. The deflection of from the standard shape is caused by the deliberately low temperature during spraying process is relatively low, which is favorable to reduce the oxidation of sprayed particles. Nevertheless, this shape has a negligible influence on the mechanical properties of the coating. For this type of coating, no evidence of hard phases in microstructure can be seen.

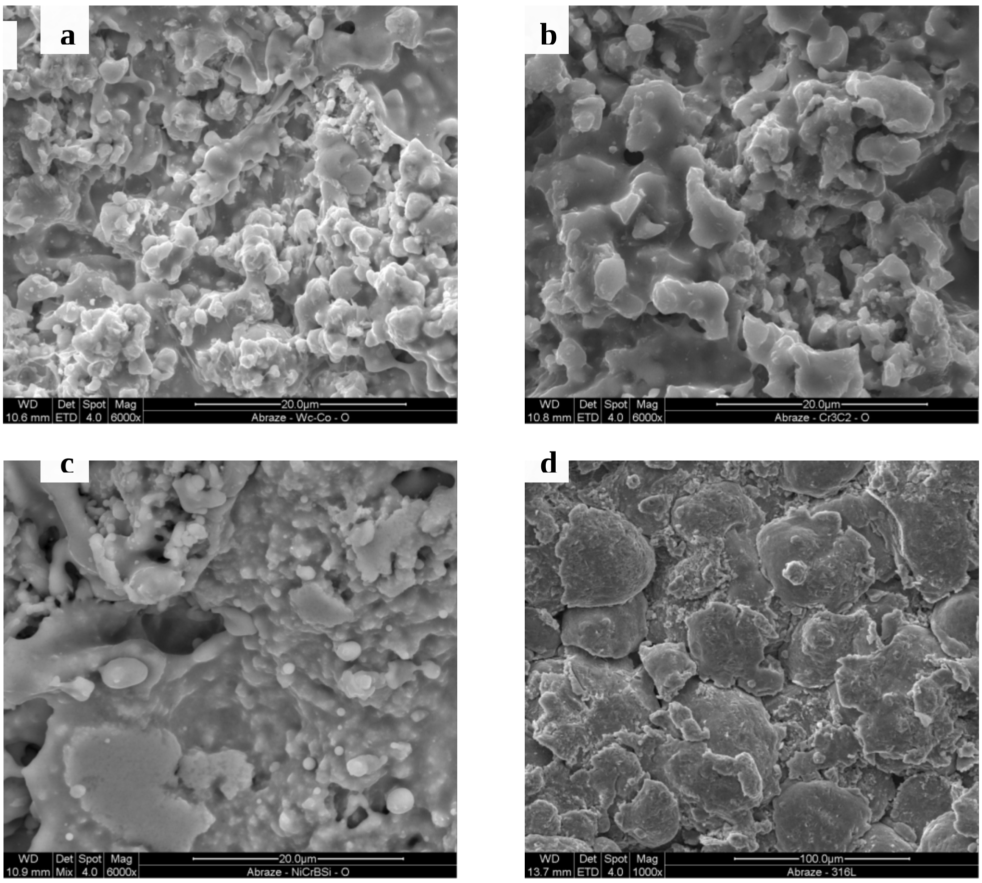

Fig. 1. SEM images of the as-sprayed coatings surface morphology a) WC-Co, b) Cr_3C_2-NiCr, c) NiCrBSi and d) 316L steel.

The tribological properties of coatings were evaluated by four wear tests. The 3-body abrasive wear tests brought information about abrasive wear rate and mechanism under dry (ASTM G-65) and wet (ASTM G-75) condition. The 2-body abrasion test (ASTM G-99), provided by pin-on-disc CSEM Tribometer equipment, enabled to measure the coefficient of friction for two kinds of counter face material - Al_2O_3 and steel. The erosive wear was evaluated using 3 different angle of particles impingement to evaluate the influence of impingement angle on wear rate and mechanism. For better comparison of coatings wear resistance, the two standard surface treatment were added in tribological tests– steel surface hardening and hard chrome coating.

The results of dry sand rubber wheel abrasion test for all tested materials are shown in Fig. 2. It represents the cumulative volume loss of coatings´ material in dependence on abrasive distance. In addition to that, the wear rate Wr [mm^3/m] and the coefficient of abrasive wear resistance K_{abr} [mm^3/Nm] was counted.

The test was provided on abrasive distance 1005 m, except of NiCrBSi, where the substrate material was revealed at 718 m abrasive distance, and hard chrome coating, where it happened at 287 m abrasive distance. The reason can be found in used abrasive medium. The sharp-edged Al_2O_3, reached number 9 at Mohs´ scale, is highly effective. It was chosen with respect to testing of wear resistant cermet coatings and probably is not the best suitable for testing of softer coatings. Also the initial thicknesses of these two coatings were the lowest.

As it can be seen from Fig. 2, the coatings can be divided in to two groups. The first group is formed by the cermet coatings with high wear resistance. The non-cermet coatings, which form the second group, reached during the test several fold higher volume loss.

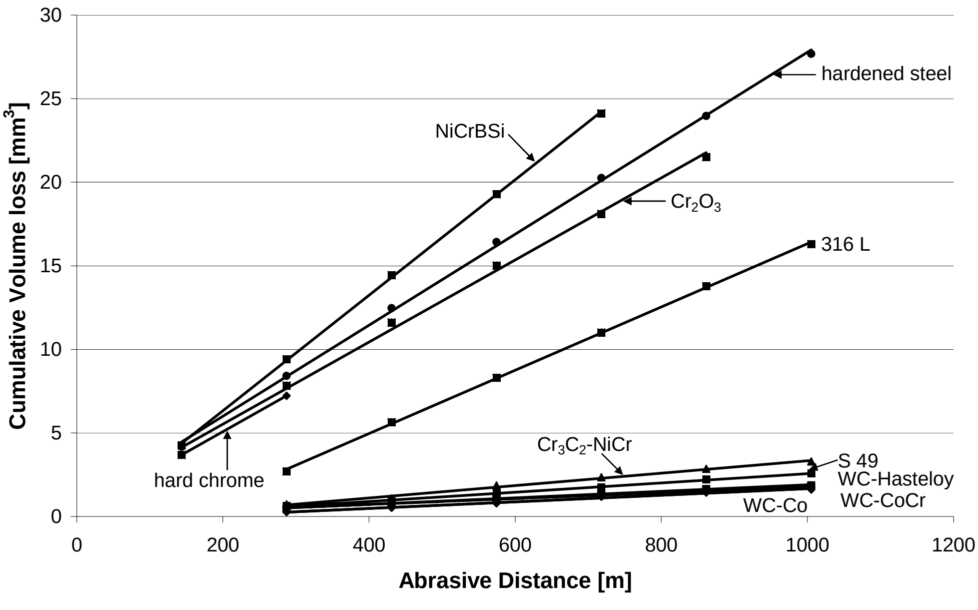

Fig. 2. Dry abrasion wear results.

In the group of cermet coatings, the highest wear resistance was measured for WC-based coatings. The differences between them are very small, as well as the difference between their hardness values (see Table 1). The hardness values can be influenced by many parameters, such as amount of porosity, carbide content, size and shape, the degree of phase transformation during spraying process etc.

The mechanism of wear is similar for all cermet coatings. The worn surface is smooth, with very shallow irregular grooves. The hard particles protect the coatings against deep penetration of abrasive particles and lower the free path of groove. The major mechanism of wear is connected with removing the matrix from the areas between coatings' hard particles, followed by weakening of their attachment and pulling off from the coating surface. In the case of Cr_3C_2-NiCr coating the mechanism of pulling off bigger parts of coating on the splat boundary was observed due to higher level of porosity, but it occurred just occasionally and can not be consider as a significant for wear.

The non-cermet coatings shown much lower wear resistivity compared to cermet coatings. The major wear mechanism for metal coatings (NiCrSiB and AISI 316L) was connected with plastic deformation, cutting and ploughing. The plasma sprayed coating (Cr_2O_3), in spite of its high hardness, does not reached high wear resistance. The reason is in its brittleness, that caused massive cracking and high volume loss. The major mechanisms of abrasive wear are illustrated in Fig. 3.

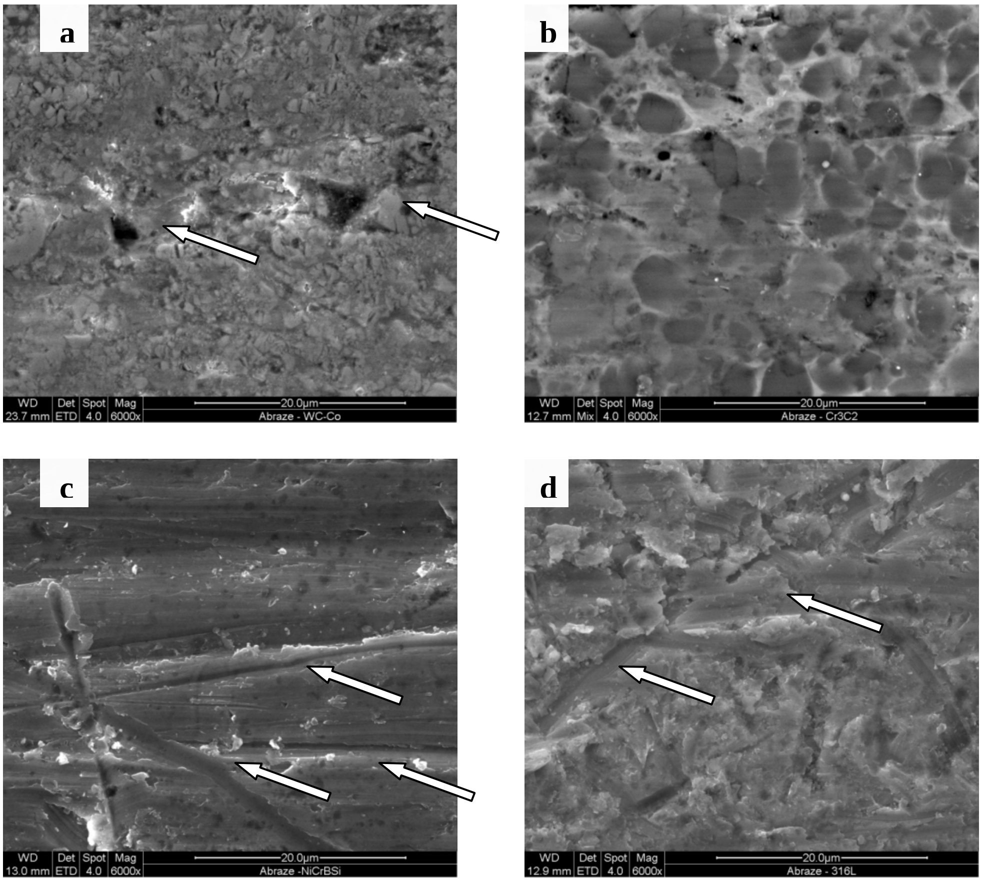

Fig. 3. SEM images of worn surfaces after dry sand abrasion test a) WC-Co, b) Cr_3C_2-NiCr, c) NiCrBSi and d) 316L steel thermally sprayed coatings.

The results of wet slurry abrasion test were similar to dry sand rubber wheel test. The influence of corrosive medium can be seen from different order of WC-based coatings, where the material of matrix played its role. Also the wear mechanisms were similar. The results are displayed in Fig. 4.

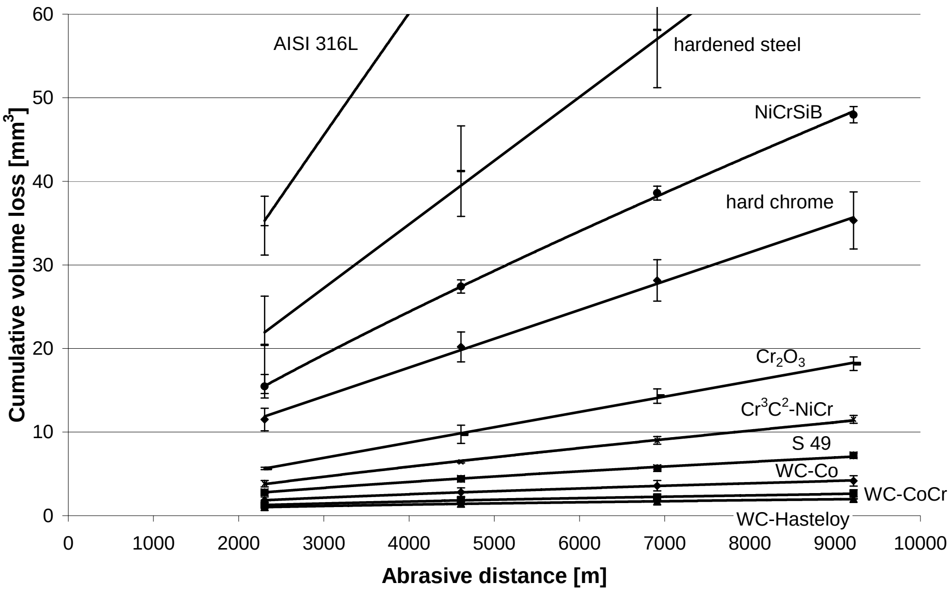

Fig.. 4. Wet abrasion wear results.

The results of pin on disc wear test were not confirmative. The volume loss for the most resistant coatings, the WC-based cermet coatings and Cr_2O_3 coating, were too small to be measured by available equipment (profilometer Homel Tester 1000). The order of measurable results match the expectation: the most resistant, immeasurable WC-based coatings and Cr_2O_3 coating are followed by other HVOF coatings, (Ti,Mo)(C,N)-NiCr and Cr_3C_2-NiCr. The next were hardened steel, NiCrSiB coating, AISI 316L coating and the worst results showed the hard chrome coatings. Compare to the coatings' values of hardness (Table 1), it can be said, that the order of pin on disc test results match the order of HR15N results.

The mechanism of wear was studied for all provided tests by SEM evaluation. Generally for cermet coatings the gradual loss of metal matrix followed by decrease of carbide-matrix cohesion and pull-off the carbides was observed. In the case of WC-based coating, the wear tracks are very shallow, without signs of plastic deformation. The wear track ground is composed from polished carbides, while the wear track sides contain the sharp-edged carbide. It leads to presumption, that carbides pulled-off from wear track sides served as an abrasive medium for wear track ground grinding and polishing. The similar mechanism is observed for Cr_3C_2-NiCr coating, however the wear track contains also deep wholes from pulled-off carbides and cracks in the matrix near the carbides, that can later caused the carbide-matrix decohesion. Besides above mentioned effects the hint of plastic deformation and loss of bigger splats parts were observed for the (Ti,Mo)(C,N)-NiCr cermet coating. The metal HVOF coatings showed much bigger amount of plastic deformation, accompanied by loss of splats cohesion, especially on the wear track edges. Completely different wear mechanism is observed for brittle plasma sprayed Cr_2O_3 coating. The numbers of cracks, created in the wear track, was followed by pull-off of coatings parts. The major mechanisms of adhesive wear are illustrated in Fig. 5.

The erosion wear results for 3 angles of particles' impingement are summarized in Fig.6X. Most of the coatings were more wear resistant to angled particles' impingement. This fact results from the primary coatings use as coatings resistant to abrasive wear. The perpendicular particles' impingement caused bigger damages in the case of more brittle coatings, such as plasma sprayed ceramic Cr_2O_3 coating, HVOF cermet Cr_3C_2-NiCr and (Ti,Mo)(C,N)-NiCr coatings and surprisingly metal NiCrSiB coating. The conventional surface treatments, hard chrome coatings and hardened steel surface, showed in erosion wear test very good results. The mechanism of wear is for small impingement angle similar to mechanism, observed for other types of abrasive wear.

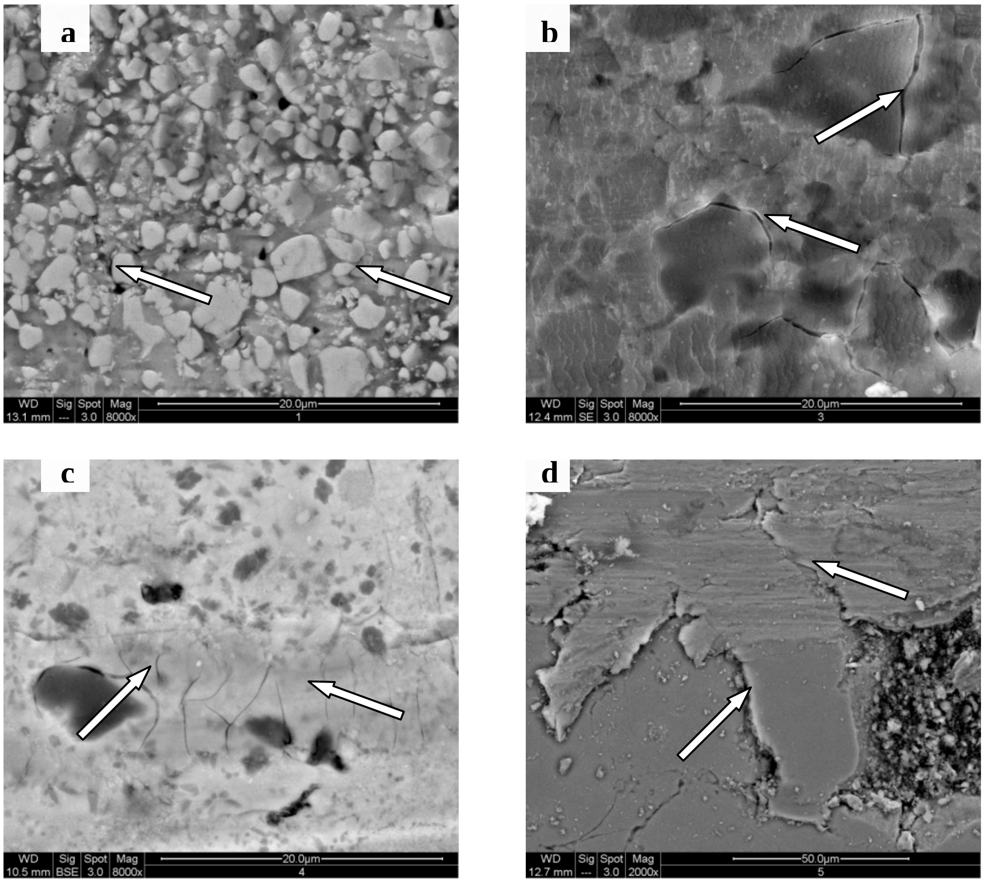

Fig. 5. SEM images of worn surfaces after pin-on-disc test at load 10 N using alumina ball indenter WC-Co, b) Cr_3C_2-NiCr, c) NiCrBSi and d) 316L steel thermally sprayed coatings.

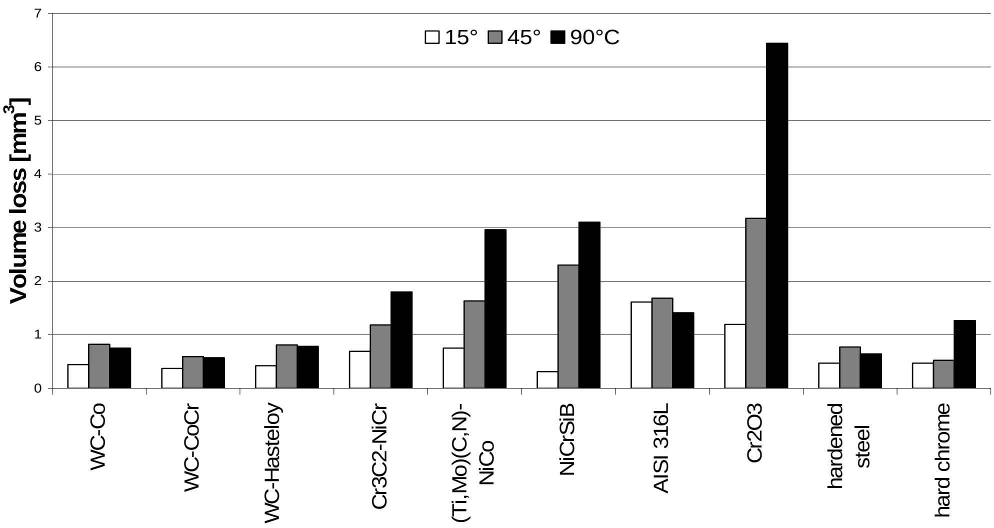

Fig. 6. Erosion wear results.

Project co-operation

The forms of co-operation used: e-mail contacts, meetings, seminars, researchers visits.

Industrial improvements in commercial use

The results will be used for new coatings application, especially as a replacement of ecologically harmless hard chrome.

Publications were project results are reported

The publications performed related to this project are the following:

1. Š. Houdková-Šimůnková, O. Bláhová, R. Enžl: Abrasion wear rate evaluation of thermally sprayed coatins, In: Acta Metallurgica Slovaca, 10, (1), 2004, p.792-794, ISSN 1335-1532.
2. Š. Houdková, O. Bláhová, P. Tichotová, K. Novotná : Tribological characteristics of thermally sprayed coatings, In: Tribology of surface layers and coatings: proceeding of the 4th international tribology conference : Prague, Czech Republic, 2004. - Prague : EDUKA, 2004. p.1-8, ISBN 80-239-3123-7.
3. F. Zahálka, R. Enžl, O. Bláhová, Š. Houdková: Study on abrassive wear resistence of different kinds of thermally sprayed coatings, In: Layers and Coatings 2005: proceedings of the conference : Demänovská dolina, Slovac Republic, 2005. - Trenčín : DIGITAL GRAPHICS, 2005, p. 224-230, ISBN 80-969310-1-6.
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5. Š. Racková, O-Bláhová, Š. Houdková, F. Zahálka: Tribological characteristic of thermally sprayed coatings, In: Layers and Coatings 06: proceedings of the conference, Rožnov pod Radhoštěm, Czech Republic, 2006, -Trenčín : DIGITAL GRAPHICS, 2005, p. 157-162, -ISBN 80-969310-2-4
6. M. Kašparová, F. Zahálka, R. Enžl: Wear resistance of thermally sprayed coatings, In: PhD 2005 [CD-ROM]: 3th international PhD conference on mechanical engineering, Srní, Czech Republic, 2005, - Plzeň, Západočeská univerzita, 2005., ISBN 80-7043-414-7.
7. R: Enžl: The Influence of Thermally Sprayed Coatings Microstructure on their Tribological Characteristic, In: COST Action 532: Triboscience and Tribotechnology: Superior Friction and Wear Control in Engines and Transmissions, Porto (Portugal), 12-15.10. 2005
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9. F. Zahálka, Š. Houdková, M. Kašparová: Evaluation of the erosive wear resistance of the thermally sprayed coatings, In: Layers and Coatings 06: proceedings of the conference, Rožnov pod Radhoštěm, Czech Republic, 2006, -Trenčín : DIGITAL GRAPHICS, 2005, p. 148-156, -ISBN 80-969310-2-4
10. M. Kašparová, F. Zahálka, R. Enžl: Mechanical properties of HVOF sprayed coatings in dependance of the spray parameters In: Layers and Coatings 06: proceedings of the conference, Rožnov pod Radhoštěm, Czech Republic, 2006, -Trenčín : DIGITAL GRAPHICS, 2005, p. 142-147, -ISBN 80-969310-2-4

11. Š. Houdková, O. Bláhová, E. Svitáková: Indentation fracture toughness of thermally sprayed coatings, In: Local Mechanical Properties 2006, Nečtiny, Czech Republic, 2006,-Plzeň, Západočeská Univerzita, p. 70-78, ISBN 80-7043-512-7

ES10 - POSITRON ANNIHILATION STUDIES OF DEFECTS IN SUBSURFACE ZONES IN MG, AL AND THEIR ALLOYS INDUCED DURING FRICTION AND WEAR PROCESSES

Co-ordinator and partners

Co-ordinator:

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Partners:

Project status and schedule

Running with full funding
Starting and ending dates 1 July 2003 and the ending date 31 March 2006.

Project aims

The project is subjected to the study of subsurface zones created during the sliding contact in poor magnesium its alloy AZ31 and aluminium and their alloys AK64 and AK 132 used in the engine's construction. In our studies we wish to use the positron annihilation techniques for detection of defects like vacancies, their clusters and dislocations induced by sliding of surface and their depth distribution.

Project results

We performed the studies of the subsurface zone induced during the sliding of the pure magnesium. For that purpose we used the slow positron beam equipment available at Delft University in Holland. The measurements of the Doppler broadening of the annihilation line were performed as the function of the positron energy, which was ranged form 0.1 keV to 25 keV. This allows us to scan the depth less than 4 μm from the top surface, which originally was exposed to the sliding. The Fig. 1 presents the obtained dependences for the well annealed and no damaged sample and samples which surface were exposed to the sliding. The value of the S parameter on the top surface is lower than in bulk it indicate that on the surface another i.e. the magnesium oxygen layer exists. This is supported by the analysis of the dependency of the S parameter versus the wing parameter, see right part of the Fig. 1b. (We analyzed only the right part of the annihilation line which is less affected by the background.) The change in the slope of the dependencies at the depth about 100 nm indicates that this is the thickness of the magnesium oxygen layer. Using the VEPFIT program, we were able to describe the experimental data for the well annealed samples assuming existence of two regions, the first one on the top and second in the interior. The thickness of the top layer evaluated from the fit was equal to 107±1 nm and the positron diffusion length was equal to 70±1 nm. This value in the interior equals to 780±150 nm. The latter corresponds to the positron diffusion in the polycrystalline bulk magnesium. For the sample which surface was exposed to the highest load of 100 N the top layer thickness increases to 150±10 nm as it arise from the fit. This results that during sliding the mixed layer is created on the top surface, its thickness increases whit increasing of the applied load. The mixed layer consists of the magnesium oxygen. The most striking feature of the obtained results is the fact that the value of the S parameter at depth more than 3 μm almost does not dependence on the sliding condition. Nevertheless, the detail analysis of the W parameter versus S parameter additionally averaged for the depth more than 2.5 μm revealed a weak dependence on the sliding condition, see Fig. 2. This can indicate that the positron trap generated during the sliding does not strongly localize positrons. This can suggest that only dislocations are present at the depth more than the top layers. The results were presented in the form of a poster during the International Conference -14 on Positron Annihilation in Canada in Hamilton.

We performed also the study of the subsurface zone in the aluminium alloys AK 64 and AK 132. Well defined decrease of the positron lifetime versus the depth has been observed in the studied samples which surface was exposed to the sliding. The total depth of the subsurface was very similar in both alloys and was ranged between 100 μm and 200 μm. It looks that under sliding conditions both alloys exhibits similar behaviour. The results were presented during the Polish Seminar on Positron Annihilation in Turawa.

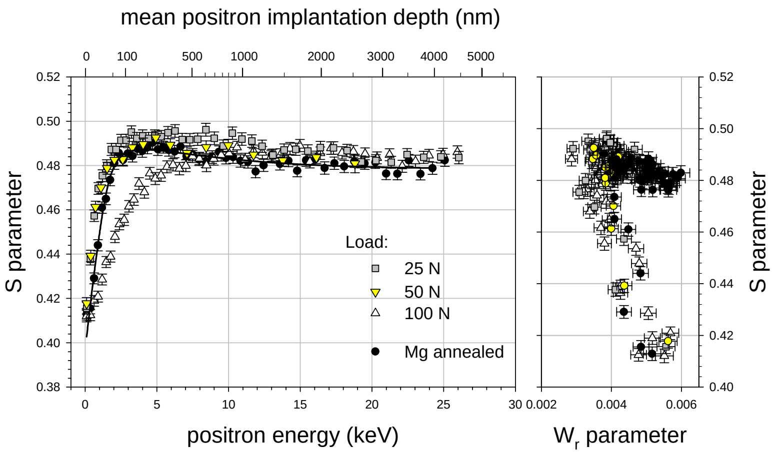

Fig. 1 The dependence of the S-parameter vs. the positron energy for well annealed magnesium sample and other magnesium samples which surfaces were damaged during sliding conditions. On the right the dependency of the S-parameter vs. the W_r –parameter extracted from the annihilation line measured for the all measured samples.

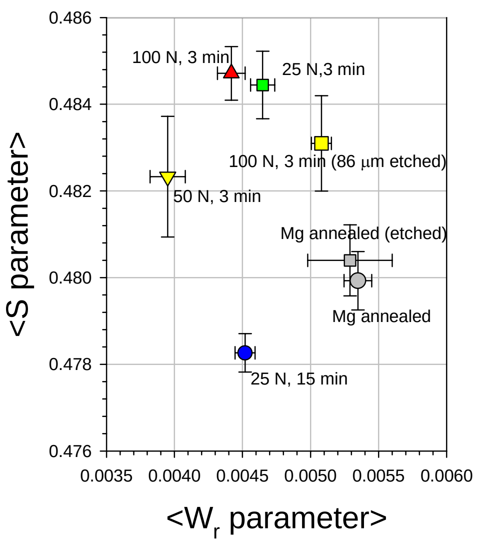

Fig. 2 The averaged value of the S-parameter vs. W_r parameter extracted from the Fig.1 (on left) measured at the depth more than 2 μm.

Our studies of magnesium and aluminium alloys we may state as follows:

The total range of the subsurface zone detected in the commercial magnesium-based alloy Mg96Al3Zn1 exposed to sliding is about 100 μm and it is much lower than that detected for pure magnesium which was between 150 μm and 440 μm and exposed to the similar treatment. In contrast to pure magnesium, the range is hardly affected by the applied load and sliding distance.

The total range of subsurface zone in aluminium alloys AK 64 and AK 132 was ranged between 50 μm and 150 μm it is much less than in pure alluminium where the zone was extended up to 450 μm. It well confirmed experimental fact that additive atoms or precipitations prevent expansion defects in deep and reduce the total depth of the zone.

The most surprising results were achieved when we found that the subsurface zone created during the blasting process exhibits similarities to the subsurface zone created during friction treatments. This points out that the impacts of the body during the friction treatment can be responsible for creating the subsurface zone below a worn surface

We correlated the short range of the subsurface zone with a high value of the wear rate found for magnesium alloy (Mg96Al3Zn1), as found before in aluminium alloys.

The detection of the long-lived component in subsurface zone of magnesium alloy (Mg96Al3Zn1) is the most surprising result of the present work. We suggest the interpretation that positronium is formed in voids of radius 0.23±0.01 nm, which initiated during sliding only at a depth of less than 30 μm. This is a new surprising result not observed yet.

New studies were performed using slow positron beam on the subsurface zone in pure magnesium. We observe the oxide zone just below the worn surface but it was very difficult to detect the defects induced during sliding. This was due to the fact that in magnesium the positron localization in atomic defects is very week and finally the positron annihilation parameters differ only slightly form the bulk values.

We established a new experimental technique named DSIP (depth scanning of positron implantation profile) which allows to study in nondestructive way the zone below worn surface. The method uses the fact that positrons emitted from the radioactive source are distributed in the material in the exponential profile. This implantation profile, typical for beta emitter may correlates with the profile of defects induced during sliding. Scaning the implantation profile we can observe the defect profile. We did interesting observation using this method in aluminium and copper samples.

Project co-operation

Delft University in Holland.
Industrial improvements in commercial use
There are the basic studies and we do not predict the commercial applications at this stage.

Publications were project results are reported

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4. J. Dryzek and D. Singleton " *Implantation profile and linear absorption coefficients for positrons injected in solids from radioactive sources 22Na and 68Ge\68Ga* ", Nuclear Instruments and Methods in Phys. Res. B 252, 197 (2006).
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ES11 - INFLUENCE OF SURFACE TOPOGRAPHY ON LUBRICATED CONTACTS

Co-ordinator and partners

Co-ordinator:

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Brno University of Technology, The Czech Republic, krupka@fme.vutbr.cz

Project status and schedule

Running with partial funding
Starting and ending dates 01-2005 to 06-2007

Project aims

The project is aimed at the experimental study of the effect of real moving asperities on lubricant film thickness within thin film lubricated point contacts. It will enable the detailed study of the influence of the orientation of surface irregularities on lubrication protective films and to relate obtained results to the machining process of friction bodies. The project is also focused on the study of the protective film forming properties of additives around real roughness features.

Project results

Literature studies. Minor modifications of experimental apparatus. Series of experiments with mineral base oils under rolling/sliding conditions using a high resolution CCD camera and xenon flash light source. Evaluation of experimental results. Experiments with formulated oil. The study of surface texturing effects on lubricant film formation under sliding/rolling conditions.

A combination of thin film colorimetric interferometry and phase shifting interferometry has been used to study the effect of slide-to-roll ratio on the micro-elastohydrodynamic action and asperity-contact mechanism on the real asperity scale. The phase shifting interferometry was used to measure in-situ initial undeformed rough surface profiles and thin film colorimetric interferometry provided accurate information about micro-EHD film thickness behaviour over a wide range of operating conditions. Lubricant film thickness distribution within mixed EHD contact has been found to change significantly as a function of a slide-roll ratio. A high resolution color camera has enabled a closer look at film thickness changes in the vicinity of surface irregularities that helped to describe these processes in detail. Obtained results indicate the presence of either a boundary film less than 1 nm thick or some solid-like contact in front of roughness features for positive slide to roll ratios (Fig. 1). No such a local film thickness reduction has been found for negative slide-to-roll ratio conditions.

The effect of slide-to-roll ratio on the micro-EHD lubrication of the roughness features of different scale in very thin film, EHD contact conditions has been studied in detail using formulated oil. Rubbing surfaces were found to be fully separated (Fig. 2).

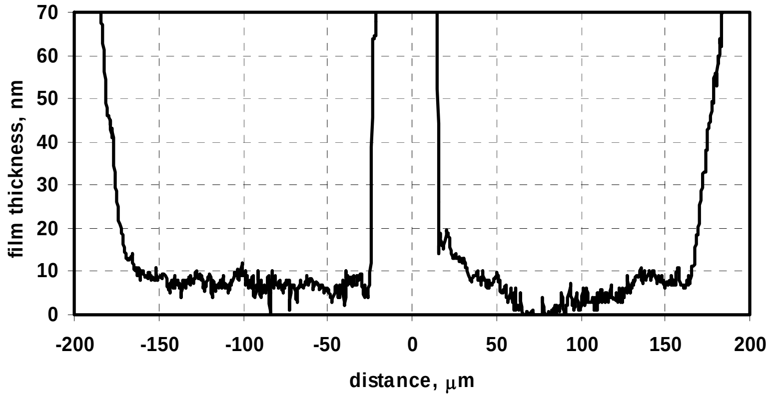


Fig. 1. Film thickness profile with paraffinic base oil for Σ = 0.5 and u = 0.0018 m/s.

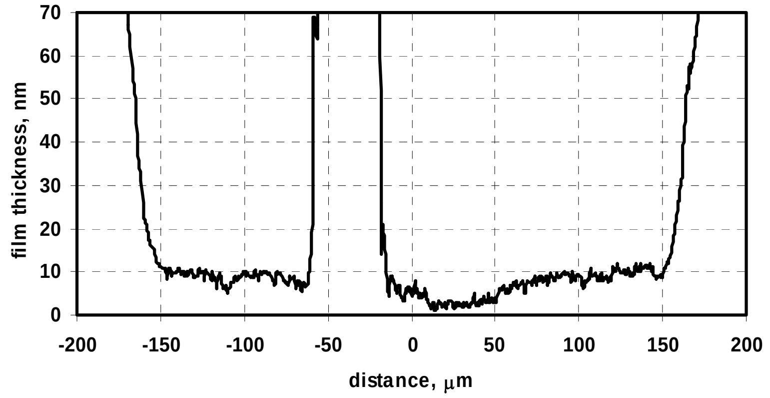


Fig. 2. Film thickness profile with the formulated oil for Σ = 0.5 and u = 0.0046 m/s.

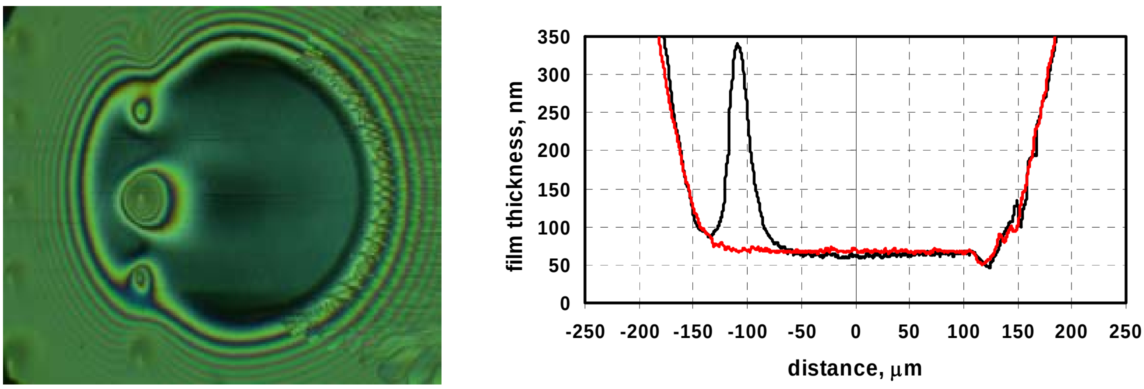
Currently, a combination of thin film colorimetric interferometry and phase shifting interferometry is applied to the study of the influence of individual additives on real surface roughness using an AISI 52100 steel ball with isotropic roughness. Its root-mean-square surface roughness measured using phase shifting interferometry is about 0.019 µm. The comparison between initial undeformed surface topography and film thickness distribution within lubricated contact enables the detailed study of the changes in surface micro-geometry influenced by the additive films formed on rubbing surfaces.

The behaviour of an array of micro-dimples within thin EHD contacts has been studied by thin film colorimetric interferometry. The influence of surface texturing on lubricant film formation has been observed under sliding/rolling conditions. The significant effect of micro-dimples depth on lubricant film thickness is observed for positive slide-to-roll ratio when the disc is moving faster than the micro-textured ball. The presence of deep micro-dimples within lubricated contact results in film thickness reduction downstream. As the depth of micro-dimples is reduced, this effect diminishes and beneficial effect of micro-dimples on film thickness formation has been observed. No significant influence of micro-dimples depth on lubricant film shape has been observed in case of negative slide-to-roll conditions when micro-dimples do not cause film thickness reduction regardless of their depths.

An array of micro-dimples was prepared by the indentation of the ball surface with a Rockwell indenter. This approach was chosen to obtain micro-dimples with well defined shape that enables to measure film thickness distribution inside micro-dimples also. It has made possible to calculate an amount of lubricant captured within the micro-dimple. Laser surface texturing has been also employed to produce micro-features of various depths and diameters. Nevertheless, obtained micro-dimples exhibit different reflectance properties comparing the rubbing surface, so that they were not used in the current study. The experimental apparatus was equipped with indenter mounted instead of microscope objective to be able to precisely adjust the position of produced micro-features on ball surface and thereby within lubricated contact. So that all procedures connected with micro-features production and topography and film thickness measurements do not require any ball replacement and repeated adjustment. Subsequent polishing with a fine diamond compound was used to study the influence of the depth of the micro-dimples on lubrication film formation. The distance between the rows is 160 μm and the distance between two adjacent micro-dimples within each row is about 100 μm. The depth of micro-dimples varies between 513 and 1435 nanometers.

Figure 3a shows the chromatic interferogram obtained at slide-to-roll ratio $\Sigma = 0.5$ with first row of micro-dimples located near the entrance to the concentrated contact. In this case the micro-dimple located near the centre-line in the direction of motion causes film thickness reduction located downstream about 30 nm. Conversely, shallower micro-dimple causes no film thickness reduction as it can be seen from Fig. 3b. Obtain results suggest that the size of micro-dimples is the key feature as to their effect on lubrication film formation. All results obtained under positive slide-to-roll ratios showed that the deeper micro-dimple causes more pronounced film thickness reduction downstream the micro-dimple. This is in a good agreement with numerical simulations by Mourier et al (Tribology International, 2006) that found a threshold value of the micro-dimple depth to be around 500 nm. They showed that such an effect is connected with the pressure distribution within the micro-dimple as when the micro-dimple is deep the pressure in it is very small or even close to zero. So that the pressure is not high enough to ensure sufficient viscosity of the lubricant entrapped in the micro-dimple and piezo-viscous effect can not longer help to improve the efficiency of lubrication film.

Obtained results suggest that micro-texturing could help to improve the efficiency of lubrication films within highly loaded contacts once shallow micro-dimples are used.



a) b)

Fig. 3. EHD interferogram and cross-section profile of film thickness depicting the effect of micro-dimples on lubrication film at $\Sigma = 0.5$.

In final series of experiments various micro-features were produced on rubbing surfaces to observe the effect of their shape on film thickness formation under rolling/sliding conditions. It was observed that the presence of deep micro-dents within lubricated contact results in film thickness reduction downstream for positive slide-to-roll ratio when the disc is moving faster than the micro-textured ball. As the depth of micro-dents is reduced this effect diminishes and mostly beneficial effect of micro-dents on film thickness formation has been observed. In case of negative slide-to-roll conditions when the disc is moving slower than the micro-textured ball an increase in film thickness upstream is the predominant feature. Both transversely and longitudinally oriented grooves, even being very shallow, caused significant film thickness reduction. The size (diameter) of micro-features is also an important parameter that must be well balanced to achieve film thickness beneficial effect on film thickness. Larger micro-feature can supply more lubricant into the contact; however they can cause lubricant film collapse near contact side-lobes even under well lubricated conditions.

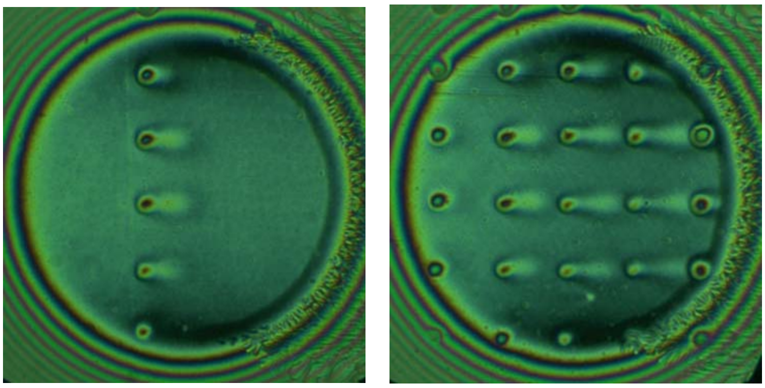


Fig. 3. EHD interferograms with a row and an array of shallow micro-dents for mineral oil and u = 0.0027 m/s and Σ = 0.5.

The effect of very thin viscous boundary films on rolling sliding point contact behaviour was studied with micro-textured surfaces (Figs. 4 and 5). Film thickness evaluated from chromatic interferograms by thin film colorimetric interferometry was compared with values obtained with mineral base oil. The use of formulated oils resulted in film thickness enhancement under very thin film conditions within both the smooth and micro-textured surfaces. Obtained results also suggest that thin viscous boundary films can provide some rubbing surface protection even under the operating conditions when thick viscous boundary films are not longer formed on rubbing surfaces.

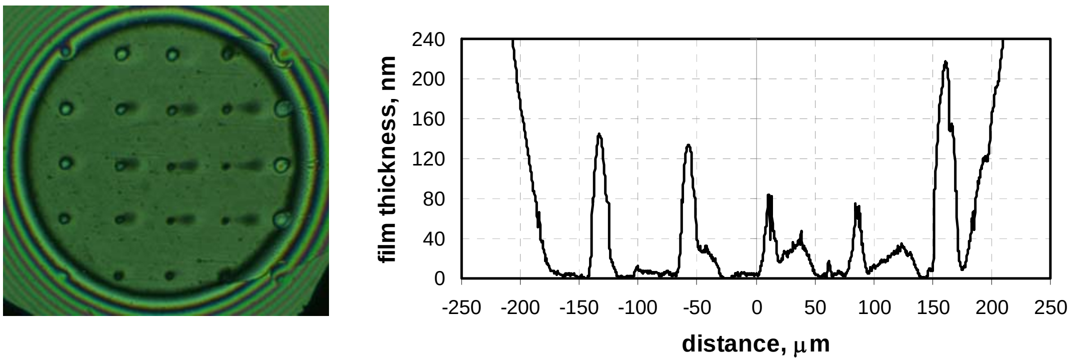


Fig. 4. EHD interferogram and film thickness profile for mineral oil and u = 0.0027 m/s and Σ = 0.5.

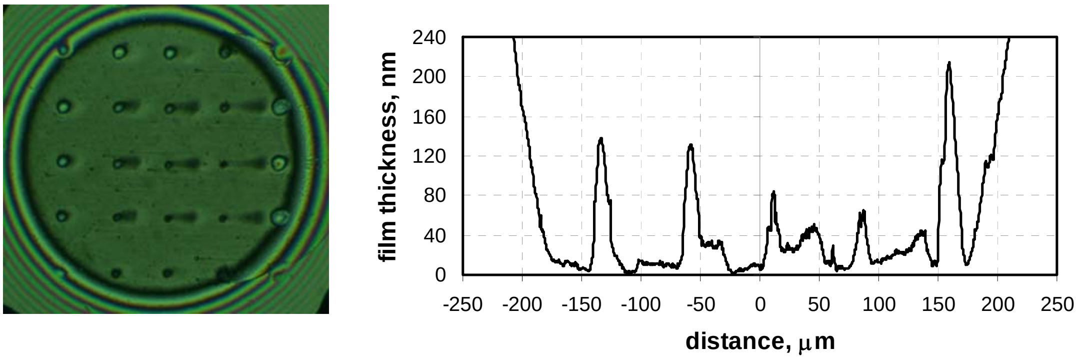


Fig. 5. EHD interferogram and film thickness profile for mineral oil with PAMA and u = 0.0027 m/s and Σ = 0.55.

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1. KŘUPKA, I.; HARTL, M.; POLIŠČUK, R.: The Effect of Boundary Films on Dented Surfaces Operated under Thin EHD Lubrication. Ecotrib 2007.
2. KŘUPKA, I.; HARTL, M.: The Effect of Surface Texturing on Thin EHD Lubrication Films. Ecotrib 2007.
3. KŘUPKA, I.; HARTL, M.: Effect of surface texturing on thin film EHD lubricated contact, In. 2007 STLE Meeting, pp. 1-4.
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CHAPTER 4 TRANSMISSION SYSTEMS, TS

4.1 Summary

By Jože Vižintin and Marian Szczerek, coordinators of WG2

Number of projects: 17 (From Poland 2, Serbia 2, Czech Republic 2, Germany , Finland , Slovenia, Ukraine, Slovakia, Belgium, Croatia, Sweden, Malta, Lithuania and Switzerland 1 each) 9 projects are finalized (100%), the other eight are between 50 and 90% of finalization. WG 2 has resulted in 281 reports of which 50 are internationally refereed journal papers, 173 are international conference papers and 58 are national reports. They have generated 10 industrial improvements already in use.

The activities within the 17 projects can be classified in 3 items.

Oil-free powertrain

Friction and wear control

New thin coatings

All 17 projects are aimed to investigate different possibilities and limits concerning possible reduction of lubricants quantity in gear transmissions without detrimental influence on load carrying capacity. The investigations cover the influence of different materials, heat treatments, coatings, lubricants, lubricated systems, gear design parameters and operating conditions on friction and wear behavior distinctive for gear transmission systems. Thin protective coatings are the subject of most projects and the elimination or minimization of lubricant quantity is seen to be strongly connected with the application of hard coatings on transmission components.

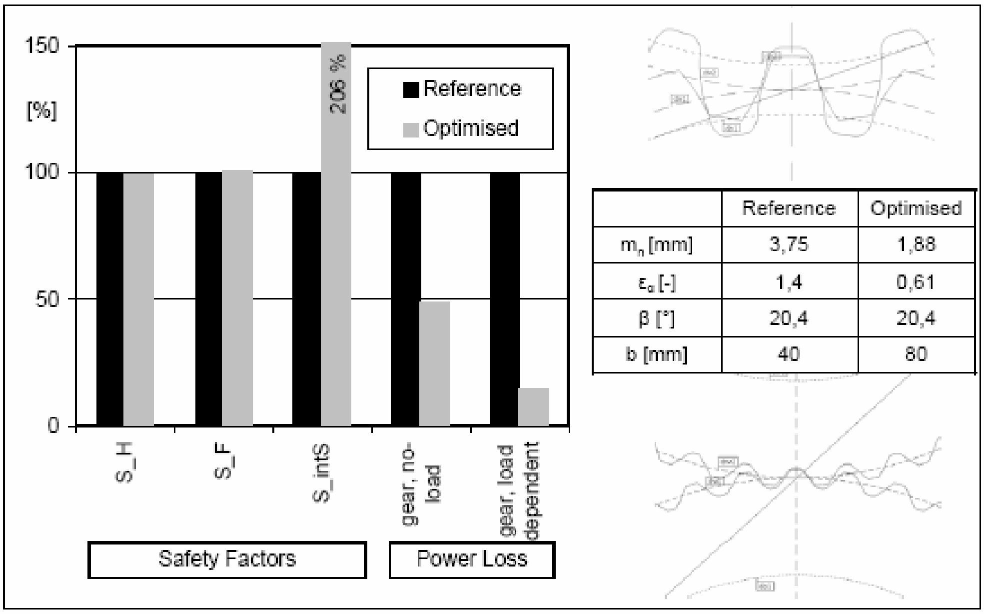
Oil-free powertrain is the most comprehensive theme. The project TS1 has been concerned with gear geometry optimization, friction optimization and coating technology optimization. All these studies are required to achieve design solutions for oil-free powertrain concept. The project has gained the improvement for commercial use.

Friction and wear control have been the main subject in TS 7, TS8, TS9, TS10, TS11, TS12, TS13, TS14 and TS15. TS12 has developed the improvement in commercial use and TS14 reported that 4 improvements have been developed.

New thin coatings were topics of TS2, TS3, TS4, TS5, TS6, TS16 and TS17. TS2 reported a development of a new technology for manufacturing steel heavy-loaded machine components; TS3 reported an industrial improvement and TS4 has developed the improvement in commercial use by the company.

Minimized lube quantity

In TS1 the first step towards the oil-free transmission systems has been done. First, the losses in bearings and gears were investigated. The main results for transmissions were that the losses in bearings are subordinate to the losses in gears. For a reduction of the losses in gears basic changes of the gear geometry have to be done, Fig.1. To get a gear with a low power loss without an effect on the load carrying capacity, sliding movements on the gear flank have to be reduced and rolling movements increased. Optimized gear geometry was designed with an expected power loss reduction of about 50% for no-load losses and about 80% for load dependent losses respectively.

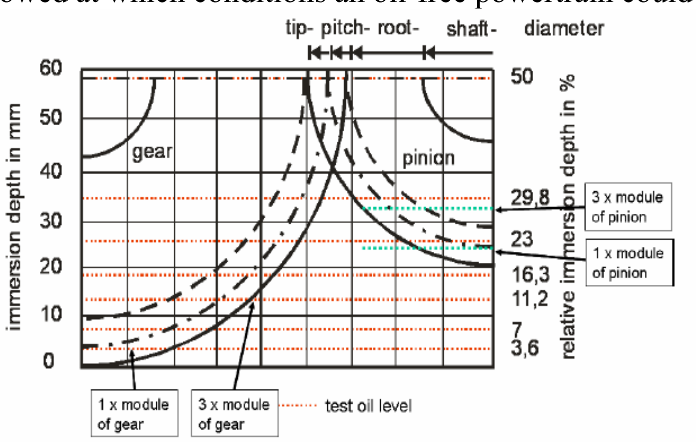


	Reference	Optimised
m_n [mm]	3,75	1,88
ε_α [-]	1,4	0,61
β [°]	20,4	20,4
b [mm]	40	80

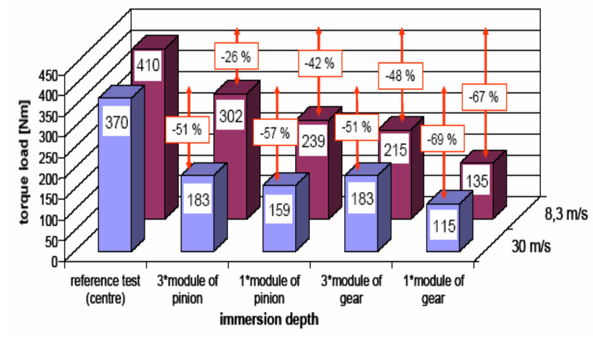
Fig. 1. Low loss gears.

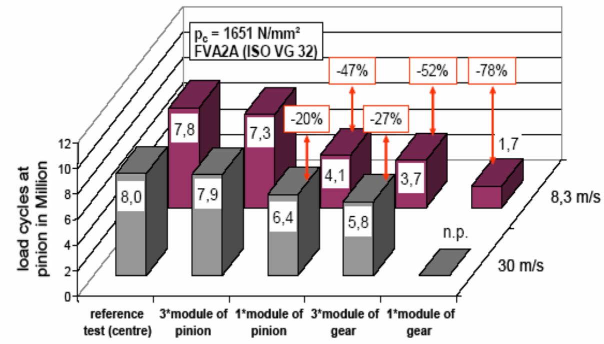
Efficiency gear tests with a reduced oil level as well as with oil/air lubrication were performed and showed the limits of the oil level and oil quantity reduction respectively. Under conditions of a low oil level or a low oil/air quantity, a high load and high speeds the bulk temperature increased above the tempering temperature of case carburized gears. Pitting load carrying capacity and scuffing load carrying capacity were also determined for different oil levels as well as very low oil quantities and both were compared to standard lubrication conditions. A reduction in pitting life of up to 85% and in scuffing load carrying capacity of up to 70% was found for minimum oil dipping depth. Oil/air lubrication resulted in an even more severe reduction and can be generally compared to dip lubrication at very low oil levels. Micro pitting tests showed a similar trend. The wear rate of the standardized gears was mostly unaffected by the immersion depth and oil quantity respectively due to the low bulk over temperatures at very low speeds. The reduction in load carrying capacity has to be taken into account in the design of gears in practice.

From the technical point of view first very promising steps to achieve an oil-free powertrain were achieved. The project showed at which conditions an oil-free powertrain could be possible in future.



a)





b) c)

Fig. 2 a) Oil levels in dip lubricated system, b) Scuffing gear test results, c) Pitting gear test results.

Coatings for heavy-loaded machine components

In TS2 tests were conducted for selections of thin, hard coating with respect to mechanical and tribological properties. The results show that single CrN and multilayer WC/C coatings exhibit good anti-wear properties and lower friction coefficient compared to the TiN coatings. The results indicate that the presence of thin coatings gives a possibility of eliminating or reducing the content of toxic AW/EP additives in lubricating oils, as well as using ecological oils made of renewable resources, without any risk of scuffing failure.

Under dry running conditions the coated gears were investigated in TS1. The most promising results were obtained with a combination of Low-loss gears and a DLC-coating (Diamor). The results for gears with thermally sprayed coatings were comparable with DLC-coated gears, but the failure mechanism differs between both coating systems. In both cases the wear is proceeding gradually at first. Thermally sprayed coatings have failed by spelling of the coating, whereas the DLC-coatings were worn off followed by fretting or increasing wear.

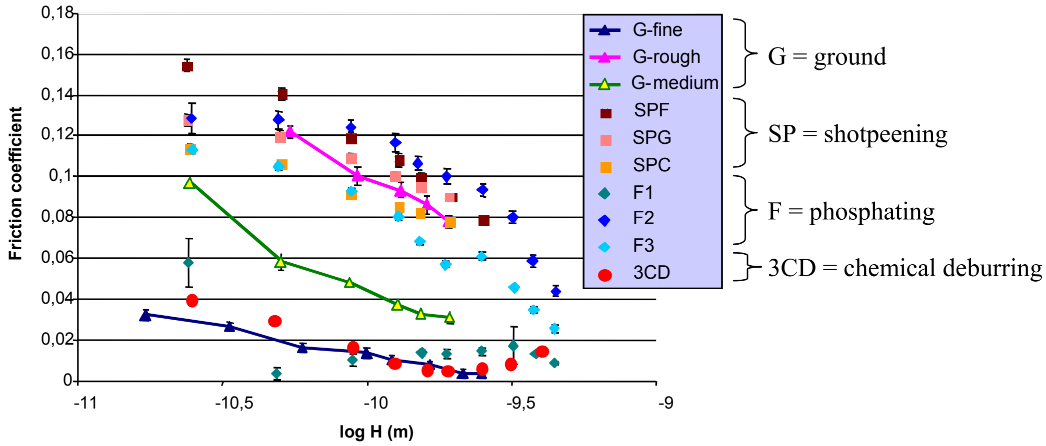
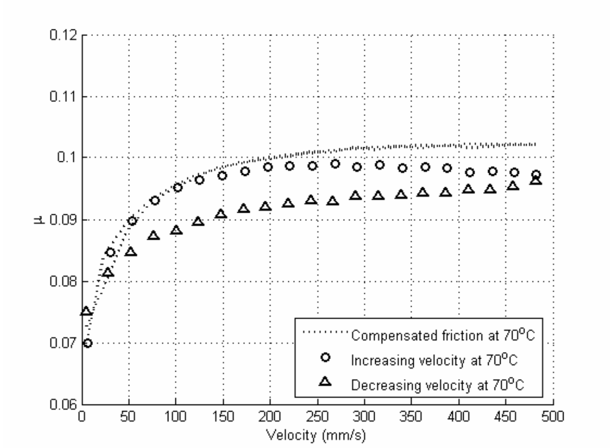


Fig. 3. The effect of surface treatment/texture on the coefficient of friction.

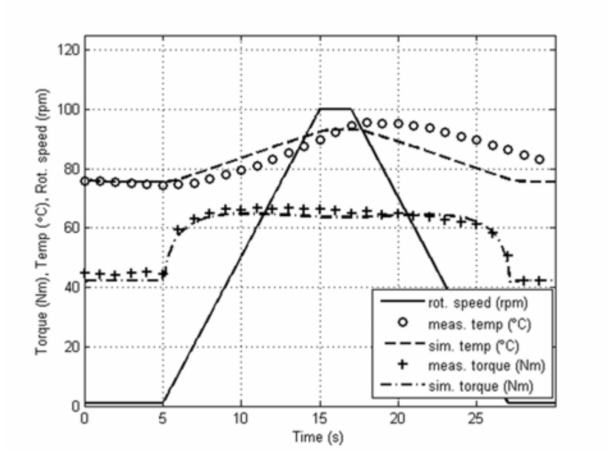
Adhesion to substrate materials is essential to suppress high internal stresses through incorporation of wear resistance coatings and is the main subject in TS4 and TS17. In TS4 a clear effect of different surface and interface preparations typical for gear transmission systems was observed on the friction behavior, Fig.3. A large-scale two disc machine was used for testing under lubricated regime and normal load of 225 MPa.

Friction and wear control

Wet clutch properties were investigated in TS9 and TS14. A test apparatus, which is able to monitor friction and temperature as a function of applied force, sliding velocity and oil flow have been developed in TS14.



a)



b)

Fig. 4 a) Friction characteristics measured during speed increase and speed decrease, and the same two curves compensated for the different conditions during measurements b) Comparison between measurements and simulation with an axial force of 25.3kN.

A method for measuring and presenting anti-shudder properties has been also developed. The friction is presented as a discrete function of velocity at a constant temperature. By using this method it is possible to compare anti-shudder properties obtained under different conditions, since the data are not influenced by the chosen test conditions, Figure 4a.
Based on the knowledge of clutch performance obtained from the research presented in this thesis, a model to predict transmitted clutch torque has been developed. This accurately determines the transferred torque from the current operating conditions and the thermal history of the clutch, Figure 4b. It can be concluded that thermal effects have a significant influence on the torque transferred by the clutch, and it is therefore necessary to have a thermal model of the clutch combined with a temperature dependant boundary friction model based on empirical friction data for the friction material/transmission fluid combination of interest.

Two projects investigated the lubricant properties. The results that indicate the interactions between materials, heat treatment and conventional lubricants have been reported in TS12. Case carburized DIN 20MnCr5 steel lubricated with the synthetic 75W-90 gear oil was recognized as the best tribological combination. TS5 was focused in novel type of solid lubricants – 2H-MoS_2 and 2H-WS_2. These solid lubricants were used as additives to paraffin oil. Significant decrease in the friction force (by a factor of 1.5) and an increase of wear resistance (by a factor of 1.5 – 2) has been observed as compared with the data on the use of natural MoS_2.

4.2 Project result reports

TS1 - OIL-FREE-POWERTRAIN

Co-ordinator and partners

There are five industrial associations (IAG) and four research institutes (RTD), which are partners within the project.

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Project status and schedule

Running with full funding
Starting and ending dates: 15.11.2002 – 15.11.2005 (36 months)

Project aims

The project "Oil-free Powertrain" was the first step towards oil-free transmission systems in engines and machines. To achieve this, the project consisted of two parts. The first part was aimed at optimising the kinematics and reducing friction in gears and engines, at minimising the liquid oil quantity and at minimising friction in the contacts by optimum material pairing with solid material or coatings. This already led to a considerable improvement in power loss and oil consumption and thus partly fulfilled the objectives. The second part aimed at a zero liquid lubricant supply making use of the development in part one with additional solid lubricant or tribological layer development. In case of an engine-related approach, one main aim was the development and integration of a new, lube-oil free piston-liner configuration for internal combustion engines. The second main aim from the engine's point of view was the development of an oil-free cylinder head.

Project results

Within the project there were different work-packages (WP), the main results are described in the following.

WP 0: Management and co-ordination

A detailed time schedule including also the interrelationships between the specific work-packages was worked out and was continuously updated. Periodic 3 months reports guaranteed a successful project progress and a very fast distribution of the latest results between the project partners. At mid-term of the project a mid-term report was written and the results were discussed together with the EU commission and independent experts. Till now six internal project progress meetings and the mid-term meeting with the EU commission were organised, see also detailed description in chapter "project co-operation".

For a successful co-operation between the different project partners a Consortium Agreement between the IAG-partners was agreed and signed, a Core Group Agreement between the SMEs was prepared. The RTD-partners signed a RTD-agreement.

WP 9: Dissemination and exploitation

The latest main dissemination and exploitation activities are listed below.

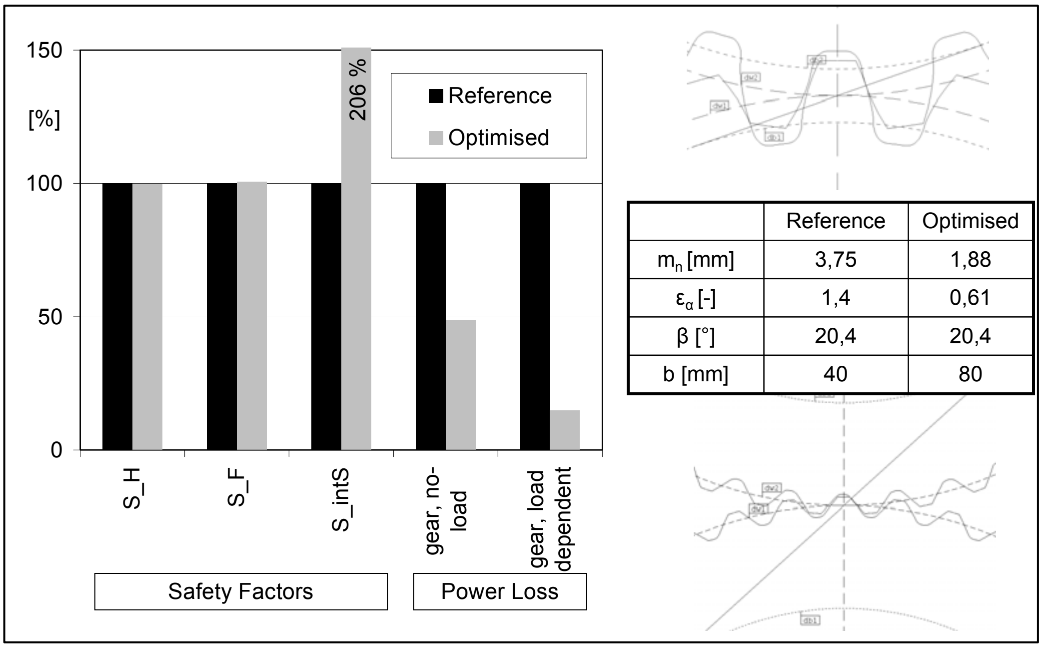
- A project's web-site www.oil-free-powertrain.de with the whole project documentation was installed and was continuously updated.
- The project's progress was periodically presented to the industry-members of the FVA (Research Association Power Transmission Engineering) within the working group meeting of the group "Lubricants and Tribology". The last presentation was done in June 2005.
- The project's progress was periodically presented to the industry members of FVV (Research Association for Combustion Engines) at the meetings of the FVV-Technical Advisory Board.
- The project's progress was presented at a conference of the FVA in November 2004 and at a conference of the FVV in September 2004.
- The project's progress was periodically presented to the European scientific community at the meetings of COST 532. Till now the progress was presented in three meetings of the COST 532 action.
- Magosz presented the project's progress at a conference in November 2004.
- FMS presented the project at a conference in October 2004.

WP 1: Analysis of oil elimination and friction minimisation in gears and engines

This work-package was finished in May 2003, the final report is available on the project's web-site (Final report WP 1).

An analysis regarding minimum oil requirements and minimum friction in transmissions and engines was done by TUM and AVL. TUM investigated the losses in bearings and gears, AVL did the analysis on the engine side.

The main results for transmissions were that the losses in bearings are subordinate to the losses in gears. Lowest losses in bearings mainly can be achieved with bearings with line contacts due to a smaller diameter. Minimum losses could be expected, when for example cylindrical roller bearings are used. For a reduction of the losses in gears basic changes of gear geometry have to be done. To get a gear with a low power loss without an effect on the load carrying capacity, sliding movements on the gear flank have to be reduced and rolling movements increased. An optimised gear geometry was designed with an expected power loss reduction of about 50% for no-load losses and about 80% for load dependent losses respectively and is currently manufactured by a SME, which is a partner within the project. Helix gears with a very low profile contact ratio below 1,0 have to be used. To get an equivalent load carrying capacity the face width has to be increased and the root height has to be reduced. **Figure 1** shows a diagram of the safety factors regarding load carrying capacity, the factors of the power loss and a drawing of the standard and optimised gear. The upper drawing shows the standard gears the lower one the optimised ones.



	Reference	Optimised
m_n [mm]	3,75	1,88
ε_α [-]	1,4	0,61
β [°]	20,4	20,4
b [mm]	40	80

Fig. 1. Reference and optimised gear.

From the engine's point of view there are three main concepts which have found to have the potential to minimise the oil requirement. One is the reduction of the oil-consumption in the piston bore interface, because 75% - 90% of the whole engine's oil consumption takes place in that interface. A second one is the reduction of the average and also the max. oil-temperature to prolong oil-changing intervals. There the oil composition itself plays an important role and therefore this part isn't investigated in this project. A third one is a concept for an oil-free cylinder head (without the need of pressurised oil), which would considerably simplify the engine architecture as for example no oil drain back channels are needed. An oil-free cylinder head could be achieved by applying electromagnetic valve train actuators. The cam-less valve actuation would also help to increase oil lifetime by eliminating the destructive high shear forces and pressures at the cam-follower interfaces. **Figure 2** shows a drawing, how a oil-free cylinder head could look like.

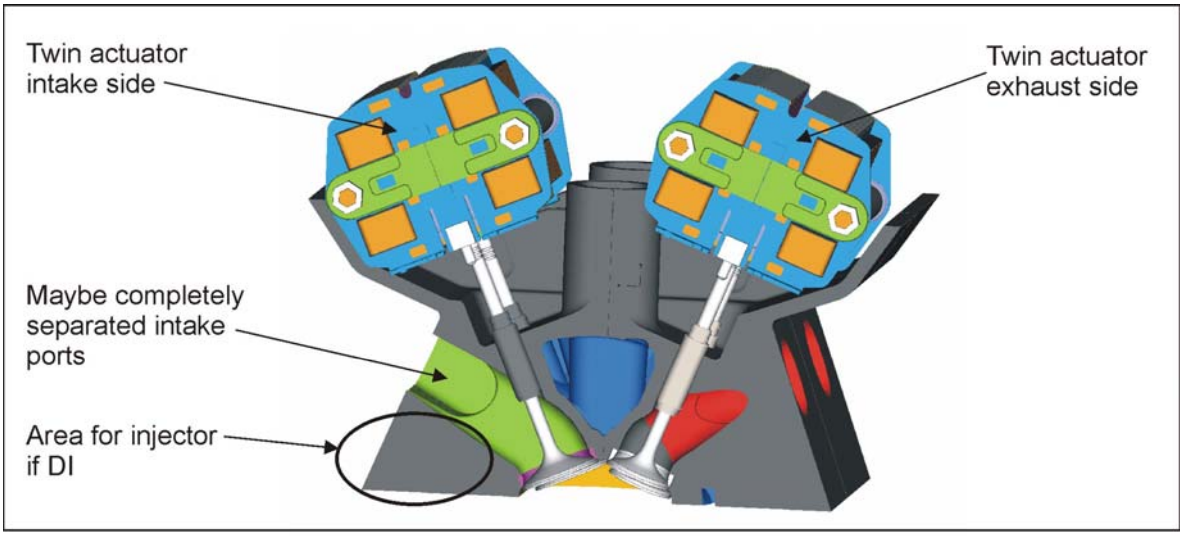


Fig. 2. Drawing of oil-free cylinder head.

WP 2: Multilayer coatings

This work-package was finished in November 2005, the final report is available on the project's web-site (Final report WP 2).

In WP 2, done by IWT, multilayer coatings on case carburised steel were developed by varying several parameters. At first an optimised coating was developed then tests with coated gears were done. For the coating optimisation the coatings were characterised with different test methods. Adhesion was evaluated with scratch tests, ultra-microhardness was measured, coating thickness and coating structure was evaluated with X-ray analyses. Wear behaviour and friction coefficients were determined with pin-on-discs tests. To avoid tempering of a case carburised steel a PVD-process (Physical vapour deposition process) was used as a coating process.

The investigated coatings consist of a chromium adhesion layer between the substrate and the real coating. The coatings itself consist of a chromium-nitride transition layer and an amorphous carbon layer with an amorphous hydrogenated carbon top layer (**Figure 1**). Between the amorphous carbon layer and the amorphous hydrogenated carbon top layer there is a gradient transition.

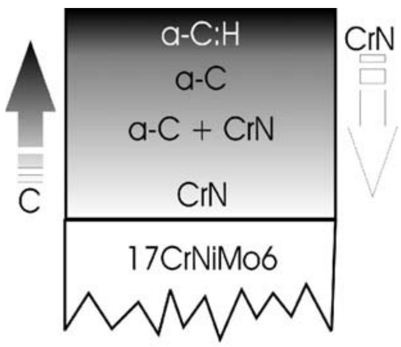


Fig. 1. Multilayer coating.

One main result of the work-package is, that the coating's wear behaviour and friction coefficient mainly depend on the coating hardness. Coating hardness can be varied by different acetylene gas flows and bias voltages during the coating process. Lower acetylene gas flows and higher bias voltages, which are responsible for the ion bombardment, result in higher coating hardness (**Figure 2**).

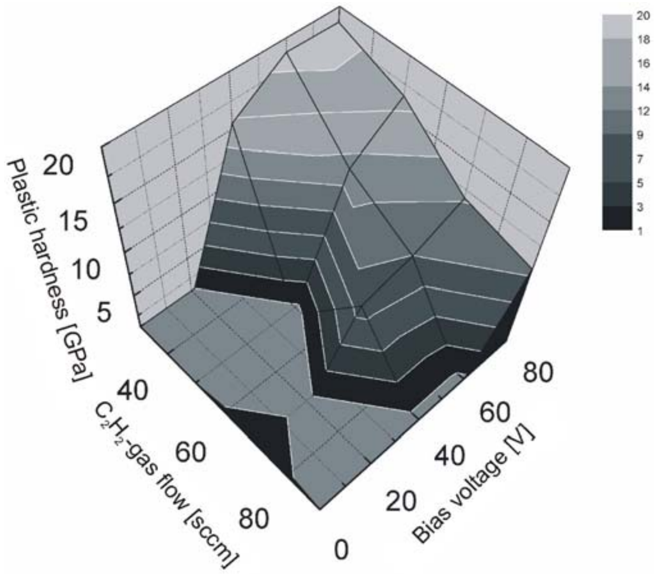


Fig. 2. Coating hardness in dependence of coating process parameters.

Pin-on-disc tests at dry lubrication under atmospheric conditions showed that "softer" coatings are superior to "harder" coatings regarding wear behaviour and friction coefficients. However "harder" coatings showed advantages under water lubricated conditions. A main problem at dry lubrication is, that cooling of the partner's contact is insufficient due to a lack of heat removal. Thus gear bulk temperature increases and can easily reach tempering region of case carburised materials. This problem can be avoided, when a water lubrication is used. Therefore besides an optimised coating for dry lubrication also an optimised coating, which can be used under water lubricated conditions, was developed within this work-package.

In the end gears were coated with the optimised coatings and tests with an FZG-gear test rig were done. There the coated water lubricated gears reached higher lifetimes compared to the coated gears, which were tested at dry lubrication.

WP 3: Ceramic coatings

TUD and the subcontractors Fraunhofer Institutes IWS and IKTS investigated DLC-coatings, thermal spray coatings and bulk ceramics. The work-package was divided into two main parts, part one was dealing with the coatings itself, in part two ceramic coated gears and gears with thermal spray coatings were investigated. Part one was finished in March 2004, the final report is available on the project's web-page (Final report WP 3.1).

The developed DLC coating, with the tradename Diamor®, showed quite good results, i.e. strong adhesion, low friction and wear rate under dry lubrication. Within the thermal spray coatings WC-based coatings showed the best results. The bulk ceramics showed the highest coefficient of friction, furthermore costs of manufacturing and finishing are very high, too. Therefore bulk ceramics aren't further investigated in the second part of the work-package. **Figure 1** gives an overview of the wear rates and corresponding friction coefficients for the different coatings.

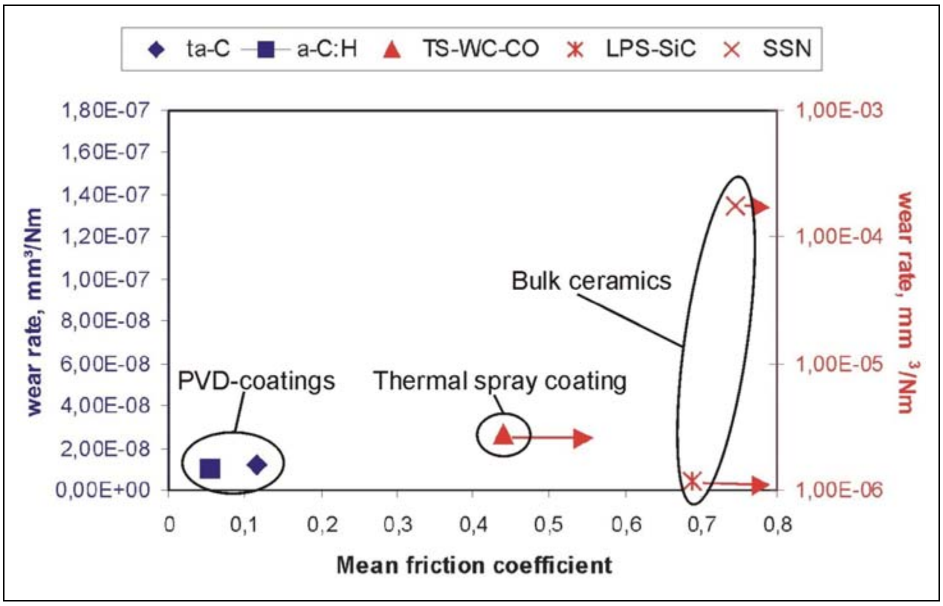


Fig. 1. Friction coefficients and wear rates at dry lubrication.

The second part of the work-package, the investigation of coated gears, was finished in February 2005, the final report is available on the project's web-page (Final report WP 3.2). Within work-package 3.2 tests with the coating Diamor® (coating thickness 3 µm) at different loads and speeds and comparative tests with different types of coatings, different coating thickness and different surface roughness were done.

Figure 2 shows the results of the tests with the coating Diamor® at different loads and speeds. As a result a clear dependence of lifetime on the load was found. A clear dependence of lifetime on speed could not be observed. In all tests the coating failed first, followed by fretting damage (high speeds and high loads) or wear (low speeds and low loads).

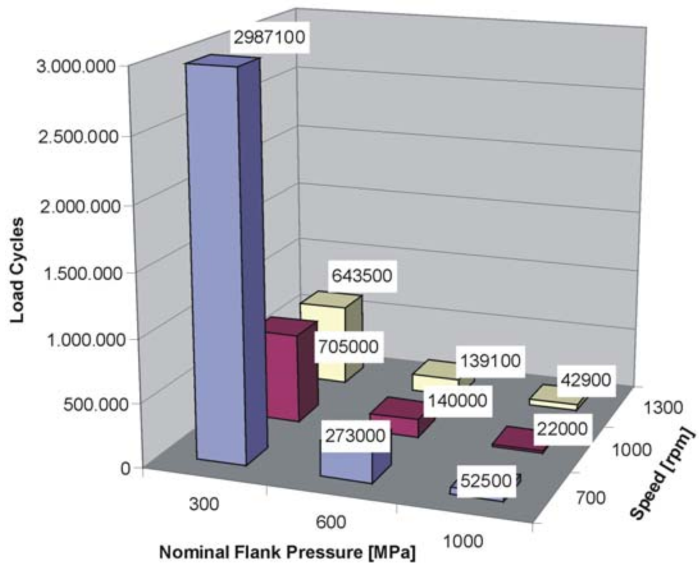


Fig. 2. Tests with the coating Diamor® at dry lubrication.

Figure 3 shows the results of the comparative tests. Nominal flank pressure was at 600 N/mm^2 and pinion speed was at 1000 rev/min. A higher lifetime could be achieved when a higher coating thickness or a better surface quality, that means a lower surface roughness, was used. Coating of just one gear was not successful. For the thermal spray coatings the higher coating thickness had to be taken into consideration. Therefore a gear geometry possible for coating with thermal spray coatings was defined. Lifetime of these thermal spray coated gears was comparable to lifetime of DLC-coated gears. However the highest lifetime by far was achieved with coated low-loss gears. Lifetime of these combination was about 18 times higher compared to lifetime of standard spur gears. These low-loss gears were developed within WP 1.1 and show very low power losses compared to standard spur gears. The idea of those gears is, that tooth contact is concentrated around the pitch point, where pure rolling occurs. Thus sliding is reduced.

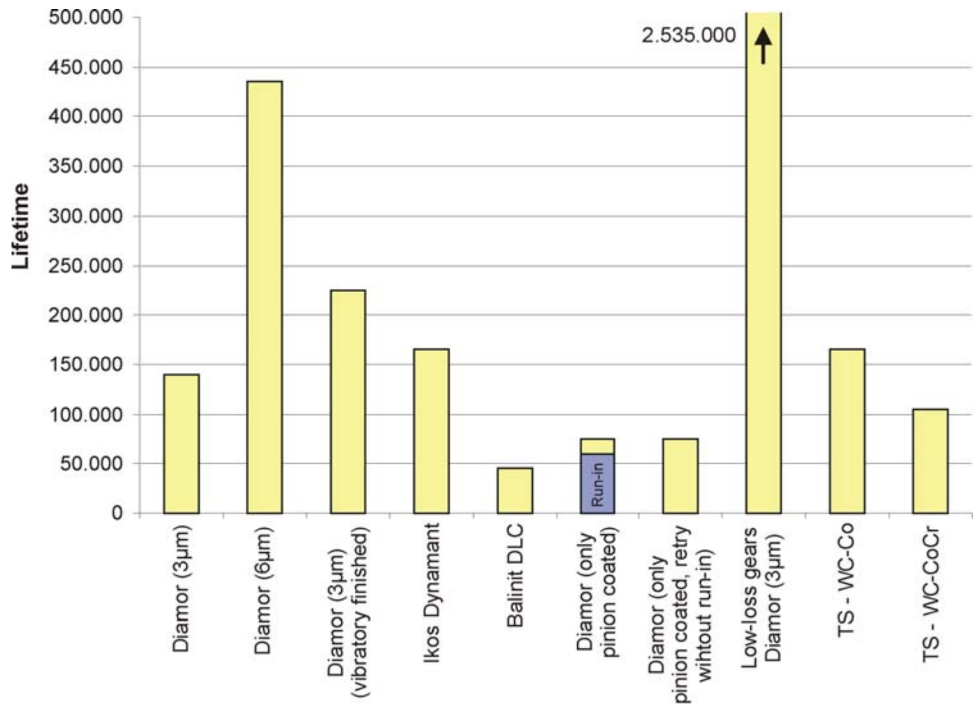


Fig. 3. Results of comparison tests.

WP 4: Solid lubricants

WP 4 dealt with a lubrication by solid powders and was done by TUD in cooperation with the subcontractors IPF and IFBL. TUD did the tests with gears, IFBL the tests with toothed couplings. The work-package was finished in December 2004, the final report is available on the project's web-page (Final report WP 4).

The investigations with gears include retardation tests, stepwise tests and longterm tests. Retardation tests with different kinds of PTFE and PE powders were done, commercially produced and modified powders were used. Optimised powders regarding the lubrication properties and the necessary swirling behaviour for a continuous renewal of the lubricating film were found, namely the powders Zonyl® MP1600 and MP 1100. The results compared to tests with common oil-lubricated gears were promising. For a continuous renewal of the lubricant film the gear box design had to be changed, different guiding plates and swirling devices were installed.

In stepwise tests, were the load was increased stepwise, losses were measured. Except of the PE powder, which showed the highest losses, the losses of the PTFE powders were in the same range as the losses of a common oil lubrication. **Figure 1** gives an overview of the measured losses for different loads. A problem, which occurred with the powders, was the increasing bulk temperature due to a missing heat removal. Thus additional cooling systems have to be used.

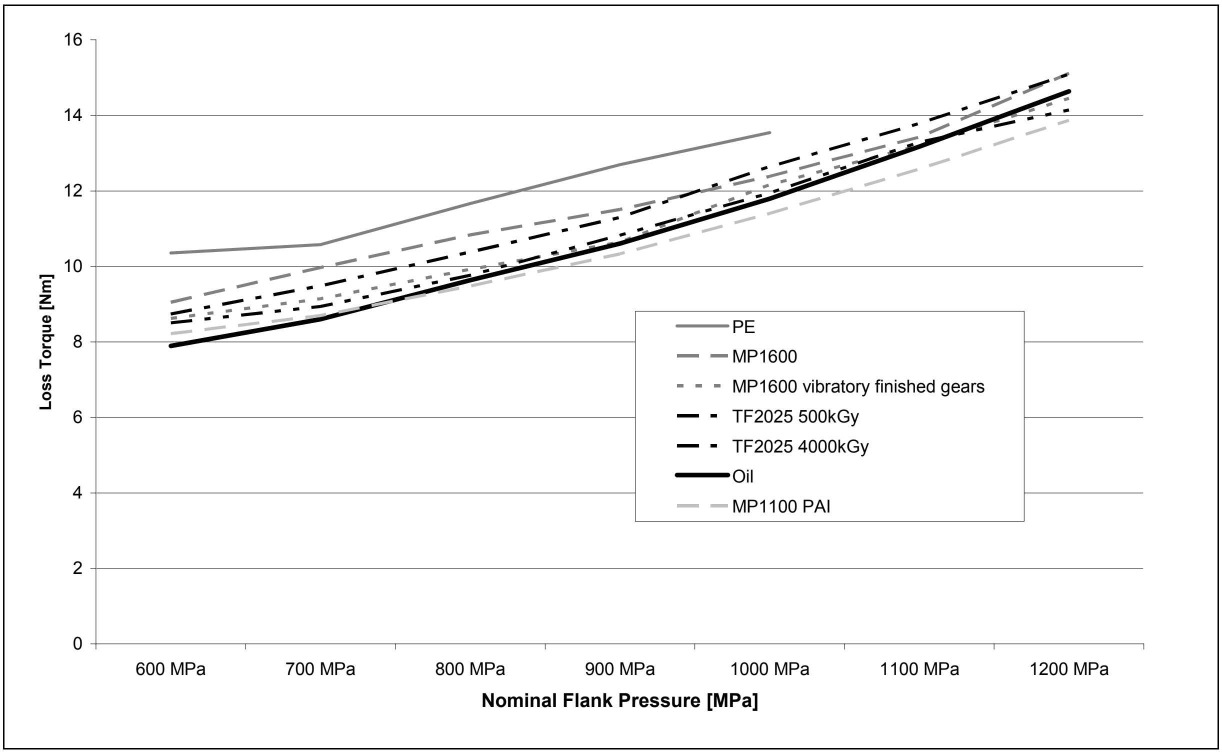


Fig. 1. Losses as a function of load and lubrication.

In a long term test with the powder MP 1600 at a pressure of 1200 N/mm^2 no gear damage occurred up to 1 million load changes.

For the tests with toothed couplings two possibilities of fixation of the powders on the tooth flanks were investigated. One was encasing the PTFE powder within the range of tooth profiles by seals the other one was a magnetically fixation of a modified powder containing also iron with magnets in the tooth flanks. However a sufficient fixation of the powders on the flanks could not be achieved by either variant. Whether the space between flanks was too large and the powder was transported away from the contact area or the low magnetic forces were too weak for a constant renewal of the sliding film.

WP 5: Phase transition lubrication

In WP 5 a new concept of lubrication, a lubrication by a phase transition, was investigated by TUM. The work-package was finished in June 2004 and the final report is available on the project's web-page (Final report WP 5).

Within the work-package there were two main tasks, a theoretical one including an extensive investigation of the literature and an experimental one including tests with a twin-disc-machine. The investigated literature can be divided into theoretical papers and literature about experiments. The theoretical papers deal with the calculation of the melting rate, coefficient of friction and the film thickness partly taking the unsteady beginning of a melting process additionally into consideration. Most of the experimental papers deal with sliding tests with different materials at various loads and speeds. Especially at high loads and high speeds, for example in guns, melt lubrication was observed. But there are also reports about experiments with ball bearings and sliding bearings. Further papers investigate possible coating procedures and necessary parameters, that dry lubrication could be possible. Based on the results of the investigation of literature the defined coatings consist of low melting alloys, resinous substances containing solid lubricants and of wax.

In part two tests with coated discs with an additional oil lubrication and under dry lubrication were done. The results show that the coatings could be used within a limited load and within a limited sliding distance. All investigated coatings showed an improvement of the friction characteristics compared to uncoated surfaces under dry lubrication and partly also in oil lubricated systems. At dry lubrication best performed a coating containing PTFE as a solid lubricant.

Additional investigations with a coating building substance were done. The substance contains magnesium and silicium and should build an iron-silicium coating, when it is added to an oil. The conclusion from these tests is, that a coating building run at the transition of boundary to mixed lubrication regime and at boundary lubrication regime has a positive impact on the lifetime under dry lubrication. The disc roughness decreased, possibly due to a kind of a lapping process of the hard silicium particles. Traces of silicium could be detected after this coating building run. However, it was not possible to detect a coating in a metallographic section of the disc surface and to improve the friction behaviour.

WP 6: Minimised liquid lubricant quantity

The reduction of the oil supply to a minimised liquid lubricant quantity should be achieved within WP 6 done by TUM. There are two analysed ways to minimise the oil quantity, a reduced oil immersion depth and an oil-air lubrication system. All kind of gear failures, that means pitting, micropitting, scuffing and wear, were investigated. Furthermore efficiency tests and gear bulk temperature measurements were done with minimised lubrication. The work-package was finished in December 2005 and the final report is available on the project’s web-page (Final report WP 6).

Efficiency tests with gears with a reduced oil level were performed and showed the limits of the oil-level reduction. The main results were, that the no-load losses decrease with decreasing immersion depths. The load-dependent torque losses were hardly influenced by the immersion depth. The gear bulk over-temperature increased with lower immersion depth, in some cases dramatically. Especially at high speeds the difference between the gear bulk temperature of the pinion and the oil temperature in the test gear increased up to more than 100 K. Those measured temperatures are in the range of the tempering temperatures of the case carburised material. With an oil-air lubrication the gear bulk temperature increased up to tempering region not only in combination with high speeds but also at low speeds in combination with high loads.

Scuffing load carrying capacity was determined for reduced immersion depth and an oil-air lubrication for two different circumferential speeds at pitch point of 8,3 m/s and 30 m/s. Scuffing load carrying capacity decreased up to 70 % at both speeds of 8,3 m/s and 30 m/s at reduced immersion depth. In combination with an oil-air lubrication the decrease was 75 % at a speed of 8,3 m/s and 85 % at a speed of 30 m/s.

Pitting load carrying capacity was determined for different oil levels and for an oil-air lubrication compared to standard lubrication conditions. A reduction in pitting life of up to

77 % was found at a speed of 8,3 m/s, when the immersion depth was only one time the module of the gear. At higher speeds of 30 m/s the decrease was not so high, due to foaming of the oil. With an immersion depth of three times the module an sn-curve for the pitting lifetime was determined. Additional tests with an oil-air lubrication with an oil volume flow of 28 ml/h were done, the results are also shown in **Figure 1**.

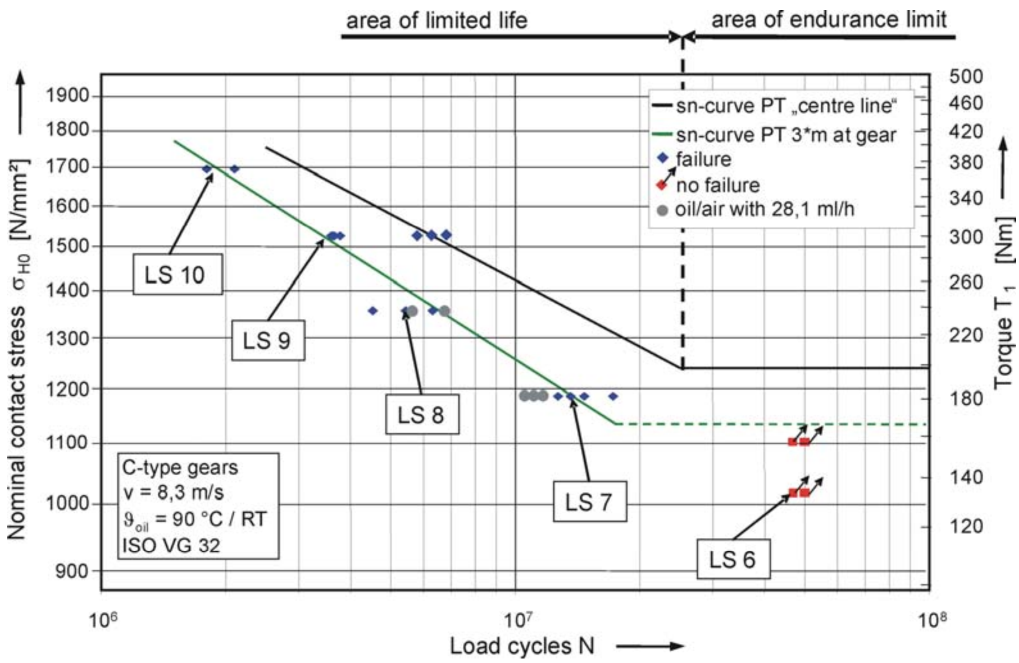


Fig. 1. Sn-curves for reduced immersion depth and oil-air lubrication.

Micropitting was investigated with reduced oil levels compared to standard lubrication conditions. The load carrying capacity regarding micropitting was load stage 10 for standard lubrication conditions and load stage 9 for reduced oil levels. In the subsequent endurance tests the gears lubricated with reduced oil levels failed due to a pitting damage, whereas no failure occurred in combination with standard lubrication conditions (**Figure 2**).

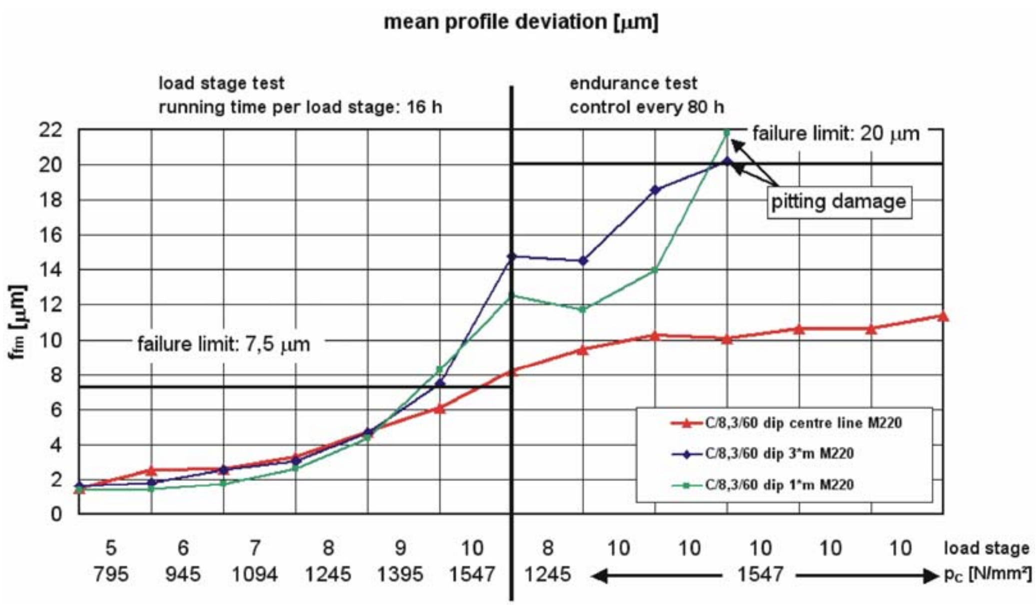


Fig.2. Results of micropitting tests.

Wear was investigated with reduced oil levels and an oil-air lubrication compared to standard lubrication conditions. Due to the low speeds at the wear test increase of gear bulk temperature is very low also at minimised lubrication. Thus the influence of a minimised lubrication on wear is very low compared to the other gear failure modes pitting, micropitting and scuffing.

WP 7: Optimisation of piston liner oil consumption and oil-free cylinder head

The engine related issues were investigated in WP 7 by AVL. Based on the outcome of WP 1 it was decided to focus the experimental investigations on the piston-bore interface and the concept of an oil-free cylinder head. Within the oil-free cylinder head the most critical part is the oil-free valve / valve guidance. The work-package was finished in July 2005, the final report is available on the project's web-page (Final report WP 7).

Current modern engines show a lube oil consumption of about 0,1 % – 0,2 % of fuel consumption. The sub-system with the highest contribution to the lube oil consumption is the piston-bore interface with about 75 % – 90 % of the total lube oil consumption. Thus the piston-bore interface experimental work was sub-divided into 3 programs:

- Rig tests with different honing types to investigate the interaction between ring pack-liner friction and the retained oil on the liner surface (directly linked to the lube oil consumption). Under the conditions of the rig test, which means lower cylinder running surface temperatures and lower gas forces compared to a running engine, the lowest friction was measured with the smoothest cylinder bore, a polished honed liner with an average surface roughness of Ra = 0,06 µm. Roughness of the standard honed liner was Ra = 0,64 µm.
  The experimental results were compared with calculations done with the simulation program "AVL GLIDE". The differences between measurement and simulation were very small at lower temperatures and lower speeds. At higher speeds and higher temperatures the correlation was still very satisfactory.
- Investigations on a small 3-cylinder passenger car diesel engine, where the major focus was the relationship between lube oil consumption and friction. Three different piston / piston-ring specifications were defined and tested. With the best piston and piston-ring specification, the friction mean effective pressure of the motored engine at a mean piston velocity of 10 m/s was about 1,70 bar – 1,72 bar, which is a value on the low side of the friction scatter band for similar engines. The lube oil consumption at rated power was reduced to about 0,03 % of the fuel consumption.
- Investigations on a heavy-duty diesel engine, where the relationship between lube oil consumption and wear on the top ring as well as on the liner at the ring reversal point was determined by radio nuclide technology. Starting from the standard piston bore interface, the cylinder liner surface was optimised by the honing process in the first development step. In a second step the lube oil consumption was further reduced with a plasma coated cylinder liner. The objective of the engine tests was the reduction of the oil consumption to a value of 0,025 % to 0,05 % of fuel consumption with the same or even better wear rates at the piston top ring and the cylinder liner. The target for the lube oil consumption at rated power was already reached with the first development step of the optimised liner honing. The lube oil consumption was about 0,03 % of fuel consumption. The potential of plasma coatings was demonstrated with again lower oil consumption to a value of about 0,02 % of fuel consumption at rated power. Furthermore it was shown, that plasma liner coatings on cylinder liner surfaces are functioning under heavy duty engine loads.

For an oil-free cylinder head four concepts have been developed. Two concepts for the electromagnetic, one for the linear motor and one for the electro-hydraulic valve actuation. On the electromagnetic valve-train system one concept features the actuators inside the cylinder head whereas on the other concept the actuators are pre-assembled and attached to the modular head using an actuator carrier. The cylinder head for the linear motor valve actuation is a one piece design with the actuators mounted directly on the head. This cylinder head can be very compact as there are no valve springs needed. For the electro-hydraulic valve actuation again a modular design was chosen, where the actuator carrier, which includes the oil supply, is mounted onto the oil-free head.

For the development of un-lubricated valve guides within an oil-free cylinder head a literature research was done to identify coating technologies that can be used for the substitution of oil as a lubricant. Friction and wear behaviour of different combinations of valve guide materials and valve stem coatings were investigated with a pin-on-disc test rig at temperatures of 250 °C and 400 °C. The selected valve guide materials are already used in series production engines without failure. At 250 °C the combination of a standard valve guide powder metallurgy steel material with a chromium or with a DLC coating withstood the tests at a normal force of 20 N for a period of 2 hours. Wear mainly took place on the valve guide material. The DLC coating provided lower wear rates and lower friction coefficients. At 400 °C none of the investigated combinations could sustain the loads during testing. They all failed due to excessive adhesive wear of the valve guide material. This was because dry friction is a much harder condition than starved lubrication, which occurs in current engines. Since the temperature was identified as a critical factor, design of the valve guides should be adjusted to cool the contact point between valve stem and guide.

WP 8: Synthesis – Design optimisation for friction minimisation and lube oil elimination in gears and engines

Within WP 8 all the results, which were achieved in the former work-packages, are synthesized. All the different advancements in the field of design optimisation, material and coating technology optimisation, friction optimisation and lubrication optimisation are merged and the most promising combinations are figured out. The work-package was finished in December 2005, the final report is available on the project's web-page (Final report WP 8).

Referring to oil-free transmissions one promising combination are gears with an optimised geometry regarding low losses, named low-loss gears (as an outcome of WP 1), coated with optimised coatings with a high wear resistance and a low friction coefficient (as an outcome of WP 2 – 4). Thus different tests with coated low-loss gears were done in the FZG gear test rig.

To get an impression of the influence of the gear geometry on the power loss efficiency tests with uncoated low-loss gears in comparison to standard spur gears at a common oil lubrication were done. The tests showed a decrease of power loss of about 40 % at higher speeds of 20 m/s and a decrease of about 70 % at lower speeds below 2 m/s. At a speed of 8,3 m/s the decrease was about 50 % (**Figure 1**).

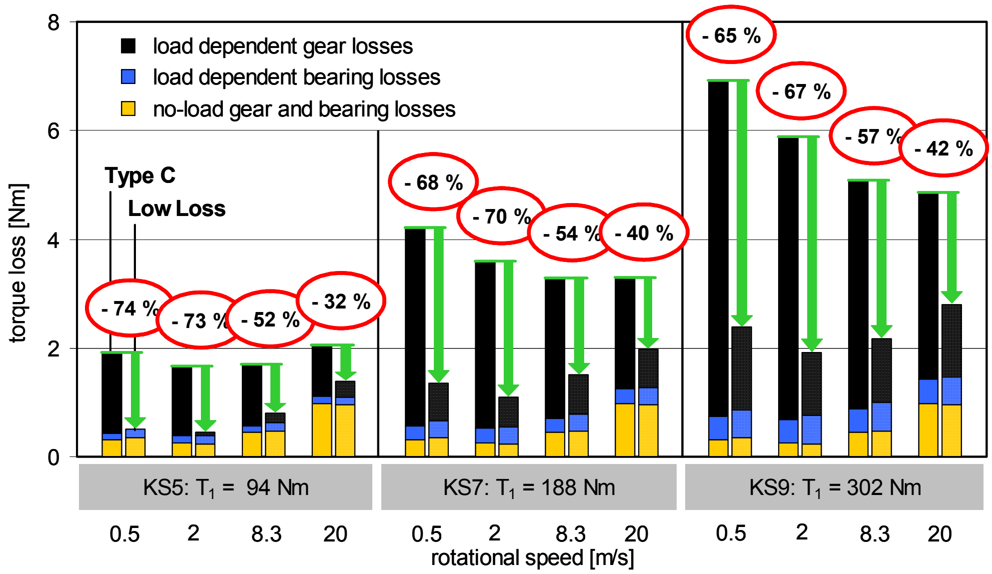


Fig.1. Efficiency tests of low-loss gears in comparison to standard spur gears.

Noise behaviour was investigated with a common dip lubrication up to centre line and with an oil / air lubrication with uncoated low-loss gears in comparison to standard spur gears. Total noise level of the low-loss gears is a little bit higher compared to the total noise level of standard spur gears. The maximum excitation level of the low-loss gears is higher compared to standard spur gears. The highest maximum excitation level was measured with the low-loss gears combined with an oil-air lubrication. However there is no decisive difference in total noise level between low-loss gears and standard spur gears at typical speeds for practical applications.

For investigations at dry lubrication the low-loss gears were coated with different kinds of coatings as an outcome of WP 3 – 4. The low-loss gears were coated with the coatings Diamor® (IWS), Balinit C® (Balzers) and Dynamant® (IKOS). Tests at a nominal flank pressure of 600 N/mm^2 and at a circumferential speed of 5,56 m/s were done. Coating failure was the limit for the test end. The result was that lifetime increased with the low-loss gears compared to the standard gears for each coating. However the highest lifetime by far was achieved with the low-loss gears coated with the coating Diamor®. With this combination the lifetime of the low-loss gears was 17 times higher compared to the lifetime of the standard gears. The average lifetime of that combination is about 7,8 million load-cycles. The conclusion is, that applications with coated low-loss gears at dry lubrication are possible at lower loads and limited lifetime.

One aim of WP 2 was the development of multilayer coatings for water lubrication. The advantage of water lubrication compared to dry lubrication is a better cooling of the gears and therefore problems with too high gear bulk temperatures are avoided. Thus tests with water lubricated gears, coated with a multilayer coating as an outcome of WP 2, were done. Nominal flank pressure was at 600 N/mm^2 and circumferential speed at 5,56 m/s. Coating failure was the limit for the test end. Lifetime of the coated water lubricated gears was about 1,6 million load-cycles. Thus applications of water lubricated coated low-loss gears are possible at lower loads and limited lifetime.

Referring to oil-free or oil lifetime filled engines the most promising combinations are figured out by AVL Graz. The synthesis referring to engines is based on the results of WP 1.2 and WP 7.

Project co-operation

In general there were three main components of the management structure, the Project management and co-ordination, the Steering committee and the Project core group.

The project management was taken over by Germany's IAG, VDMA. VDMA acted as a co-ordinator and interface between the European Commission, the co-operating associations FMS, Magosz, SST and AIA, the SME partners and the RTD-performers. For the technical co-ordination VDMA was supported by the RTD-performer TUM.

The Steering committee was formed by one representative of each participating IAG and by representatives of the SMEs. The Steering committee was responsible for reviewing and controlling the good progress of the project and to help the Project manager to solve any issues or conflicts. The Steering committee met twice a year or if one of the partners called for an extra meeting.

The Project core group played the key role for the technical management of the project. This group of experts of especially interested SMEs watched over the project very intensively and the SMEs were directly involved in the defined work-packages. They guided the project in terms of content, used the results on-line and steered the project's plans for exploitation and dissemination of knowledge. The Core group met twice a year.

The respective work-packages were performed by the RTD-performers. The RTD performers co-operated closely with the SME in the Core group and regularly submited reports there. They exchanged the necessary project results among themselves co-ordinated by VDMA and TUM. The institutes were responsible for the content of seminars and workshops for the dissemination of results.

Besides the periodic meetings twice a year, 3 months reports regarding the continuous progress of the project were prepared. The distribution of the information was handled through the project's web server.

For a wide exploitation and dissemination of the results different workshops, seminars and meetings were held for the whole European industry and scientific community. In October 2005 a symposium will be held together with the COST 532 action in Porto, Portugal with a half day session on "Oil-free powertrain". In November 2005 the project's progress will be presented at a conference of the FVA in Würzburg, Germany.

Till now the following meetings took place:

- Kick-Off Meeting, 18. - 19.11.2002, at FMS, Vienna
- Progress meeting, 12. - 13.05.2003, at SST, Prague
- Progress meeting, 24. - 25.11.2003, at TUD, Dresden
- Mid-term meeting, 06. – 07.05.2004 at EU Commission, Brussels
- Progress meeting, 02. – 03.06.2004 at VDMA, Frankfurt
- Progress meeting, 22.- 23.11.2004 at SST, Prague
- Progress meeting, 23.- 24.05.2005 at TUM, Garching
- Final project meeting, 07. – 08.11.2005 at FMS, Vienna

Planned or achieved industrial improvements in commercial use

The European automotive engineering industry (OEM and suppliers) has a decisive influence on the development of the whole European economy. In the EU more than 3 million people work somewhere along the whole automobile value added chain, approximately 1,7 million of these in the components supply industry. The supply industry is dominated by SMEs, SMEs produce nearly 90% of all parts. A reduction of 20% of the lubricants in car powertrains will result in a saving of 500000 tons/year of used lubricants in Europe. SMEs played the key role within the project and therefore a success strengthens the European SMEs. At the same time a success of the field of the PR-effective automobile technology will radiate positive effects to the other fields of application in the machines and equipment sector.

Already in commercial use is the developed DLC-coating Diamor®. The optimised gear geometry (Outcome of WP 1) was manufactured and different experimental tests were done. Industry is very interested in this kind of gear geometry and is doing further investigations with these gears for their own. This could be a first step for a future commercial use in series production.

Publications were project results are reported

1. VDMA: 3 months report (February 2003) – Oil-free Powertrain, 14 pages
2. VDMA: 3 months report (May 2003) – Oil-free Powertrain, 14 pages
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4. VDMA: 3 months report (August 2003) – Oil-free Powertrain, 14 pages
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8. VDMA: 3 months report (February 2004) – Oil-free Powertrain, 13 pages
9. Martens S., Weihnacht V., Berger L.-M., Zieris R., Schulz I., Kleemann C.: Final report WP 3.1: Ceramic coatings, March 2004, 43 pages
10. VDMA: Mid-term report (April 2004) – Oil-free Powertrain, 51 pages
11. Grossl A.: Final report WP 5: Phase Transition Lubrication, June 2004, 65 pages
12. VDMA: VDMA-Euro-Newsletter, Edition No. 15, 04.06.2004
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15. Diesselberg M., Stock H.-R., Zoch H.-W.: Multilayer Coatings, Proceedings of the COST 532 Symposium, 18. - 20.Oct.2004, Ghent, Belgium, p. 234 - 239
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18. Höhn B.-R., Michaelis K., Grossl A.: Phase Transition Lubrication, Proceedings of the COST 532 Symposium, 18. - 20.Oct.2004, Ghent, Belgium, p. 259 - 268
19. Höhn B.-R., Michaelis K., Otto P.: Minimised Liquid Lube Quantity, Proceedings of the COST 532 Symposium, 18. - 20.Oct.2004, Ghent, Belgium, p. 269 - 278

20. Haslinger R., Herbst H.: Reduction of Piston–Liner Oil Consumption & Oil Free Cylinder Head, Proceedings of the COST 532 Symposium, 18. - 20.Oct.2004, Ghent, Belgium, p. 279 - 289
21. VDMA: 2nd year progress report, November 2004, 36 pages
22. Martens S., Mothes M., Lehmann D.: Final report WP 4: Solid lubricants, December 2004, 38 pages
23. VDMA: 3 months report (February 2005) – Oil-free Powertrain, 13 pages
24. Martens S., Weihnacht V., Berger L.-M., Zieris R.: Final report WP 3.2: Ceramic coated gear wheels, February 2005, 33 pages
25. VDMA: 3 months report (May 2005) – Oil-free Powertrain, 13 pages
26. Aschaber M., Blaha J., Benediktov A., Haslinger R., Herbst H., Sauerwein U., Xin J.: Final report WP 7: Optimisation of piston-liner oil consumption & Oilfree cylinder head, July 2005, 75 pages
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28. Martens S., Weihnacht V., Berger L.-M.: Ceramic coatings, Proceedings of the COST 532 Symposium, 12. – 14.Oct.2005, Porto, Portugal
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TS2 - CHEMOMECHANICAL SYNERGY OF PVD/CVD COATINGS AND ENVIRONMENTALLY FRIENDLY LUBRICANTS IN ROLLING AND SLIDING CONTACTS

Co-ordinator and partners

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Project status and schedule

Running with full funding
Starting and ending dates: 1.01.2003 – 31.12.2006

Project aims

The project was aimed at determining the materials, lubricant and operation factors governing the scuffing resistance and fatigue life of the PVD/CVD coated elements in heavily loaded contacts lubricated with non-toxic lubricants.

The technological objective of the project was to elaborate a new technology for heavy-loaded machine elements, lubricated with ecological oils (e.g. gears, rolling bearings), based on nanostructured coatings, in order to increase the service-life of crucial machine components and reduce environmental hazards. These components are especially important in automotive, manufacturing and energy industry.

Project results

INTRODUCTION

Increasing attention on environmental issues and more restrictive environmental regulations drives the lubricant industry to increase the ecological friendliness of its products. As ecological lubricants one considers lubricants manufactured from renewable resources, which are biodegradable and non-toxic. Today, the main candidate for ecolubricants are oils without toxic extreme-pressure (EP) and anti-wear (AW) additives. The crucial aspect in environmentally friendly lubricants is their effective lubricating action under extreme working conditions. To promote the application of lubricants without environmentally hazardous additives, the authors postulate a new concept**: taking over the function of lubricating additives by thin, hard coatings** deposited on sliding elements.

The coatings used today are known not to interact chemically with lubricants or their additives in the way metals do. This is because lubricants and their active additives were once developed to form protective films, by physical and chemical reactions, not on coatings but on contacting metals (mainly steel). Therefore, we researched the possible synergetic action between the lubricant and coating, with particular emphasis on the ecology of lubricants.

It is well known that the durability of heavy loaded machine components working in non-conformal contacts depends on two phenomena: scuffing of mating elements and rolling contact fatigue – pitting.

THE SELECTION OF COATINGS

Standard single **TiN and CrN coatings** with thickness of about 2 μm was selected and deposited by the arc-vacuum method (PVD technique), at the Surface Engineering Department of ITeE-PIB.

The low friction coatings were selected and deposited by industrial partners. The low friction coatings are based on carbon or molybdenum disulphide. The coatings containing carbon exhibit unique properties, which depend on the deposition method and doped elements. In coatings the carbon is in amorphous form or crystalline form.

The **WC/C (a-C:H:W)** coating is DLC type representing a-C:H:Me group. The coating consisted of an elemental Cr adhesion layer adjacent to the steel substrate, followed by an intermediate transition region consisting of alternating lamellae of Cr and WC, and an outermost W-containing hydrocarbon (a-C:H:W) layer. The composition of the outermost a-C:H:W layer, in atomic concentration is approximately 12% W, 70% C, 15% H, and 3% Ni. The coating was deposited using PVD process (Physical Vapour Deposition) by reactive sputtering in cooperation with Balzers Ltd., Poland.

In cooperation with Blösch AG, Switzerland, **Movic (MoS_2) coating** was deposited by the PVD technique (thickness 2 μm).

In cooperation with Teer Coatings, UK, **MoST (MoS_2/Ti) coating** was deposited. The MoST coating is deposited by DC Magnetron Sputtering using a CFUBMSIP process (closed field unbalanced magnetron sputter ion plating). The coating procedure starts with ion cleaning, followed by a 70 nm Ti layer, a 200 nm MoS_2/Ti multilayer, a 900 nm MoS_2/Ti (non-multilayer) and a last step of 50 nm layer of MoS_2 for coloration.

The comparison of standard and low friction coatings in dry sliding conditions was presented in Fig. 1.

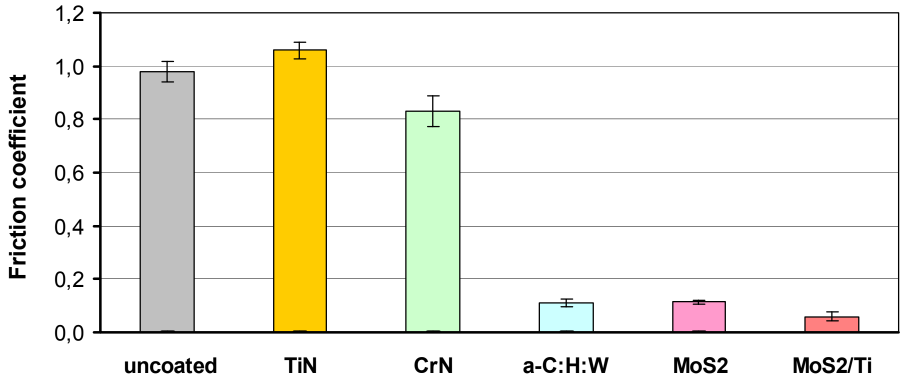


Fig. 1. Comparison of friction coefficient obtained for the tested coatings (ball-on-disk method elaborated in the VAMAS programme and COST 516 research project - alumina ball, load 10 N, sliding velocity 0,1 m/s, debris removal through draught of dry argon).

Usually thin hard coatings do not exhibit satisfactory resistance to fatigue life. Today the most promising are so called duplex coatings. The rolling contact fatigue investigation of duplex TiN, CrN and multilayer CrN-TiN coatings were tested in a co-operation with the Research Centre Bechovice from Czech Republic.

THE SELECTION OF ECOLOGICAL LUBRICANTS

The main candidate for ecolubricants are oils without or with very low content of toxic extreme-pressure (EP) and anti-wear (AW) additives. The crucial aspect in environmentally friendly lubricants is their effective lubricating action under extreme working conditions.

The tribosystems were lubricated with a **mineral base oil** (denoted RL-144/4 with viscosity at 100° - 7.2 mm^2/s), **synthetic base oils** (PAO 8 and PAG 8 - viscosity at 100° was 8 mm^2/s) and **vegetable base oils** (rapeseed and sunflower oils).

Also a commercial hydraulic-gear oil intended for lubrication of high-power transmissions, automotive gear oils of API GL-3, GL-4 and GL-5 performance levels, as well as an eco-oil intended for lubrication of industrial transmissions (ELAS-B) were used. The hydraulic-gear oil and all the automotive gear oils contain toxic AW/EP additives. The eco-oil is a fully formulated vegetable-based, environmentally friendly oil with no AW/EP additives. This oil has been elaborated at ITeE-PIB.

EXPERIMENTAL METHODS

The tribological experiments were performed using five types of tribotesters: ball-on-disk tester (T-10), four-ball tester (T-02), high frequency ball-on-disk tester (T-19), cone-three balls pitting tester (T-03), as well as T-12 gear test rig (FZG type).

The **wear and friction** were measured using T-10 ball-on-disk type testing machine. The stationary steel ball, 10 mm in diameter (made of chrome alloy bearing steel), is pressed from above at the load 80 N against the coated disc rotating in the horizontal plane at the speed of 0.1 m/s. The sliding track radius is 18 mm.

The **wear tests** under high-frequency oscillatory regime were conducted at the load of 200 N, amplitude 1 mm, duration 3600 s., frequency 50 Hz, and ball diameter 10 mm. After a run the wear of the coated disk and steel ball were measured. The balls and disks were made of chrome alloy bearing steel with hardness of 60-65 HRC.

The **scuffing resistance** was measured using the T–02 tester employing four–ball tribosystem in a sliding contact. The scuffing resistance was characterised by the so-called limiting pressure of seizure (p_{oz}). The higher p_{oz} value, the better resistance to scuffing. A very important feature of the T–02 tester is the possibility of continuously increasing load during a run, owing to an independently controlled motor moving the weight along the lever.

The **fatigue life (pitting)** was characterised by the 10% fatigue life L_{10}. The procedure of its determination is presented in IP 300 standard. The value of L_{10} represents the life at which 10% of a large number of test cones, lubricated with the tested lubricant, would be expected to have failed. L_{10} life was determined using the T–03 tester.

The **load-carrying capacity of lubricated gears** was investigated using T-12 Back to Back Gear Test Rig, employing test conditions according to DIN 51 354 and IP 334 standards, procedure A/8,3/90.

The wear scars were analysed using scanning electron microscopy, (SEM), X-ray microanalysis (EDS), glow discharge emission optical spectrometry (GDOES), infrared spectrometry (IR) and air force microscopy (AFM).

MAIN RESULTS AND DISCUSSION

The investigations of chemomechanical synergy between thin hard coatings and lubricants have been performed. This was confirmed by results of tests performed in sliding contacts (method ball-on-disc, T-10 testing machine), in oscillatory motion (ball-on-disk, T-19 tester), as well as in scuffing conditions (four ball apparatus, T-02) and in rolling contact (cone-three balls, T-03).

An enhancement of the knowledge about mechanisms of coating wear and coating-lubricant interaction under different friction conditions (sliding, sliding-rolling, rolling) play an important role in extension of the spectrum of coated machine components.

In sliding conditions for all investigated coatings in ball-on-disk tribosystem the lowest friction coefficient and lowest wear was obtained for oil bases containing polar components – PAG 8 and vegetable ones.

The behaviour of heavy-loaded friction pairs was also determined at high-frequency oscillating movement. Under such conditions wear may be reduced by application of an oil containing additives, mainly AW type, or by using antiwear coatings. Under oscillating sliding movement it is more effective to apply oils with AW additives, which beneficially modify the surface layer, than use antiwear coatings. The presence of AW additive changes the wear mechanism from fatigue to corrosion independently of the presence of the coating. This probably explains the wear reduction for AW additives.

Quite another situation is in the case of lubrication with high performance oils containing EP additives. These additives show corrosion aggressiveness which leads to the creation on the lubricated surface of numerous defects, which are potential nuclei for wear. **a-C:H:W coatings, like in rolling contacts, reduce the negative action of the EP additives, and in this way reduce wear.**

Comprehensive research on scuffing indicates that PVD coatings do display a satisfactory scuffing resistance. The effect of oil coating type on the scuffing resistance for coated steel balls is presented in Fig. 2. The best scuffing characteristics were obtained for standard coatings.

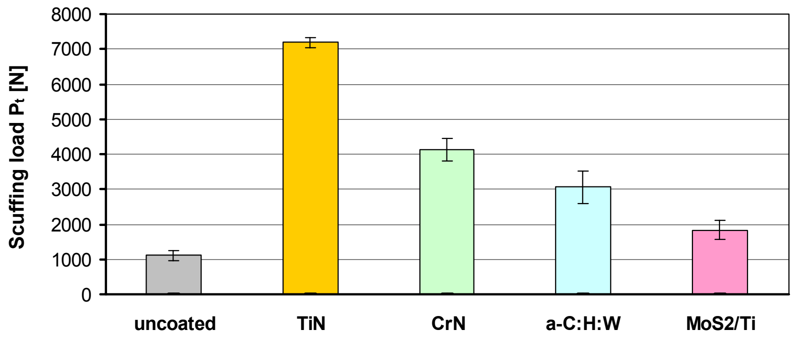


Fig. 2. The effect of oil base type on the scuffing resistance for all a-C:H:W coated steel balls (four-ball sliding test).

So, the mechanism of improving antiscuffing properties by chemical modification of the surface layer of steel specimens (e.g. by sulphur) in the tribochemical way of lubricant-surface interaction, is replaced with the mechanism of antiscuffing action of the coatings, probably by preventing adhesive bonds creation.

The durability of highly loaded friction joints depends not only on the load-carrying capacity but also on the fatigue life (resistance to pitting wear). Comprehensive research on rolling contact fatigue indicates that PVD coatings do not display a satisfactory fatigue life. The fatigue behavior depends on a number of factors and their influence on this phenomenon is very far from clear. The additives influence the rolling contact fatigue of uncoated and coated steel elements is presented in Fig. 3. For mineral base oil the fatigue life for uncoated and a-C:H:W coated cones is similar.

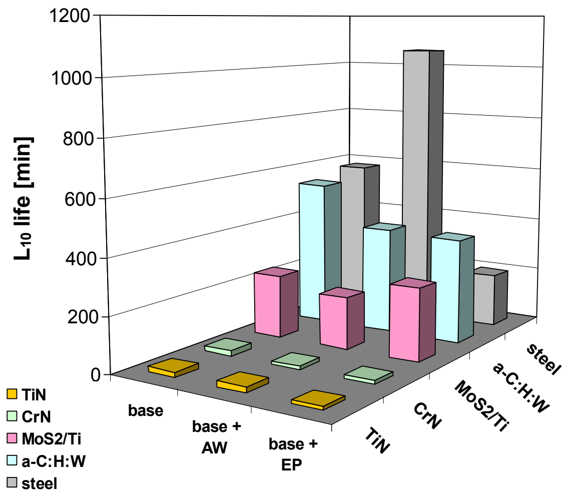


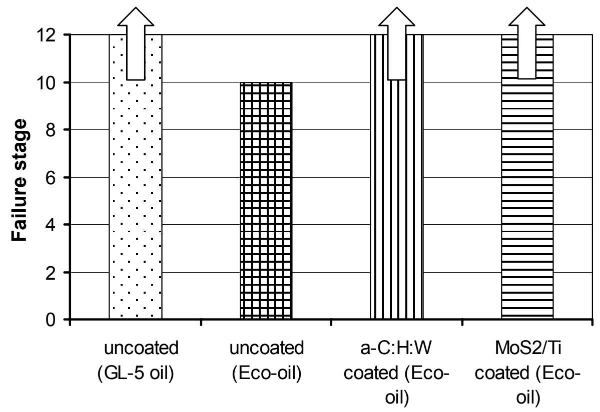
Fig. 3. L_{10} lives for uncoated and coated elements (cones) lubricated with the base oils with lubricating additives.

A content of AW additive in the base oil may extend the time to pitting failure of uncoated tribosystems, but reduces the life of a-C:H:W coated specimens. EP additives significantly reduce the fatigue life for the steel-steel tribosystem, but for the a-C:H:W coated specimens their effect is similar to AW ones.

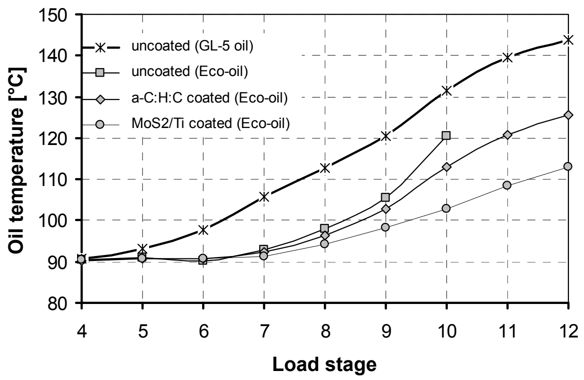
As concerns WC/C coated specimens lubricated with the mineral base oil or ecological oil, they show a much higher fatigue life than usually obtained for the steel-steel tribosystem lubricated with oils containing EP additives. **This confirms the suitability of a-C:H:W coatings for application with heavy-loaded machine components.**

The idea of taking over the functions of AW/EP additives by a thin hard coating, was verified during gear testing the Eco-oil (ELAS-B) using a-C:H:W and MoS_2/Ti coated test gear. The results were compared to the ones obtained for uncoated, steel test gears lubricated by the commercial gear oil which contains toxic AW/EP additives Fig. 4.

a)



b)



c)

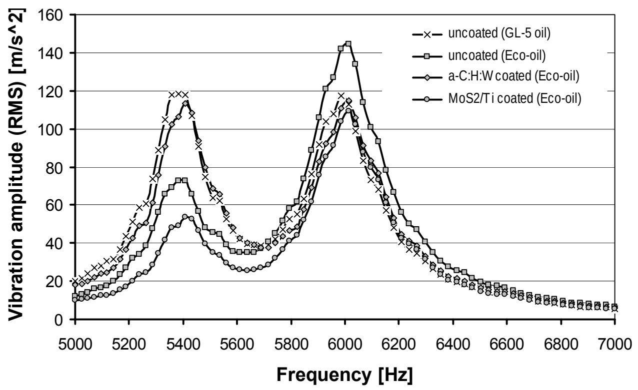


Fig. 4. Results from FZG tests: a) failure stage, b) oil temperature, c) vibration amplitude at the 8^{th} stage, for gears lubricated with commercial high-performance oils with AW/EP additives, and coated and uncoated gears lubricated with ELAS-B vegetable-based oil without AW/EP additives.

The failure load stage obtained for a-C:H:W and MoS_2/Ti coated test gear lubricated by the eco-oil without any AW/EP additives is the same or better than this measure given by commercial gear oils containing toxic AW/EP additives. Furthermore the operating temperature and vibration level were lowered.

So, it has been shown here that **under extreme-pressure conditions low friction coatings can take over the functions of AW/EP additives.**

CONCLUSIONS

The results indicate that surface coatings technologies have great potential to extend the service-life of machine components. It was confirmed by gear tests - PVD coated gears gave much higher resistance to scuffing than usually obtained for the steel-steel tribosystem.

Unfortunately, typical PVD coatings (like TiN) do not exhibit a satisfactory fatigue life. This radically limits the area of application of such coatings to machine components subjected only to scuffing. In situations where resistance to pitting is an important factor (gears, rolling bearings) the application of these coatings is still limited. However, it is possible to optimize the coating-substrate system to increase the resistance to fatigue wear – a satisfactory fatigue behavior was observed for a-C:H:W coating.

The beneficial influence of the presence of a-C:H:W coatings on scuffing prevention and their accompanying satisfactory fatigue-preventive behavior imply a possibility for their application with heavy-loaded machine components.

The tribological results were explained on the basis of chemomechanical interactions between thin hard coatings deposited on heavy-loaded machine elements and lubricants.

Additionally, the results indicate that the presence of thin coatings on the surface of machine components gives a possibility of eliminating or reducing the content of toxic AW/EP additives in lubricating oils, as well as using ecological oils made of renewable resources, without any risk of a scuffing failure.

On the basis of the research performed so far, it is apparent that the scuffing resistance can be improved by thin coatings deposited on the surface of machine components, even without the application of active additives in lubricants. However, a factor limiting the scope of application of the coatings is their poor performance under conditions of cyclic contact stress, which leads to accelerated fatigue failures (pitting).

Industrial improvements in commercial use

A new technology of manufacturing of steel heavy-loaded machine components (e.g. gears) covered with nanostructured coatings which increase the service life of components and allow lubricating with environmentally friendly oils. This will increase the reliability of machines and reduce pollution.

Project co-operation

1. The expertise, selection and deposition of low friction coatings for application in heavy-loaded friction joints working under cyclic stress regime is realised in a co-operation with Balzers - an industrial partner from Poland, Blösch AG and Teer Coatings Ltd. - industrial partners from Switzerland and UK respectively.

2. In 2-29 April 2005 Tribology Department of ITeE-PIB hosted Dr. Krešimir Grilec from Faculty of Mechanical Engineering and Naval Architecture Zagreb, Croatia in frame of Short Term Scientific Mission (reference code: COST-STSM-532-01448).
3. The rolling contact fatigue investigation of duplex coatings in a co-operation with Research Centre Bechovice from Czech Republic.
4. The collaboration between partners have been discussed and dissemination of the results were performed during the following meetings, symposiums and conferences:

- 1st MC meeting, 22 March 2002, Brussels (Belgium),
- 2nd MC meeting, 8 Novemeber 2002, Lyon (France),
- 3rd MC meeting and Kick-off meeting, 2-3 October 2003, Radom (Poland),
- 14th International Colloquium Tribology, 13-15 January 2004, Esslingen (Germany),
- Working Group meeting, 19-20 February 2004, Brussels (Belgium),
- 11th Nordic Symposium on Tribology NORTRIB, 1-5 June 2004, Tromso, Harstad, Hurtigruten (Norway),
- 4th MC meeting, 31 May 2004, Tromso (Norway),
- VTI & COST Symposium, 18-19 October 2004, Ghent (Belgium),
- 5th MC meeting and Working Group meeting, 17-18 February 2005, Praha (Czech Republic),
- 25th IRG-OECD meeting, 13-14 June 2005, Uppsala University (Sweden),
- III World Tribology Congress, 12-16 September 2005, Washington (USA),
- 5th International Conference "The Coatings", 5-7 October, 2005, Kallithea - Chalkidiki (Greece),
- Working Group meeting, 20-21 April, 2006, Dubrovnik (Croatia),
- Working Group meeting, 2-3 November, 2006, Uppsala (Sweden).

5. In co-operation with COST partners the ITeE-PIB formed the consortium for preparing the project (STREP) titled "New technology of multifunctional, nanostructured, coated materials for heavy loaded machine components working with ecological lubricants". Consortium coordinated by Institute for Terotechnology consisted of 12 partners (including 4 industrial) from 8 countries: Technical Research Centre of Finland, University of Ljubljana, Technische Universität München, Fundacion Tekniker, Uppsala University, Ecole Centrale de Lyon, Vlaamse Instelling voor Technologisch Onderzoek, Equipamientos Técnicos Comerciales, Röchling Getriebe, DIARC Technology and NAFTOCHEM.
   Although the proposal did not pass all the evaluation thresholds and was rejected, it was evaluated as good and interesting and that the research areas tackled could have had potential important impact on European industry.
6. In co-operation with COST partners the ITeE-PIB participated in the consortium for preparing the project (Marie Curie Research Training Networks - RTN) titled "Characterisation of wear mechanisms and surface functionalities with regard to life time prediction and quality criteria - from micro to the nano range". (Contract MRTN-CT-2006-035589), acronym WEMESURF.

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TS3 - TRIBOLOGICAL OPTIMISATION OF COATED SURFACES BY DETERMINATION OF STRESS AND STRAIN DISTRIBUTIONS AND CALCULATION OF THE FRACTURE TOUGHNESS

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Project status and schedule

Running with planned funding
Starting and ending dates 1.5.2003-31.8.2007

Project aims

The aim of the project is to further develop and assess by empirical studies a new three dimensional FEM modelling based computer simulation method for the optimisation of the mechanical and geometrical properties of a surface coated with a thin coating and sliding against a counterface. The stress and strain analysis method is combined with experimental scratch testing to characterise and identify coatings and assess their fracture toughness.

Project results

The research work is based on a new analysis method recently developed by (Holmberg et al., 2003) that combines experimental scratch testing with simulation analysis to develop a new quantitative procedure for calculating stress and strain values, determining the principal stresses at which the first failures begin to appear and calculation of the fracture toughness of coatings.

In order to verify and develop the method different type of coatings were deposited for the study. The coatings deposited were two different TiN coatings with two coating thicknesses, two types of diamond-like carbon (DLC) coatings and two types of molybdenum disulphide (MoS_2) coatings. The coatings were deposited with different coating deposition techniques on high speed steel substrates. The basic properties of these coatings were determined for the modelling work.

During the reporting period experimental work, stress modelling and simulation was carried out for the coatings described in *Table 1*.

Stress and strain modelling and stress field computer simulations are carried out in the project. In Finite Element Method (FEM) modelling the ploughing component of friction is integrated in the model while the adhesive component needs to be determined as input value for stress simulations. In the resent work adhesive friction component has been determined for the TiN and DLC coatings in order to further improve the simulation results.

The test samples were prepared of power metallurgical high speed steel (HSS, Böhler S790 ISOMATRIX). The samples were hardened to 7.5 GPa (63 HR_C) and polished to surface roughness R_a 0.01μm prior to deposition. Two different coating types were used in the study, namely commercial titanium nitride (TiN) coating deposited by magnetron sputtering and diamond-like carbon (DLC) coating prepared by plasma enhanced CVD process. The details of the coatings are represented in Table 1.

Table 1. The thickness, hardness and Young's modulus of the coatings used in the tests.

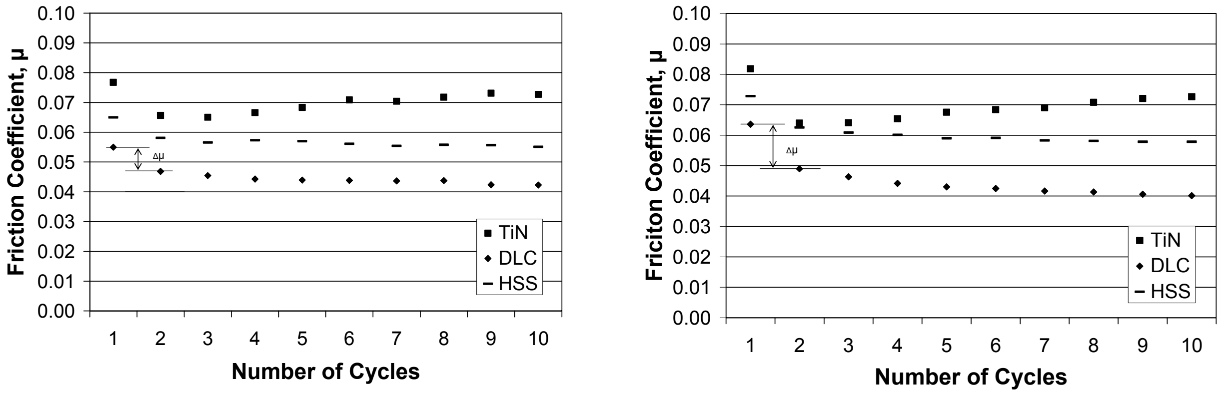
Coating	Deposition method	Coating thickness [μm]	Hardness [GPa]	Young's modulus [GPa]
TiN	magnetron sputtering	1.8	35±10	475±90
DLC	PACVD	0.9	5±0.4	39±2

Multi-pass friction measurements were performed for the coatings and for the uncoated HSS substrate by using the scratch tester in the multi-pass mode performing reciprocating movement. In multi-pass testing a static normal load of 5 and 10 N were applied and the sliding speed was 10 mms^{-1}. The distance of one sliding cycle was 5 mm and the sliding was performed in the same track during the 10 sliding cycles. The friction was measured during multi-pass testing continuously. After the tests the mean value of friction for each sliding pass was calculated and this value represented the friction during one sliding cycle. The tests were performed in normal air at 50 ±5 % RH and 21±2 ^{o}C.

The friction evolution in multi-pass testing for the ten sliding cycles is represented in Fig. 1 for the TiN coated, DLC coated and uncoated samples. The adhesive friction component was determined based on these multi-pass friction test results. The friction coefficient of the first sliding cycle was considered to contain both adhesive and ploughing friction. As the sliding occurred in the same track for the repeated sliding cycles, it was assumed that the friction coefficient measured during the second sliding cycle represented mainly the adhesive friction component. The drop between the first and the second sliding cycles Δμ, was considered to be equal to the ploughing component μ_p of friction as described in the Bowen and Taber model:

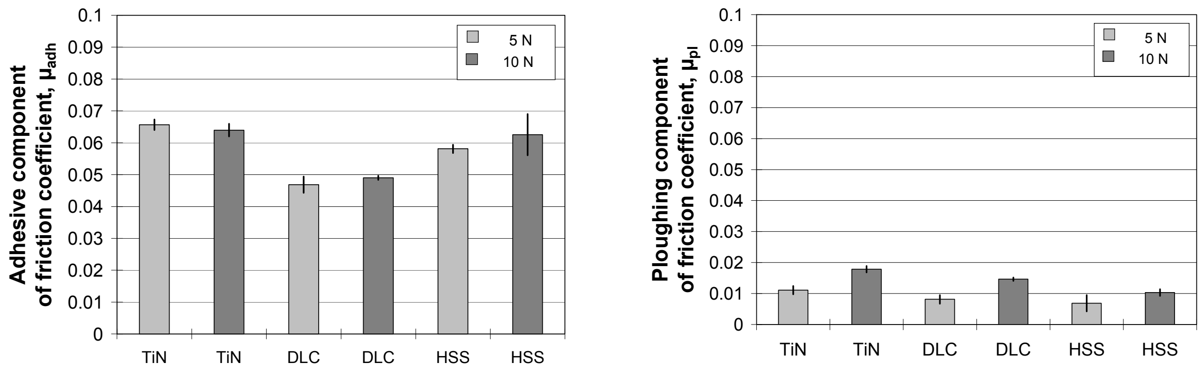
$$\mu = \mu_a + \mu_p \qquad (1)$$

The values determined for the adhesive and ploughing friction of the TiN and DLC coated and the uncoated substrate are presented in Fig. 2. The adhesive friction was the lowest for the DLC coated (0.047) and highest for the TiN coated (0.065) substrate. The change in the adhesive friction as the normal load was varied was within the scatter limits in all cases. The ploughing friction presented clearly lower values compared to adhesive friction and increased as the normal load was increased from 5 to 10 N. The dimensions of the wear scar were measured after the test and the width of the wear scar changed from 0.032 to 0.049 mm and the depth of the wear scar from 0.33 to 0.83 μm as the normal load was increased for 5 to 10 N.



(a) (b)

Fig. 1. The friction values measured in the multi-pass tests with (a) 5 N normal load and (b) 10 N normal load for ten sliding cycles. Sliding speed was 10 mms^{-1} and sliding distance/cycle 5 mm.



(a) (b)

Fig. 2. (a) The adhesive component of friction coefficient and (b) ploughing component of friction coefficient determined from the friction data collected in multi-pass sliding tests.

When the adhesive friction component was calculated based on the results of multi-pass testing, the adhesive friction turned out to be the main constituent of friction coefficient, being 0.065 for the TiN coating, 0.047 for the DLC coating and about 0.060 for the uncoated HSS substrate. The ploughing component increased from 0.011 to 0.017 for the TiN coating, from 0.008 to 0.015 for the DLC coating and from 0.007 to 0.010 for the uncoated HSS substrate as the normal load was increased from 5 to 10 N. In the present study the ploughing components was determined as the difference between the first and the second sliding cycle. However, the ploughing action was probably not completed during the first sliding cycle, since the friction coefficient still decreased for the DLC coated and uncoated substrates. For the TiN coated sample similar effect was not observed, probably due to higher hardness and stiffness of the coating. An other approach would be to determination the ploughing component as the difference between the initial value and the stabilised values of friction as diamond stylus was sliding against coated surface. When this approach was applied for the present data, the ploughing component value was change from 0.011 to 0.019 for the DLC coating and from 0.0095 to 0.015 for the uncoated sample. These values are very close to the values determined for the TiN coating, namely 0.011 to 0.017, which is in better agreement with the actual determination of ploughing friction. In that case the adhesive friction would be lower for the DLC coated and uncoated samples. Since the determination of friction components is not unambiguous, the values determined need be treated as tentative. The adhesive friction data is determined for the TiN (μ_a=0.065) and DLC (μ_a=0.047) coatings from experimental friction measurements will be used as input values in the three dimensional finite element micro-model that simulates the spherical tip sliding on a DLC coated flat substrate with increasing load similar to the conventional scratch test contact.

Numerical FEM analyses were carried out in order to further interpret the development of contact stresses during the sliding contact, and as such evaluate the relative proportions of adhesive and ploughing friction components. The analyses were carried out using the ABAQUS and WARP3D software packages. The friction related results were computed based on the contact area, contact pressure and shear stress calculations. Comparison of numerical and experimental results of friction evolution during scratch testing, containing both the adhesive and ploughing friction, is presented in Figure 3. The adhesive friction, μ_{adh}=0.047, in the analyses, being an input value to the numerical model, is naturally identical. It can be seen that the development of the ploughing component in the numerical approach is quite similar in comparison to experimental friction evolution. The numerical model beginning to drift from the experimental results, when the sliding distance increases. For comparison an other numerical model with different initial adhesive friction values (μ_a=0.1) is also presented in Figure 3. The numerical 3D FEM analyses contain both elastic and plastic deformation and therefore it gives rather realistic friction results compared to analytical approach. The numerical 3D FEM analyses give results closely related to experimental values as long as the coating remains reasonably untouched. As soon as a dense crack field is generated in the deformed coating, relaxation in the surface will occur and the experimental values do not follow the theoretical numerical results.

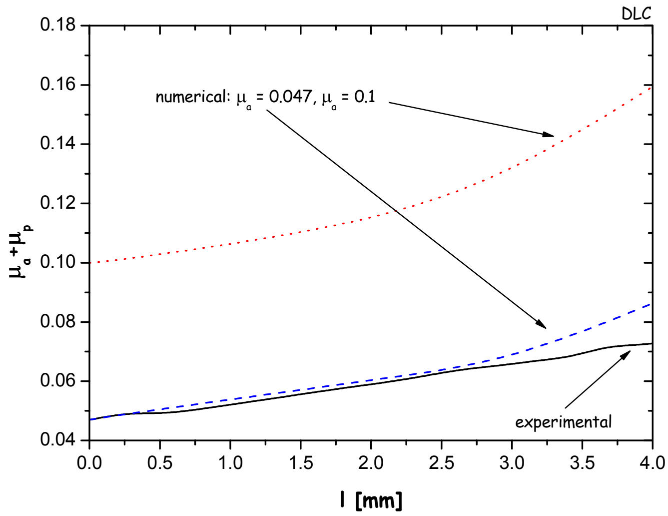
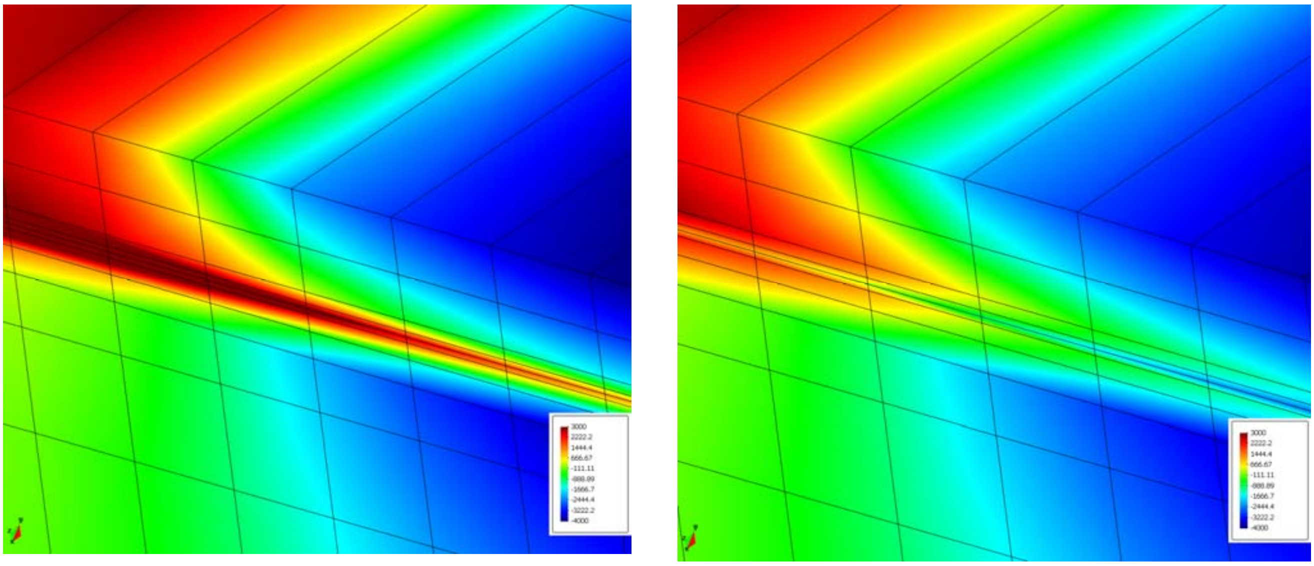


Fig. 3. Comparison of the numerical and experimental results of friction evolution in scratch testing for the DLC coated steel substrate. The graphs contain both the adhesive and ploughing friction. The adhesive friction values, μ_a=0.047 and μ_a=0.1, are used as input values to the numerical model.

Bond layer model was developed to describe the performance of the coated system consisting of more the one layer. In this case an intermediate layer and the coating layer were modelled and the stress state generated in the scratching action was simulated. In Figure 4 are examples of the stresses generated when the bond layer is harder or softer that the coating. If the bond layer is hard, high stresses are generated in the bond layer. Whereas with soft bond layer stresses are lower, but higher stains will be generated in the bond layer.



(a) (b)

Fig. 4. The stress field map of the bond layer-coating system with (a) hard bond layer and (b) soft bond layer.

Adhesion model is generated to describe the performance of the coated system as a crack is generated in the interface. Five different cases are modelled, namely no crack, interface crack, through coating to interface crack, interface crack from a density of through coating cracks and density of through coating cracks. Figure 5 represents an example of the stress field generated on a coated system that has a crack in the interface between the substrate and the coating when the system is under load. As can be seen, high tensile stresses are generated in the crack tip areas that act as a driving force for the crack propagation.

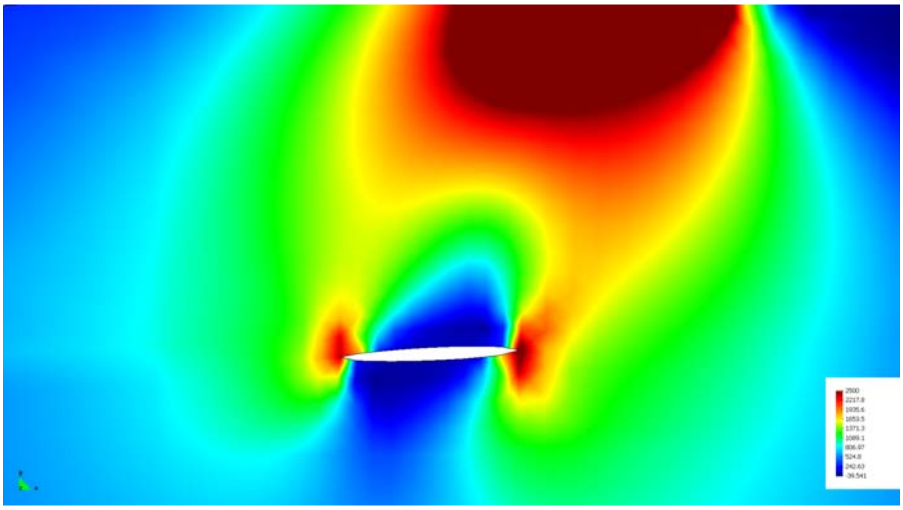


Fig. 5. The stress field map of a coated system with a crack in the interface.

Project co-operation

Three project planning and co-ordination meetings have been held during the reporting period: 2.11.2006 in Uppsala, Sweden, 18.4.2007 in Montreal, Canada and 25.4. in San Diego, USA.

Planned or achieved industrial improvements in commercial use

The plan is to develop a new modelling and scratch testing based quantitative tool for the characterisation and identification of coated surfaces and the determination their fracture toughness. The method can be used to design improved friction and wear properties of surfaces of transmission components and other components in mechanical and electronic products.

Publications were project results are reported

Articles in refereed journals and book chapters:

1. Holmberg, K. & Matthews, A., Tribology of Engineered Surfaces. In: Wear - Materials, Mechanisms and Practice, G. Stachowiak (Ed.), Tribology in Practice Series, John Wiley & Sons, Chichister, UK, 2005, 123-166.
2. Holmberg K, Laukkanen A, Ronkainen H, Wallin K, Varjus S, Koskinen J., Tribological contact analysis of a ball sliding on a flat coated surface, Part I: Modelling stresses and strains. Surface and Coatings Technology, 200 (2006) 3793-3809.
3. Holmberg K, Laukkanen A, Ronkainen H, Wallin K, Varjus S, Koskinen J., Tribological contact analysis of a ball sliding on a flat coated surface, Part II: Material deformations, influence of coating thickness and Young's modulus. Surface and Coatings Technology, 200 (2006) 3810-3823.
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5. Holmberg, K., Laukkanen, A., Ronkainen, H. and Wallin, K. Tribological analysis of fracture conditions in thin surface coatings by 3D FEM modelling and stress simulations. Tribology International, 38 (2005) 1035-1049.
6. Ronkainen, H., Laukkanen, A. & Holmberg, K., Friction in a coated surface deformed by a sliding sphere, Submitted to Wear, 2007, 9 p.
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8. Holmberg, K., Ronkainen, H., Laukkanen, A. & Wallin, K., Friction and wear of coated surfaces – scales, modelling and simulation of tribomechanisms, Submitted to Surface and Coatings Technology, 2007, 30 p.

Conference proceedings and other reports:

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1. Geneva, Switzerland
2. Holmberg,K., Laukkanen,A., Ronkainen,H., Wallin,K. & Koskinen,J., Coating fracture measurements by scratch test modelling, Proc. of Mikkeli Int. Industrial Coatings Seminar MIICS-2004, 18-20.3.2004, Mikkeli, Finland, 6 p.
3. Holmberg,K. & Laukkanen,A., Coatings for wear and friction control, Proc. of ISFF4, 26-28.5.2004, Lyon, France, 2 p. (short abstract)
4. Holmberg,K., Laukkanen,A. & Ronkainen,H., Tribological optimisation of coated components by stress modelling and surface fracture assessment, Proc. COST 532 Conf. Superior Friction and Wear Control in Engines and Transmissions, 18-19.10.2004, Ghent, Belgium, 161-170

5. Holmberg,K. & Laukkanen,A., Tribological performance of coated surfaces, Proc. of 14th Congr. Int. Fed. Heat Treatment and Surface Engineering, 26-28.10.2004, Shanghai, China, IFHTSE 14 Congr. Shanghai, China, 20-27
6. Holmberg, K. & Sainio, H. VTT Instrumented Automated Tape Test Device - Users Manual, Version 01.3 /17.1.2005, VTT Industrial Systems, 11 p.
7. Holmberg, K., Ronkainen, H. & Laukkanen, A., Tribological analysis of TiN and DLC coated contacts by 3D FEM stress modelling and frcture toughness determination. Proceedings of NORDTRIB 2006 - Nordic Symposium on Tribology, 6-9.6.2006, Helsingör, Denmark
8. Holmberg, K., Ronkainen, H., Laukkanen, A., Tribological analysis of TiN and DLC coated contacts by 3D FEM stress modelling and fracture toughness determination, VTT Symposium on Applied Materials, 8.6.2006, Otaniemi, Finland, 13 p.
9. Ronkainen H., Holmberg, K. & Laukkanen, A., Coatede surface design by modelling and simulation, Proceedings of MIICS 2006 - Mikkeli International Industrial Coating Seminar, 16-17.3.2006, Mikkeli, Finland
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TS4 - ROLLING AND ROLING-TO-SLIDING CONTACT FAILURE MECHANICS OF DIAMOND LIKE COATINGS

Co-ordinator and partners

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Project status and schedule

Finished.
Starting and ending dates: start July 2003, finish March 2007

Project aims

The proposed project will focus on failure mechanisms of DLC-coated steel and different surface roughness and surface treatment techniques under dry and lubricated rolling and rolling-to-sliding contact conditions. Hard coatings, especially diamond like coatings (DLC) are promising materials to help achieving: operation under poor lubrication conditions, the need for increased transmitted power in gears, or lowering friction and energy consumption. Moreover, bearings and gears with coated raceways and gear flanks are already used and investigated, but the amount of knowledge on possible failure mechanisms, and thus the reliability of DLC-hybrid bearings and gears still limit their broader use. Moreover, there are different surface treatments, presumably well-known, but their industrial implementation and effects caused on the components are sometimes still limited. The project brought new knowledge and understanding of the rolling contact failure mechanisms for different DLC coatings and surface treatments and compared it to conventional steel materials.

Project results

1. Two types of tests were performed: i) real scale shaver test rig with full-scale gear wheel (without teeth produced), i.e. disc-on-disc rolling tests – having different surface roughness and surface

treatments, and ii) model tribological rolling tester for DLC-coated bearing and gear steel surfaces under dray and lubricated conditions.
2. A substantial literature search was performed on investigated topics.
3. Testing machine (CTD-ROL) adoption was performed to achieve the direct friction comparison between the two devices that are used in the project.
4. Many of planned experiments at Halmstad university are perfomed on gear-shaver full-scale machine and the work is finished. In the last period, focus of the experiments was put on the effect of different oils (Figure 1 and 2), but still with the industrially-used case-hardened steel substrates. A clear effect of surface treatments was observed on the friction behaviour (Figure 3). A PhD work was finished in Sweden out of the project results.
5. At the small-scale heavy loaded rolling tester, several substrates were investigated in addition to oils (Figure 4 and 5). The results suggest that presently used industrial substrates are not appropriate for direct deposition of DLC coating without prior modification when used at high loads. Namely, case hardened substrates, with lower hardness than bearing steel, performed poor with the coated surfaces. At low loads, however, the results are much more beneficial when using DLC coatings. In addition, harder 100Cr6 substrate was tested, with and without coating. 100Cr6 is harder than Case Hardened steel. The results suggest much better wear resistance than for the case hardened steel and the results are beneficial for DLC-coated surfaces, in particular in dry conditions (Figure 6). Lubrication did not promote wear resistance of DLC-coated surfaces, obviously due to poor interface compatibility between the oils and coatings, which suggest that better tailoring of the oil-surface interface is needed. However, DLC-coated surfaces were better than non-coated under dry conditions, even at high loads.
6. More analyses are needed to evaluate surface morphologies and detailed wear mechanisms.
7. Industrial improvement was achieved with a clear indication of the effect of different surface and interface preparation. The project results enable more in-expensive and more tailored interface properties with using the different surface roughness, oils and coatings.

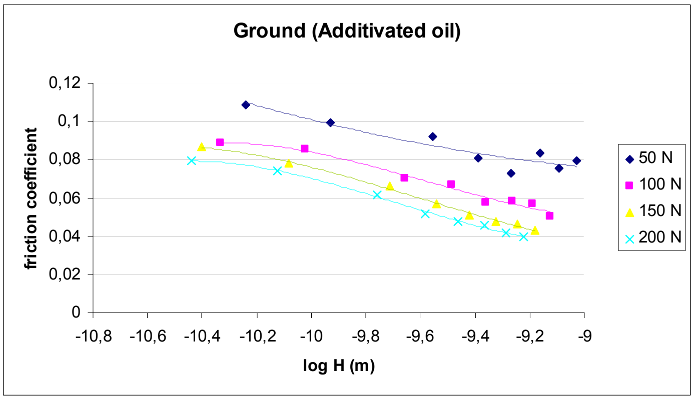

Fig. 1. Friction measurements on ground surface in additivated oil [gear-shaver tester, ground surfaces, additivated oil].

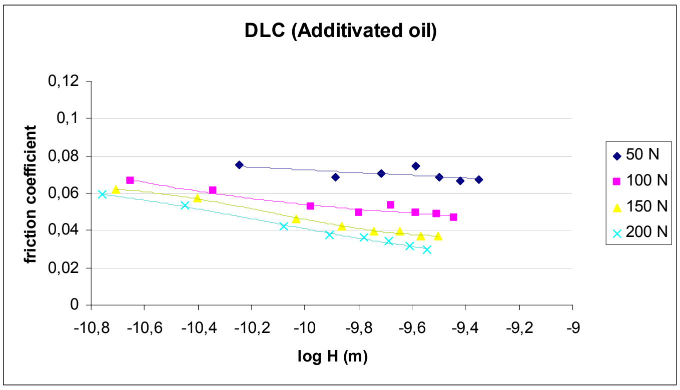

Fig. 2. Friction measurements on DLC-coated surface in additivated oil [gear-shaver tester].

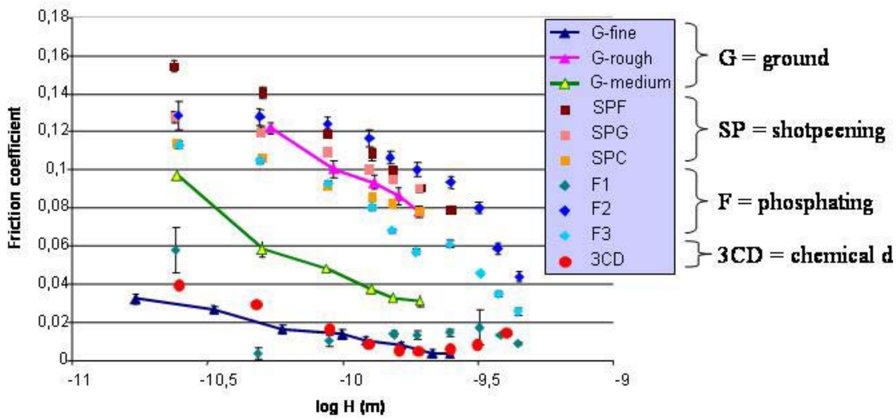

Fig. 3. Friction as a function of different surface treatment (substrate case hardened steel), [gear-shaver tester, Base oil, 225 MPa contact pressure].

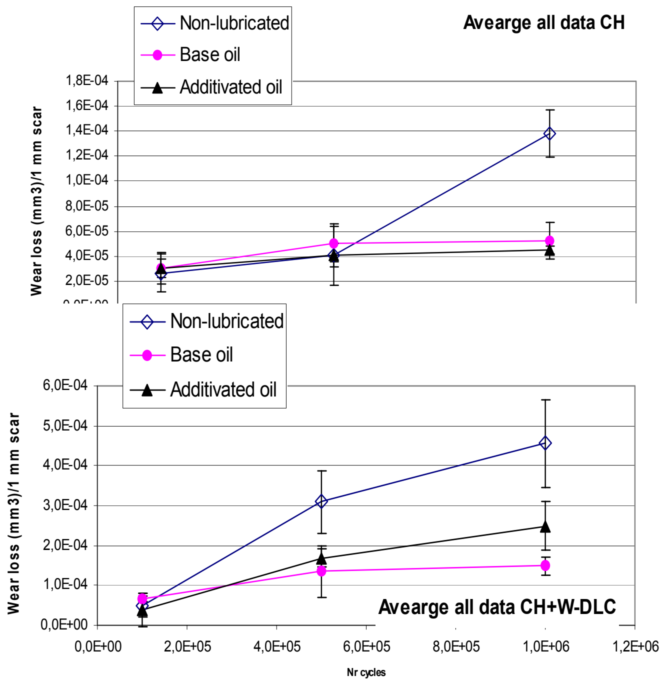

Fig. 4: (A) plain case hardened steel, (B) coated case hardened steel [rolling-wear tester, 1 million cycles, frequency 5 Hz, load 100 N].

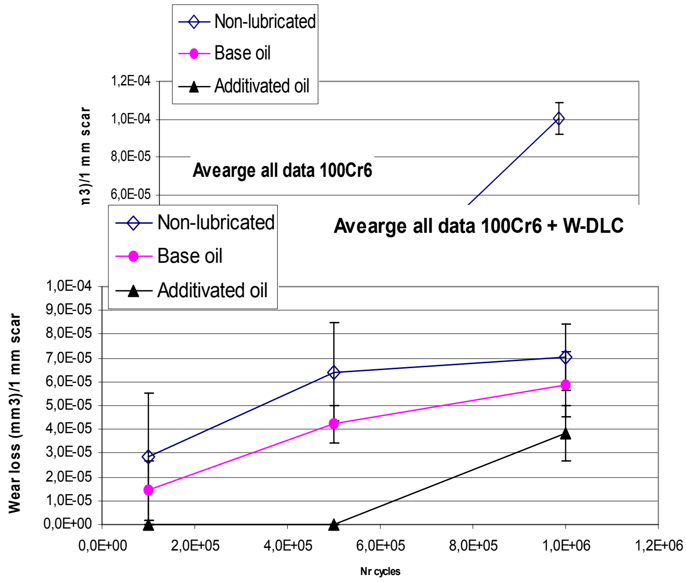

Fig. 5. (A) plain 100Cr6 steel, (B) coated 100Cr6 steel [rolling-wear tester, 1 million cycles, frequency 5 Hz, load 100 N].

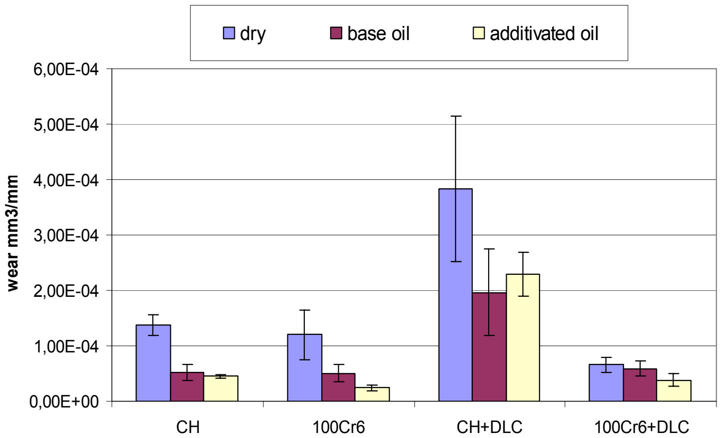

Fig. 6. Overall wear data of different materials/substrates and oils [rolling-wear tester, 1 million cycles, frequency 5 Hz, load 100 N].

Project co-operation

E-mail contact were regularly used between the partners.
A meeting about the detailed future work and coordination was organized on October 3 2004 at Halmstadt University in Sweden.
A meeting about the results and work was organized in Ljubljana in March 2004.
Joint paper was presented at the Leeds-Lyon conference in Leeds, September 2004.
Results were presented and meeting between the partners was held in Ghent, October 2004.
Communication between the partners is done by e-mail throughout the year 2005.
Results were presented and discussed in Dubrovnik, April 2006.
Communication between the partners is done by e-mail throughout the year 2006 and 2007.

Planned or achieved industrial improvements in commercial use

Industrial improvement was achieved with a clear indication of the effect of different surface and interface preparation. The project results enable more in-expensive and more tailored interface properties with using the different surface roughness, oils and coatings.

The results of the effect of DLC coatings, but also other surface modifications (3CD, phosphating) and effect of substrates (through- and case-hardened steels) were gained and implemented to improve the performance of transmission systems at Volvo Cars. New results are directly related to industrial use and enable implementation to production.

The result will be used in Volvo Cars, but also by Volvo Technology for transfer of knowledge to other Volvo companies.

Publications were project results are reported

1. M. Kalin, J. Vižintin, L. Xiao, B.-G. Rosén and P. H. Nilsson, Rolling and rolling-to-sliding behaviour of DLC coated case hardened steel, COST 532 Ghent October 2003
2. L. Xiao, N. Amini, B.-G. Rosén and P. H. Nilsson, A study on the effect of surface topography on rough friction in roller contact, Wear, vol 254, 11 2003, 1162-1169
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4. M. Kalin, J. Vižintin, L. Xiao, B.-G. Rosén and P. H. Nilsson, Rolling and rolling-to-sliding contact failure mechanisms of DLC coatings, COST 532, Brussels, February 2004
5. L. Xiao, S. Björklund and B. G. Rosén, The influence of surface roughness and contact pressure distribution on friction in rolling/sliding contacts, Tromso, Norway, Nordtrib 2004.
6. L. Xiao, S. Björklund and B. G. Rosén, The influence of surface roughness and contact pressure distribution on friction in rolling/sliding contacts, Tribology International Volume 40, Issue 4 , April 2007, Pages 694-698.
7. L. Xiao, B. G Rosén, P. H. Nilsson, M. Kalin and J. Vižintin, Rolling and rolling-to-sliding contact behaviour of DLC coatings, Leeds 2004, proceedings of the 31th Leeds-Lyon Sympoium on Tribology, Tribology and interface engineering series, 48, Amsterdam: Elsevier, 2005, p. 213-220.
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TS5 - ADVANCED NANOSTRUCTURED MATERIALS ON THE BASES OF INTERCALATED SYSTEMS – LAYERED TRANSITION METAL DICHALCOGENIDES (TMD) USING IN HIGH-TECH LUBRICANT DESIGN

Co-ordinator and partners

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Project status and schedule

Finished
Starting and ending dates 01.01.2003-21.03.2007

Project aims

The aim of the project is the study of a new tribological systems include ordered / disordered Transition Metals Dichalcogenides layered nanostructures (solid "nanolubricants") with structural-sensitive tribological properties for new nanostructured lubricating materials design.

In the research project, we present the results of the further studies of the tribological properties of some lubricating compositions with participation of the 2H-MoS_2 and 2H-WS_2 layered nanostructures and compare them with those of the micronic powders of natural molybdenum disulfide.

Project results

Nanotechnologies have found practical application in motor industry in trans-missions, to lessen the designs weight, in converters of energy, for reduction in deterioration and emissions CO_2 in an atmosphere, etc.

The widest spectrum of the application of nanotechnologies is considered in the prognosis of their development by 2010 "Nanotechnology Research Directions" made by the National council on science and technology of the USA [1] and in the concluding remarks by R. A. Andrievsky to its Russian edition [2]. The practical aspects of the use of nanotechnologies in the processing of petroleum and the petroleum chemistry were analyzed in the report by M. Youngk at the 16th annual conference of ELGI [3].

At present, the studies of the application of nanocrystalline TMD in lubricating materials are, in essence, on the initial stage. However practically there are no data concerning development of lubricants with nanopowders additions for application, for example, in motor transport. Layered TMD tribological properties are determined by the common influence of effects of transition into nanostate, their intercalation and layered structures partial disordering, and also an opportunity of Fullerene-like (IF) structures and nanotubes formation. There are no works on the determination of the efficiency of the additives of nanocrystalline layered TMD to plastic lubricants because of their complexity. On the whole, the available, though scanty results testify to the perspectives of the application of various nanostructures of TMD as solid lubricants or their additives to oils and lubricants in order to improve the operational characteristics.

The progress in improvement of lubricant capacity with TMD was achieved in the IPMS by application of CVD method for TMD recently developed, ultrasonic procedures for disperse particles TMD in base lubricant, and original tribology test methods in the static and dynamic mode.

Authors of the project have made before the essential contribution to the theory and technique of CVD syntheses TMD. In the beginning with the help of CVD method pure micron homogenous TMD and intercalated TMD (ITMD) powders were obtained. It is known that the TMD with layered structures of 2H-MCh_2 (M=Nb, Ta, Mo, W; Ch=S, Se) (Table l, Fig.1, 2) and, in the first turn, natural molybdenum disulfide are the efficient solid lubricants possessing a number of advantages, in particular, the low friction coefficients and the possibilities of the operation at high and cryogenic temperatures under conditions of space or vacuum (see, e.g., [4]).

Table 1. Some examples of the results of X-ray studies of nanocrystalline 2H-MoS_2 and 2H-WS_2 powders.

Compounds and numbers of specimens	Parameters of the-unit cells, nm		Average sizes of particles in crystallographic directions, nm	
	a	c	[013]	[110]
2H-MoS_2 [1] *(11)*	0.3136(1)	1.258(1)	2.7(2)	9.4(6)
2H-MoS_2 [1] *(14)*	0.3136(1)	1.257(1)	3.1(2)	11.3(7)
2H-MoS_2 [2] *(8)*	0.31495(9)	1.2520(9)	3.1(5)	8.5(4)
2H-WS_2 [1] *(55)*	0.31367(3)	1.2529(4)	3.9(2)	8.1(3)
2H-WS_2 [1] *(13)*	0.31565(4)	1.2480(5)	3.8(3)	17(1)
2H-MoS_2[3] *(DM-1)*	0.31598(4)	1.2992(2)	61(4)	97(6)
2H-$NbSe_2$	0.3446(2)	1.2607(9)	25.4(8)-	62(2)
2H-WSe_2	0.3286(2)	1.299(1)	4.5(3)	18.7(1.2)
2H-$MoSe_2$	0.32876(1)	1.2923(2)	6.5(4)	36(2)
$Ti_{0,67}WSe_2$	0.3290(2)	1.2980(1)	9,7(9)	29(2)

Notes: space group – $P6_3/mmc$; structural type – 2H-MoS_2 (for 2H-$NbSe_2$ - 2H-TaS_2), 1, 2 – insignificant and essential disorders of the layered nanostructures (by the metal atoms positions), respectively; 3 – natural 2H-MoS_2 after the dispersion of a micron powder by ultrasound action in oil I-20.

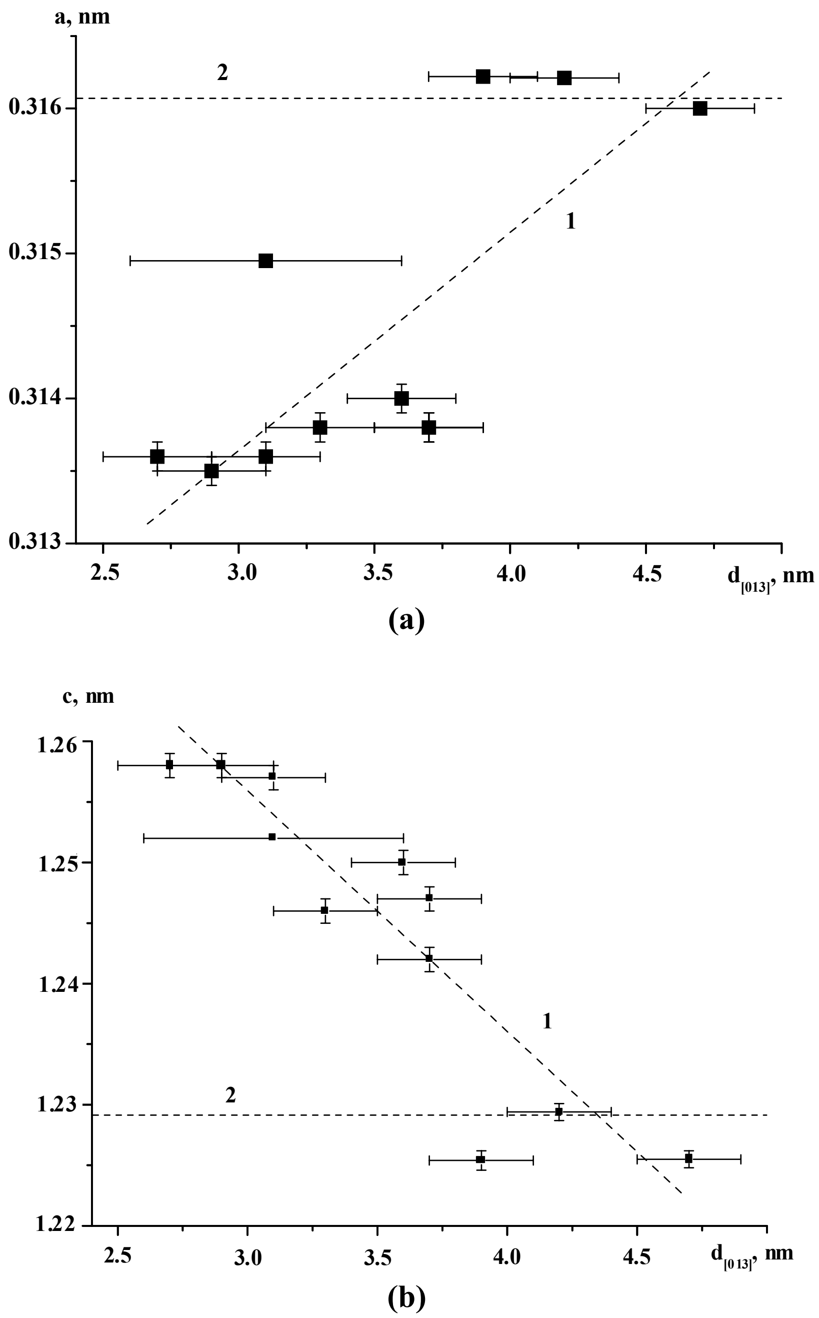
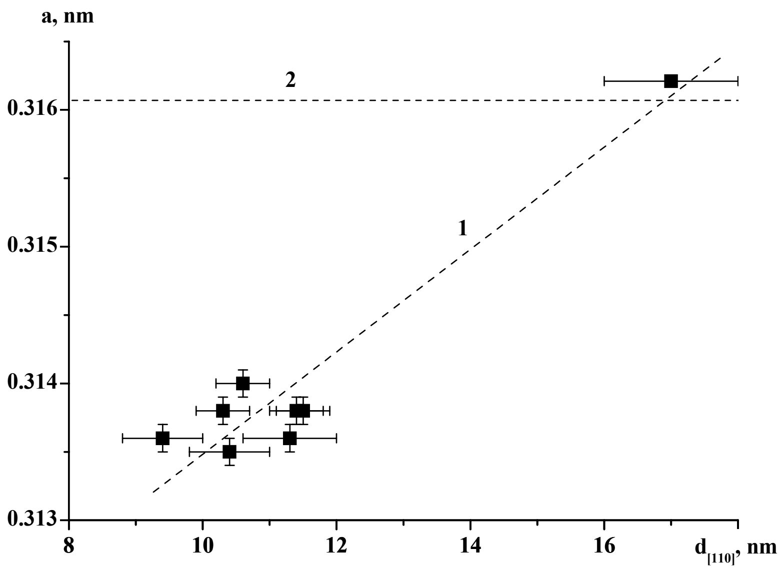
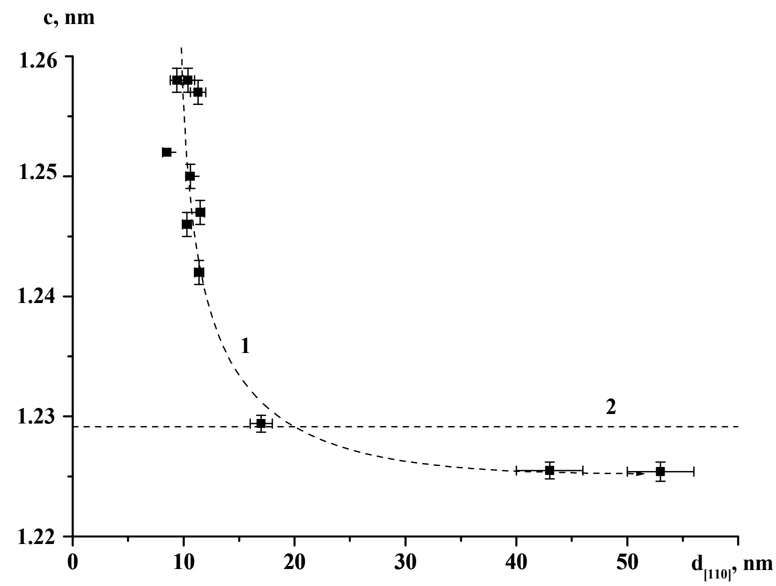


Fig. 1. Dependences of the unit cell parameters a (a), c (b) vs. average dimensions for 2H-MoS_2 nanoparticlesin the crystallographic direction [013], $d_{[013]}$, (1); for well crystallized micron-sized 2H-MoS_2 powders, (2): a = 0.3160 nm, c = 1.2294 nm.



(a)



(b)

Fig. 2. Dependences of the unit cell parameters a (a), c (b) vs. average dimensions for 2H-MoS_2 nanoparticles in the crystallographic direction [110], $d_{[110]}$, (1); for well crystallized micron-sized 2H-MoS_2 powders (2): a = 0.3160 nm,c = 1.2294 nm.

The micron powders of natural molybdenum disulfide, 2H-MoS_2, are applied on the mass scale as solid lubricant additives to oils and lubricants: the assortment of domestic antifriction oils and pastes with fillers includes about 50 names [5]. Recently, the annual application of oils which contain natural 2H-MoS_2 increases by at least 30 times. We also mention the successful experience of the analogous use of the micronic powders of tungsten disulfide [6], molybdenum diselenide [7, 8], and other layered TMD [9-12] and, in some cases, nanocrystalline TMD (see, e.g., [13-14]).

The achievements in the field of nanotechnologies favor the further development of the studies of phenomena and mechanisms of the processes of wear on the nanolevel, which ensures the comparison of the traditional conceptions of lubrication and nanolubrication [15].

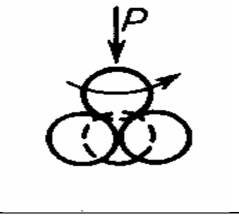
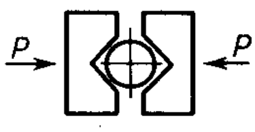
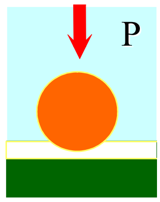
In result of Dr. Kulikov and other authors researches on synthesis by Chemical Vapor Deposition (CVD) for the first time are prepared anisotropic 2H-MeS_2 nanoparticles (Me=W, Mo) with extremely small average sizes (~4 nm and ~8 nm in crystallographic directions [013] that [110], accordingly and are homogeneous and do not contain the admixtures of extraneous phases, including X-ray amorphous ones, or the other ~~kinds~~ types of nanostructures. It was established that average sizes of nanoparticles are regulated at wide rangers: (for crystallographic directions [013] and [110]): 2H-MoS_2 - $d_{[013]}$=2,7(2) - 4,7(2) nm, $d_{[110]}$=8,5(4) - 53(3) nm; 2H-WS_2 - $d_{[013]}$=2,7(2) - 8,0(5) nm, $d_{[110]}$=7,9(4) - 123(8) nm; 2H-$MoSe_2$ - $d_{[013]}$=5,2(3) - 44(3) nm, $d_{[110]}$=25,4(1,6) - 50(3) nm, 2H-WSe_2 - $d_{[013]}$=4,5(3) - 33(2) nm $d_{[110]}$=18,7(1,2) - 82(5) nm. After the execution of the additional annealing (at 830÷920 and 670÷870 K, respectively, the layered nanostructures of 2H-MoS_2 and 2H-WS_2 have a relatively small level of disorder (except for the mentioned cases) and are characterized by a single structural type – 2H-MoS_2. It has been established that the unit cell parameters *a* and *c* for prepared layered nanostructures, as well as their *c*/*a* ratio, correlate with the average dimensions of nanoparticles in the specified directions,. As a rule, exceed the corresponding values for micron-sized 2H-$MoS_2$and 2H-WS_2 powders. In other hand was shown that at ultrasonic dispersion in cavitation regimes in various liquid mediums it have been prepared 2H-MeS_2 nanoparticles (Me=W, Mo) with the average anisotropic sizes 2.7 nm that of 10-20 nm in crystallographic directions [013] that [110], accordingly, and with in part disordered layered structure concerning equilibrium positions of W atoms.

A special attention is attracted by the study of the possibilities to apply the fullerene-like structures of disulfides of tungsten and molybdenum as new solid lubricants - “nanolubricants” (see, e.g., [16-19]). We indicate the comparative estimates of the efficiency of the additives of micronic powders of TMD, nanoparticles of molybdenum trisulfide [20], and nanocrystalline layered TMD [21] to lubricants and antifriction composites [22].

As additives to the lubricants, we used the TMD micronic powders including natural 2H-MoS_2 (DM-1, performance specifications 48-19-133-75), 2H-$MoSe_2$ (performance specifications 88 134-26-80), ITDM and nanocrystalline 2H-MoS_2 and 2H-WS_2. The lubricating compositions on the base of industrial oil I-20 and the layered ultrafine powders and nanostructures of 2H-MoS_2 and 2H-WS_2 (5% mass.) were prepared with the help of their ultrasonic treatment on an improved setup UZVD-6 (the resonance frequency – 18 kHz, specific acoustic power – 0.5÷10 $W \cdot cm^{-2}$, the protecting medium – argon) in cavitation modes. To decrease the destruction of molecules of the oil, its ultrasonic treatment was carried out in concentrated mixtures. Then these mixtures were additionally diluted by the oil. On the whole, the content of oil I-20 after the ultrasonic treatment was less than 10% mass. In the case of the stratification on the long-term storage, the lubricating ability of liquid compositions was restored by the mechanical mixing

The tribotechnical properties of lubricants with the TMD additives were studied under various friction conditions Table. 2: Due to reciprocating sliding with dynamic loading on CATC influence of chemical components TMD and ITMD, type of structure and size are determined easily and carefully.

Table 2. Scheme and conditions of the experiments.

				
	Four Ball Test	FALEX-1	SRV	CATC
loading	200,400,600N	1100N	100N	50N
material	ШХ 15 HRC 60 ∅12,7 mm	SAE 3135 Hb 87-91 ∅ 6.35 mm 1=31.75 mm	ШХ 15 HRC 62	ШХ 15 HRC 62
counterbody		V-prisms AISI 1137 HRC	ШХ 15 HRC 62	Hardmetal ∅5,96mm
test duration	1h	0.12h	1h	0.75h
speed		230±10 min $^{-1}$		0.013 m/s
tangential frequency			50	
tangential amplitude			1mm	8mm
normal frequency; amplitude				25Hz; Δ±5 N

The X-ray studies of the nanocrystalline powders of 2H-MoS_2 and 2H-WS_2 were performed on an automatic powder diffractometer HZG-4A (Cu-K_α-emission). The indication of X-ray diffraction patterns, as well as the correction of the parameters of elementary cells by the method of least squares and structural parameters, were carried out with the help of the own package for computerized structural calculations CSD [23]**.** The mean sizes of anisotropic nanoparticles of 2H-MoS_2 and 2H-WS_2 were determined by the method of analysis of the broadening of X-ray lines (the Scherer formula). In the analysis of the physical broadening functions, the possible effect of distortions of the crystalline structure (the Stokes formula) was taken into account. The X-ray diffraction study of anisotropic nanoparticles was performed with the use of the standard for reflexes [013] and [110], whose intensity allowed us to rather exactly describe the functions of profiles, which is more correct as compared with the data of calculations of the mean sizes for quasispherical particles. The relevant computer calculations of the mean sizes of nanoparticles in crystallographic directions [013] and [110] were carried out with the help of the package of improved programs CSD [23].

Table 3. Results of X-ray studies of nanocrystalline 2H-MoS_2 powders.

Parameters	Annealing temperatures, K			
	870	910	950	1020
Half-width, (direction [013]), rad	0.05004	0.04536	0.04452	0.04440
Average dimension, $d_{[013]}$, nm	3.3(2)	3.6(2)	3.7(2)	3.7(2)
Half-width (direction [110]), rad	0.01722	0.01673	0.01555	0.01541
Average dimension, $d_{[110]}$, nm	10.3(4)	10.6(4)	11.4(4)	11.5(4)
Unit cell parameters, nm: a	0.3138(1)	0.3140(1)	0.3138(1)	0.3138(1)
c	1.246(1)	1.250(1)	1.242(1)	1.247(1)
Cell volume, nm^3	0.1062(2)	0.1067(2)	0.1059(2)	0.1063(2)
Calculated density, $g{\cdot}cm^{-3}$	5.004(9)	4.980(9)	5.0017(8)	4.998(9)
Divergence factor: R (intensity)	0.1204	0.1745	0.1287	0.1156
Texture axis and parameter	[110]; 0.24(2)	[110]; 0.33(2)	[110]; 0.28(2)	[110]; 0.24(4)
Atomic parameters, (x, y, z)	Mo – (1/3, 2/3, ¼) S – (1/3, 2/3, 0.6090(5))	Mo – (1/3, 2/3, ¼) S – (1/3, 2/3, 0.6134(5))	Mo – (1/3, 2/3, ¼) S – (1/3, 2/3, 0.6112(5))	Mo – (1/3, 2/3, ¼) S – (1/3, 2/3, 0.6117(6))

Note: radiation, wavelength – Cu, 0.154185 nm; diffractometer – powder; mode of refinement - full profile; space group - $P6_3/mmc$, structural type - 2H-MoS_2; 2θ = 138.40; sin $\theta/\lambda_{(max)}$ = 0.606; for well crystallized micron-sized 2H-MoS_2 powders with ordered structure: *a* = 0.3160 nm, *c* = 1.2294 nm.

As the objects of studies, we also took the model specimens of lubricants, whose dispersion phase is lithium soaps of 12-hydroxystearic acid (12-HoSt), and the dispersion medium was paraffin liquid with addition of nanocrystalline 2H-MoS_2 and 2H-WS_2. The specimens of lubricants were produced in a reactor equipped by a mechanical mixing unit and heated with the help of a high-temperature lubricating heat-carrier. To produce the lubricants, we use commercial lubricant 12-HoSt. To obtain a soap thickener of lubricants, we applied commercial lithium hydroxide (LGD-3, GOST 8595), the mass part of the basic substance being 53.0% (item 4.4, GOST 8595). As the dispersion medium, we used Paraffin liquid (GOST 3164) with the index of kinematic viscosity equal to 30 mm^2/sec at 50 ^{0}C (GOST 33).

The preparation of specimens was carried out according to the common technology used in the production of lubricants on lithium soaps of 12-hydroxystearic acid [24]. In a digester, we loaded

Paraffin liquid (2/3 of the rated amount), heated up to 75–80 ^{0}C, and added a finely divided 12-HoSt. On the constant mixing, we continued the heating up to 85–90 ^{0}C and added an aqueous solution (10%) of lithium hydroxide (LiOH) by small portions, not admitting a sharp foaming of the reaction mass. Up to100 ^{0}C, the temperature of the mixture was increased slowly. The further rate was 1 degree/min, and the maximum temperature was 210 ^{0}C. Then we carried out the treatment of the reactor contents by the rest (1/3 of the total amount) of paraffin liquid l, decreasing the temperature in a digester to 180–185 ^{0}C. At this temperature, the mass was kept for 30 min. Then we stopped the supply of a hot heat-carrier and cooled the reactor on the continuous mixing up to 40–50 ^{0}C. The further cooling up to ambient temperature was carried out without mixing. In order to homogenate the obtained product, we subjected it to the further mechanical treatment by pressing through narrow (0.3 mm) slits of a laboratory three-roll machine. The mixing of the additives under study was realized at room temperature, and the obtained specimens of the lubricant were repeatedly pressed through slits of a three-roll machine. In one day after the production, the specimens of lubricants were analyzed, and the reproducibility of the obtained lubricating compositions was controlled by theological indices.

The semiliquid lubricants were produced from model specimens of the lithium lubricants with the content of the TMD additives of 3% mass., on the increase of the content of the dispersion medium relative to a thickener by 12-HoSt – 5% mass. In the last case, the content of TMD was 2.2% mass.

In the tests on a FBFM in the range of small loads, nanocrystalline 2H-MoS_2 and 2H-WS_2 have better characteristics as compared with those of commercial micron powders of 2H-MoS_2 and 2H-$MoSe_2$, but approximately on the level of the base lubricant, which is conditioned by an insignificant load-velocity mode. As the load increases, the lubricants with nanocrystalline 2H-MoS_2 and 2H-WS_2 are also characterized by better characteristics as compared with those of the base lubricant and the compositions with micronic powders of 2H-MoS_2 and 2H-$MoSe_2$ (Tables 4, 5).

Table 4. Tribological properties of lithium lubricants with the additives of micronic and nanocrystalline powders of TMD.

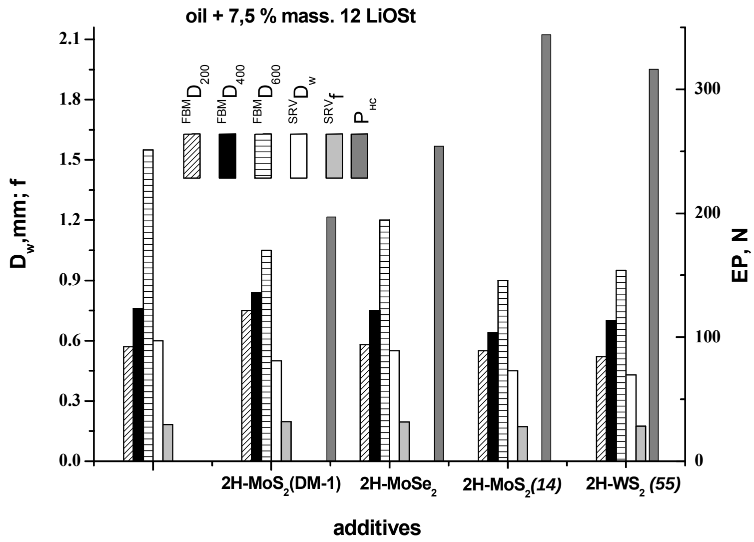
Lubricant composition		FBFM			Falex-1
Dispersion medium, thickener	Additive, 3% mass.	Wear spot diameter, D_w, mm, under load			
		200 N	400 N	600 N	P_{ba}, N
Paraffin liquid + 7.5 % mass. 12 LioSt	-	0.57	0.76	1.55	Welding
	2H-MoS_2 (DM-1)	0.75	0.84	1.05	197
	2H-$MoSe_2$	0.58	0.75	1.20	254
	2H-MoS_2 *(14)*	0.55	0.64	0.90	344
	2H-WS_2 *(55)*	0.52	0.70	0.95	316
Paraffin liquid + 10 % mass. 12 LioSt	-	0.48	0.64	2.10	Welding
	2H-MoS_2 (DM-1)	0.56	0.63	1.20	254
	2H-$MoSe_2$	0.58	0.70	1.20	316
	2H-MoS_2 *(14)*	0.45	0.58	0.85	416
	2H-WS_2 *(55)*	0.42	0.60	0.88	344

Under conditions of the reciprocal motion, the lubricants with the additives of nanocrystalline 2H-MoS_2 and 2H-WS_2 have better characteristics by the index of the wear spot diameter (D_w), than the lubricants with commercial micron powders of 2H-MoS_2 and 2H-$MoSe_2$, but on the level of the data for the base lubricant. The last fact is related to the conditions of the inflow of a lubricant into the friction zone which are more favorable for the base lubricant. On the whole, by the friction coefficient, the lubricants with the additives of nanocrystalline 2H-MoS_2 and 2H-WS_2 have better characteristics, than those of the base lubricant and the lubricants with the additives of commercial micron powders of 2H-MoS_2 and 2H-$MoSe_2$.

In a case of use the additives of commercial micron powders of 2H-MoS_2 and 2H-$MoSe_2$ to oil forecasts increasing resource of efficiency of friction unit into 1.5-2 times.

Additives of commercial micron powders of 2H-MoS_2 and 2H-$MoSe_2$ improve tribological characteristics of bentonitic oil: given oil compositions have better tribological characteristics according to bentonitic oil that produced by foreign firms (Shell, Mobil). Obtained results are evidence of prospect uses of new oil compositions in friction units, that is used in high temperatures (-10-220^{0}C) and temperate speeds (metallurgy industry etc.).

In addition, the obtained data (Table 6) yield that the semiliquid lubricant with the additive of nanocrystalline 2H-WS_2 *(55)* has better antiwear properties as compared with the case of micron powders of natural 2H-MoS_2, but they are practically such as those of the lubricant with nanocrystalline 2H-MoS_2 (*14)*.



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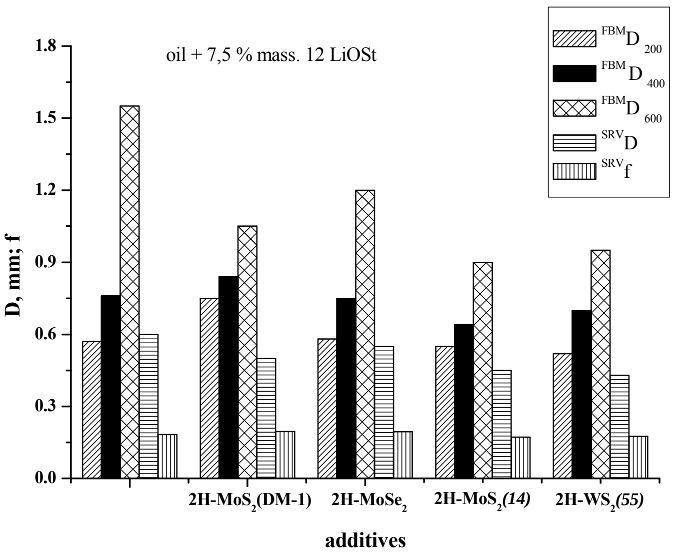


Fig. 3. Tribological properties of lithium oil with the additives of nanocrystalline 2H-MoS$_2$ and 2H-WS$_2$ comparison with micron powders of 2H-MoS$_2$ and 2H-MoSe$_2$ (a, b).

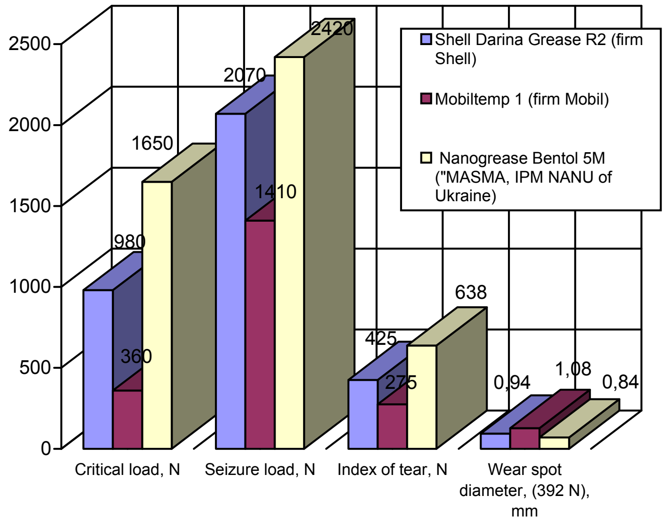


Fig. 4. Tribological characteristics of bentonitic oil.

Table 5. Effects of the additives of micronic and nanocrystalline powders of TMD on antiwear and antifriction properties of lithium lubricants.

Composition of luboil		tribometer SRV			
Dispersion medium, thickener	Additive, 3% mass.	Wear spot diameter, D_w, mm	Friction coefficient		
			steady, f_{st}	minimum, f_{min}	maximum, f_{max}
Paraffin liquid + 7.5 % mass. 12 LioSt	-	0.60	0.183	0.143	0.195
	$2H\text{-}MoS_2$ (DM-1)	0.50	0.196	0.175	0.188
	$2H\text{-}MoSe_2$	0.55	0.195	0.191	0.198
	$2H\text{-}MoS_2$ *(14)*	0.45	0.172	0.172	0.190
	$2H\text{-}WS_2$ *(55)*	0.43	0.175	0.173	0.194
Paraffin liquid + 10 % mass. 12 LioSt	-	0.55	0.185	0.183	0.185
	$2H\text{-}MoS_2$ (DM-1)	0.54	0.185	0.183	0.196
	$2H\text{-}MoSe_2$	0.58	0.190	0.185	0.190
	$2H\text{-}MoS_2$ *(14)*	0.48	0.165	0.182	0.186
	$2H\text{-}WS_2$ *(55)*	0.49	0.175	0.155	0.177

We note that, under similar conditions of the reverse sliding in the medium of oil I-20, larger nanoparticles of $2H\text{-}WSe_2$ have also advantages as compared with nanoparticles of $2H\text{-}MoSe_2$ [21, 23, 25].

Table 6. Tribological characteristics of semiliquid lithium lubricants with the additives of micronic and nanocrystalline powders of TMD.

Lubricants with the additives of TMD	Wear index, μm		Friction force, N	
	Friction modes		Friction modes	
	Quasistatic	Dynamical	Quasistatic	Dynamical
Base lubricant	18.5	39.65	19.86	8.95
2H-MoS_2(*DM-1)*	14.65	34.32	18.05	9.15
2H-MoS_2 *(14)*	13.8	34,25	17.99	9.14
2H-WS_2 *(55)*	11.8	27.9	16.37	7.33

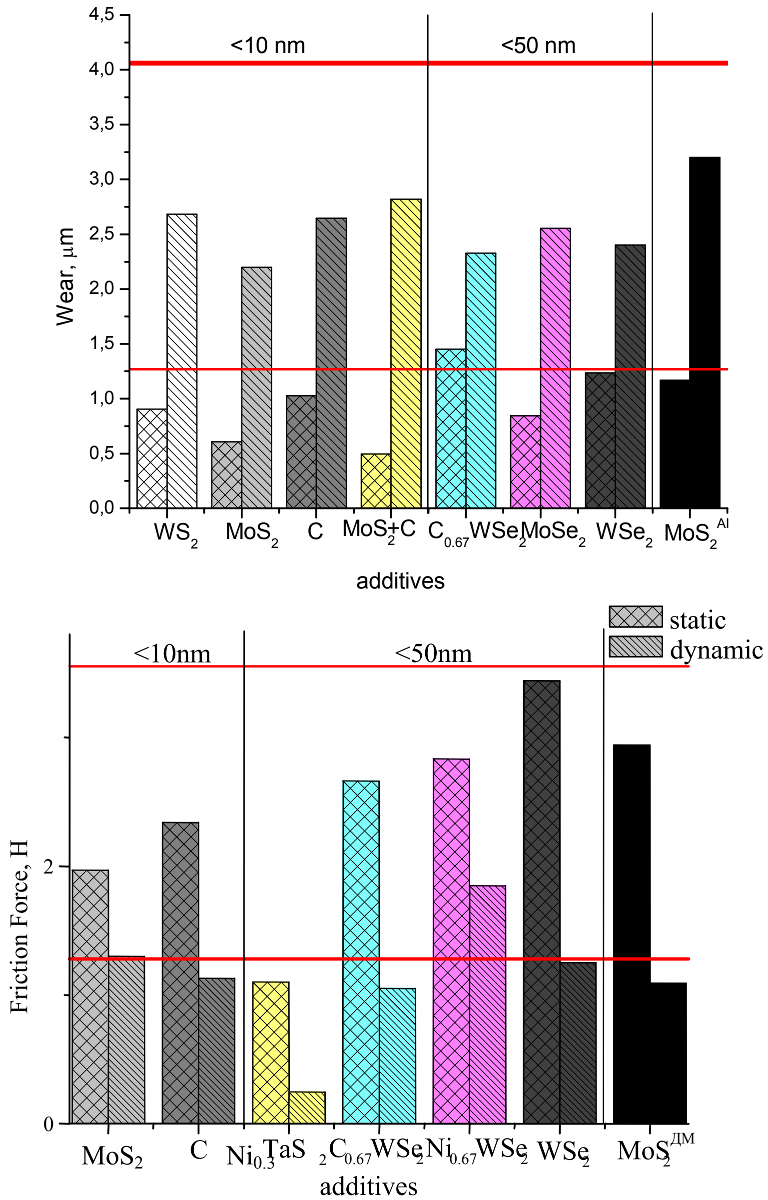


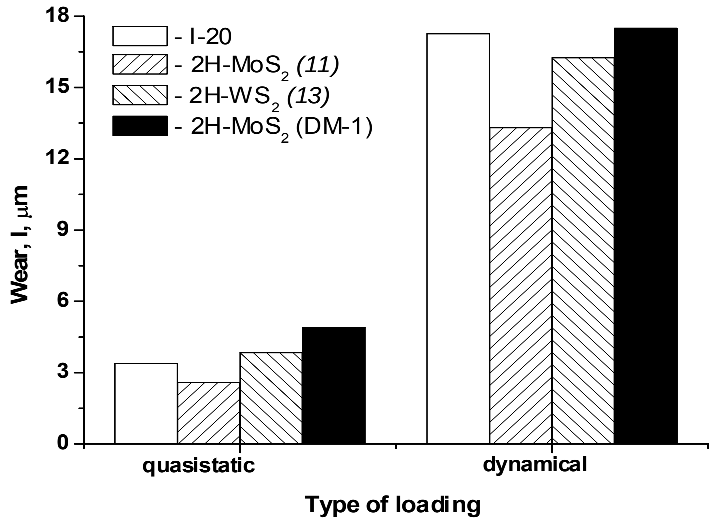
Fig. 5. The tribological properties of lubricant compositions with TDM intercalation compounds additives into base liquid oil.

However, on the reciprocal sliding on a vibrotribometer SRV, a great positive effect is conditioned by the additive of nanocrystalline 2H-MoS_2 *(14),* (Table 5), and, on ATCD, respectively – the additive of nanocrystalline 2H-WS_2 *(55)*, (Table 6), i.e. the action efficiency of an additive depends essentially on the parameters of tests. In this case, under various friction conditions, the lubricants containing the additives of nanocrystalline 2H-MoS_2 *(14)* and 2H-WS_2 *(55)* have much better tribotechnical properties as compared with those of the lubricants with the additives of commercial micron powders of 2H-MoS_2 and 2H-$MoSe_2$. It is assumed that the action efficiency of 2H-MoS_2 in lubricating materials significantly increases with the dispersion of powders. But the analysis of works [26 – 29], in which the effect of the dispersion of particles of 2H-MoS_2 on the tribological properties of lubricating materials is considered, allows us to assert that the available experimental data differ significantly, and the conclusions are not unambiguous. In particular, the effect of the size of only micron particles of 2H-MoS_2 (0.3; 0.7, and 7 μm) was analyzed in works [26 – 29], i.e., a very narrow fraction of micron powders was considered. In the opinion of I. G. Fuks [30], the contradictory results concerning the effect of the dispersion of particles of 2H-MoS_2 on the tribological properties of lubricants are related with the differences in methods of the execution of tests and in the compositions of lubricants which are quite complicated systems.

In this connection, as the base data for the comparative analysis, we chose the tribotechnical characteristics of micron powders of natural 2H-MoS_2 (DM-1, performance specifications 48-19-133-75) dispersed by the ultrasonic action in oil I-20 up to nanocrystalline sizes (Fig. 6).

As compared with the additives of nanocrystalline 2H-$MoSe_2$ and 2H-WSe_2 [21, 23, 25, 31], the introduction of nanocrystalline 2H-MoS_2 (*11)***,** 2H-WS_2 (*13)* with extremely small sizes of nanoparticles (see Table 1), especially in the case of 2H-MoS_2 *(11)*, ensures better tribotechnical characteristics. Thus, the use of nanocrystalline layered TMD with the extremely small sizes of anisotropic nanoparticles leads to a qualitative improvement of operational properties of the tribosystem.It is probable that, in the case of nanocrystalline 2H-MoS_2 and 2H-WS_2 with small sizes of anisotropic nanoparticles, the negative effect of sulfur on the processes of wear is neutralized. In this case, the tribochemical processes of interaction of the TMD additives with the surface of friction couples begin to play a greater role. The last assertion is in agreement with the results concerning the effect of intercalating elements and the composition of nanocrystalline TMD on the structure formation processes in the near-surface layers of friction couples and tribological characteristics [31]. Hence, the action efficiency of 2H-MoS_2, as a solid lubricant additive to the oils and lubricants under study, considerably increases under a significant decrease in the size of anisotropic layered nanoparticles.

By the example of the additives of nanocrystalline powders of 2H-MoS_2 in oil I-20, we studied the effect of mid-size anisotropic nanoparticles on the tribotechnical properties of the compositions with their participation. The obtained data (Table 1, Fig. 2) yield that the mean sizes of nanoparticles of 2H-MoS_2 in direction [013] are correlated with the wear index in the static loading mode, and the sizes in direction [110] – with the wear index in the dynamical mode. On the whole, the less the mean sizes of nanoparticles 2H-MoS_2, the less is the wear level: the best wear indices under static conditions are characteristic of nanoparticles of 2H-MoS_2 *(11)*, under dynamical conditions – 2H-MoS_2 *(8)*.



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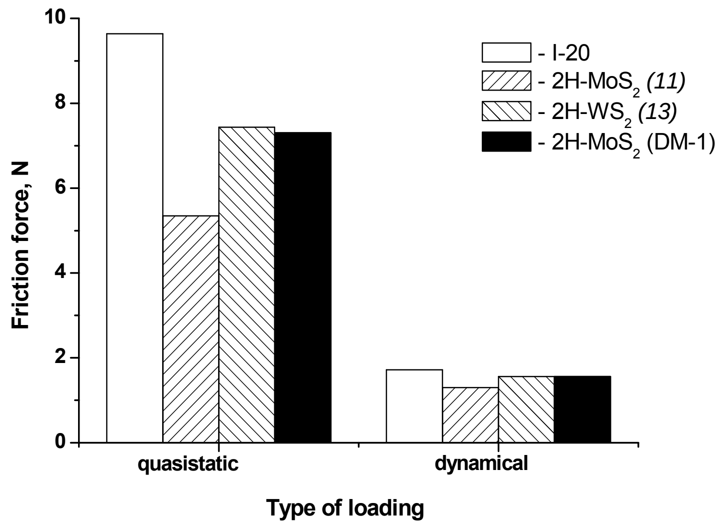
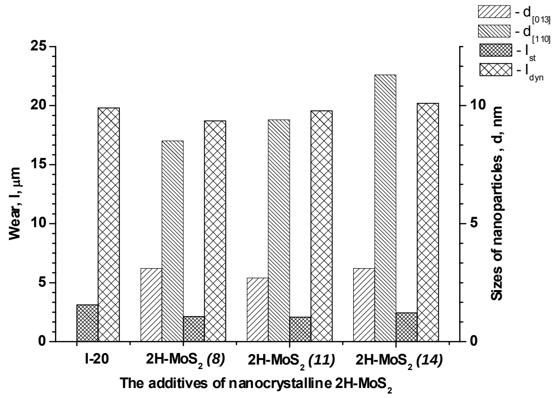


b)

Fig. 6. Tribological characteristics of oil I-20 with the additives of layered nanocrystalline TMD in comparison with the natural molybdenum disulfide under conditions of quasistatic and dynamical loading (a – wear; b – friction force).

Such an approach well explains the significant improvement of the tribotechnical indices of 2H-MoS_2 *(11)*, ($d_{[013]}$=2.7(2) nm; $d_{[110]}$=9.4(6) nm) as compared with those of 2H-WS_2 *(13)*, ($d_{[013]}$=3.8(3) nm; $d_{[110]}$=17(1) nm) for oils*,* as well as their more significant improvement for 2H-WS_2 *(55)*, ($d_{[013]}$=3.9(2) nm; $d_{[110]}$=8.1(3) nm) as compared with 2H-MoS_2 *(14)*, ($d_{[013]}$=3.1(2) nm; $d_{[110]}$=11.3(7) nm) for lubricants. Nevertheless, the least mean sizes of nanoparticles do not always ensure the least losses by friction under the studied conditions. For example, the least value of the friction force in both loading modes is characteristic of nanoparticles of 2H-MoS_2 *(11)*. In addition, the observed differences, especially under dynamical loading conditions, can be related to different levels of the disorder of real nanostructures of 2H-MoS_2. In particular, the disorder of real nanostructures, which is conditioned by the statistical distribution of atoms of the transition metal or chalcogen over equilibrium and nonequilibrium positions, can induce the changes in their reactivity in tribochemical processes. The same factors can affect also the structure formation processes in the near-surface layers of friction couples, as compared with the action of nanostructures possessing a slight disorder. We note that, on the production of lubricating compositions, the ultrasonic treatment of layered nanostructures of 2H-MoS_2 and 2H-WS_2 in the medium of liquid industrial oil I-20 can induce, in the cavitation modes, the further dispersion and disorder of real nanostructures. By the available data, the layered nanostructures of 2H-WS_2 are characterized by a greater stability as compared with that of the nanostructures of 2H-MoS_2 in the processes of ultrasonic treatment in various liquid media. The disorder of the initial real layered nanostructures of TMD and the possibility of their further disorder on friction can enhance the reactivity of nanostructures in the tribochemical processes under their interaction with the surface of friction couples as compared with that of micron powders. The obtained correlations of tribotechnical characteristics with mean sizes of anisotropic nanoparticles of 2H-MoS_2 and 2H-WS_2 (Fig. 6, 7) agree qualitatively with the assumption that the important parameters for the optimization of the tribological characteristics of compositions with participation of nanotubes of WS_2 are the ratio of the radius to the length of nanotubes and the level of their defectiveness [32].



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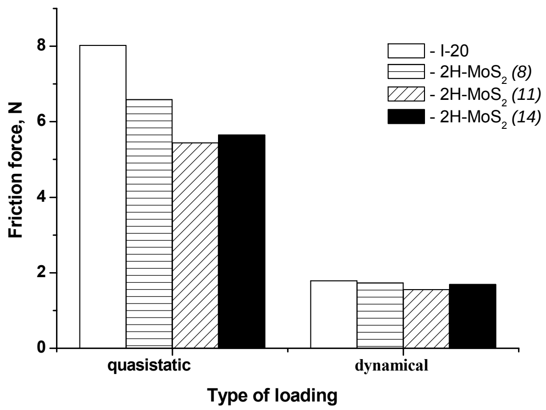


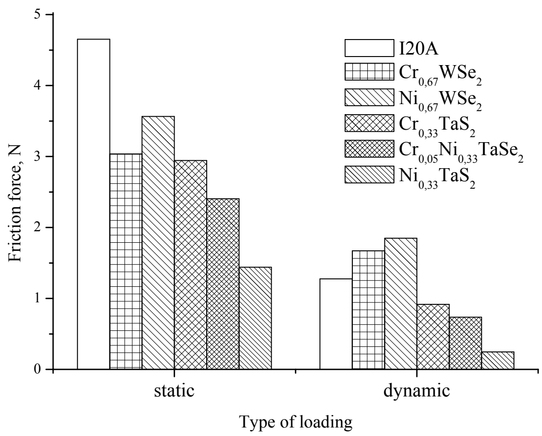
b)

Fig. 7. Tribological characteristics of oil I-20 with the different additives of nanocrystalline molybdenum disulfide for quasistatic and dynamical conditions of loading (a – wear, sizes of nanoparticles; б – friction force).

On the whole, the above-presented results yield that the use of nanocrystalline layered 2H-MoS_2 and 2H-WS_2, as the additives to industrial oils (the I-20 type), improves significantly the tribotechnical properties of compositions in the quasistationary and dynamical loading modes: there occur the significant decrease in the friction force (by a factor of 1.5) and the increase in the wear resistance (by a factor of 1.5–2) as compared with the data for micron powders of natural molybdenum disulfide.

It was also investigated influence of structure type and intercalated elements on tribology behaviors. It is established ris x , that intercalation by Ni, in comparison with Cr, reduces linear wear**,** both for systems WSe_2, and for TaS_2, that will be coordinated to known researches on introduction of Ni ultradisperse powder at greasing for reduction of wear of pair friction. The least linear wear was provided with a composition with intercalate $Ni_{0,67}WSe_2$ (structural type 2H-MoS_2) addition, at transition to structural type 2H-TaS_2 the linear wear increases. Introduction of $Ni_{0,33}TaS_2$ intercalate provides in force friction sharp decrease (almost in 3 times) in comparison with base oil. Introduction $Cr_{0,33}TaS_2$ also reduces force of friction, but is less effective.

Determining role in force of friction decrease in chemical properties of nickel as replacement of small amount Ni on Cr results friction in increase of force will play. Essential increase of force friction occurs at full Ni replacement on Cr. Thus, deterioration at introduction of additives on basis TaS_2 very high, that is entirely explained by presence of sulfur. The best compounds on Se basis comparable on force of friction with sulfur compounds of nevertheless provide smaller deterioration. Reduction of influence of sulfur by deterioration at preservation of high antifrictional properties such nanostructure additions, in our opinion, probably at using of other TMD structural types (in particular Fullerene-liked, nanotubes, etc.). Received tribology properties of industrial oil I20 with additions are resulted on Fig 8.



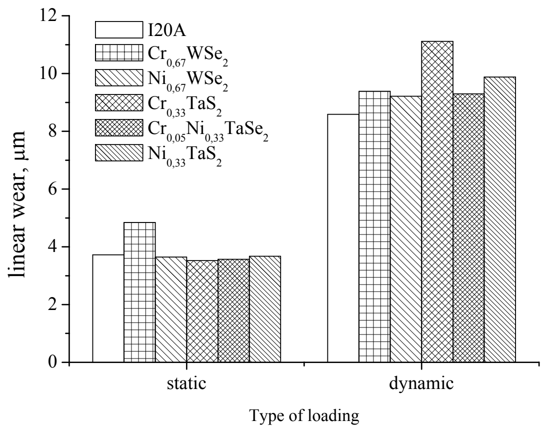


Fig. 8. The tribological properties of lubricant compositions with TDM intercalation compounds additives into base liquid oil I20.

Under real conditions of the operation of facilities, both the constant (static) and variable (dynamical) components of of loads are always present. Therefore, the determination of the optimum intervals of the mean sizes of anisotropic nanoparticles of solid lubricants is the important practical problem, and the control over these parameters is the significant advantage of the proposed nanotechnology of the production of solid lubricant additives, namely the layered nanostructures of disulfides of molybdenum and tungsten.

Thus, as compared with micronic powders of natural molybdenum disulfide, the use of the new class of solid lubricant additives, namely the layered nanostructures of disulfides of transition metals, allows one to significantly improve the tribological properties of semiliquid plastic lubricants and oils different by the production technology and the concentration of additives.

On the whole, the presented results of studies of the tribotechnical characteristics of lubricating compositions with participation of layered nanostructures of 2H-MoS_2 and 2H-WS_2 coincide qualitatively with the data on the compositions with participation of fullerene-like structures of WS_2 (see, e.g., [16-19, 33-38]). We note that the tribological properties of nanocrystalline TMD are defined by the influence of effects of the transition in a nanostate with the formation of different types of nanostructures (layered nanostructures, fullerene-like structures, onion-like nanoparticles, multiwalled nanotubes, etc.), the processes of ordering-disordering of real nanostructures, and their intercalation, which defines a change in the structure-sensitive tribological properties of nanostructures in a wide scope. The indicated factors must lead to remarkable differences in the tribochemical interactions of nanostructures of TMD with the near-surface layers of friction couples and to changes of the tribotechnical characteristics of systems on the whole.

The presented results testify to the perspectives of studies of the tribological properties of the systems with participation of the ordered/disordered layered nanostructures of TMD with structure-sensitive tribological properties aimed at the creation of new nanostructural antifriction materials. As for the last, there exists a number of actual problems which can be successfully solved with the help of the application of nanocrystalline layered TMD as solid lubricant additives. In particular, it seems to be expedient to use the layered nanostructures of TMD in the development of new lubricants, including high-temperature ones, for hard-loaded friction units of the metallurgical equipment; semiliquid lubricants with the improved tribological properties for hard-loaded reducers and centralized systems of lubrication of the industrial facilities; and solid lubricants and pastes for friction units which operate at high temperatures and loads.

Conclusion

1. The original equipment for studying friction processes at dynamic loading is suitable to the express method of evaluation of wear and friction force at controlling rang of alternate (dynamic) loads for creation new high-tech lubricant, because the change type of loading greatly affects both tribology characteristics and, which is more important, mechanism of wear processes in tribosystems with TMD and ITMD nanoparticles.
2. It was elaborated a nanotechnologies of the anisotropic 2H-MeS_2 (Me=W, Mo) layered nanoparticles preparation with extremely small average sizes (~4 nm and ~8 nm in crystallographic directions [013] that [110], accordingly) without admixtures of foreign phases, including X-ray amorphous ones, or the other ~~kinds~~ types of nanostructures.
3. On the determination of the tribological characteristics of lubricants with the additives of nanocrystalline powders of layered 2H-MoS_2 and 2H-WS_2 and on the comparison of those with the additives of commercial micronic powders of natural 2H-MoS_2 and 2H-$MoSe_2$, we obtain the following characteristics:

- antiwear properties on a four-ball friction machine are improved by 10-25%;
- score resistance on a friction machine Falex-1 increases by 25-70%;
- antifriction properties on a vibrotribometer SRV are improved by 10-14%.

The obtained results concerning the tribological properties of lubricants with the additives of nanocrystalline powders of layered disulfides of molybdenum and tungsten allow one to expect the increase in the service life of friction units by a factor of 1.5–2 under operational conditions.

4. We have established that the nanocrystalline powders of layered 2H-MoS_2 and 2H-WS_2 used as solid lubricant additives to oil I-20 improve significantly the tribotechnical characteristics as compared with the use of micronic powders of natural molybdenum disulfide. For the layered nanostructures of 2H-MoS_2 and 2H-WS_2, we have observed a significant decrease in the friction force (by a factor of 1.5) and an increase in the wear resistance (by a factor of 1.5–2) under conditions of quasistationary and dynamical loadings as compared with the data on the use of natural molybdenum disulfide. The values of wear resistance in the presence of nanocrystalline layered disulfides of molybdenum and tungsten are correlated with the mean sizes of their anisotropic nanoparticles.
5. Tribological systems with participation of the ordered/disordered layered nanostructures of dichalcogenides of transition metals with structure-sensitive tribological properties are perspective for the production of new nanostructural antifriction materials.
6. We have two ways to obtaine nanosize powders as lubricant additions. Said above proves that such researches are very perspective for creation of new high-tech lubricant design.
7. Layered nanostructures of disulfides of molybdenum and tungsten – a new class of efficient solid lubricant additives to oils and lubricants aimed at the improvement of their operational characteristics.

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Project co-operation

Mention the forms of co-operation used: e-mail contacts, meetings, seminars, researchers visits, joint publications, joint presentations, COST Short Term Scientific Missions etc

This work was carried out in close cooperation with Ivan Franko Lviv National University, Ukrainian Oil-Refinery Research Institute "MASMA".

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Industrial improvements in commercial use

Description of the planned industrial improvements or improvements already in commercial use. Appropriate company and product names can be mentioned but do not include confidential information

Publications were project results are reported

1. Ukraine Patent "Method of the nanocrystalline Molybdenum Dichalcogenides preparation", Kulikov L. M., Kenig N.B. Filing Date: 03.2007.
2. Ukraine Patent "Method of the nanocrystalline Tungsten Dichalcogenides preparation", Kulikov L. M., Kenig N.B. Filing Date: 03.2007.
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TS6 - STUDY OF CONTACT FATIGUE MECHANISMS OF DUPLEX TREATED LOW ALLOY STEELS

Co-ordinator and partners

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Project status and schedule

Running with partial funding
Starting and ending dates: 8/2003-6/2007

Project aims

The scientific aim of the study is the degradation mechanisms of duplex treated low-alloyed steels in the conditions of contact fatigue and adhesive wear. The technological aim is to produce data for selected range of duplex treatment technologies applied to structural steels. The objective is to contribute to the design of duplex treated systems with optimized friction and minimized wear and thus to enable materials to be used in different applications.

Project results

In the first phase of the project there were prepared specimens for analysis of parameters pulse plasma nitridation, specimens for tribological tests (pin-on-disc, ring-on-plate) and specimens for twin disk tribometer and modified four-ball tester. All the specimens from the low-alloyed steels 31CrMoV9 were heat treated (hardening 865-870°C/N_2 + tempering 600°C/2h), pulse plasma nitrided and PVD coated. The changes of chemical composition of duplex treated steel 31CrMoV 9 were studied by EDAX and GDOES.

Adhesive wear tests

In the second phase of the project the duplex treated specimens from the steel 31CrMoV 9 were tested with the ring-on-plate tribometer. The tested duplex treated specimens:

- plasma nitriding + PVD TiN (1 and 3 μm),
- plasma nitriding + PVD CrN (1 and 3 μm),

- plasma nitriding + PVD TiAlN (3 μm),
- plasma nitriding + PVD (CrN-TiN)×3 (3 μm)

After plasma nitriding the specimens had the thin surface layer of nitrides. Therefore, it was necessary to remove this layer by lapping before the deposition of PVD coatings.

The two-step plasma nitriding produces surfaces without this layer of nitrides. The specimens were coated only with PVD CrN coating. The results of tribological tests both duplex treated steels with tribometer Amsler given in fig. 1, 2, 3 and 4.

Thin PVD TiN coatings (1 μm) were worn-out during the tribological tests. At the beginning of tests (F_N = 50 N) the surface of the PVD TiN coatings (3 μm) was coated by thin layer of iron and iron oxides transferred from the opposite member of sliding pair. After increasing load the coating TiN was strongly deteriorated.

Contact fatigue tests

The **2-disc test ring Amsler** was used for the evaluation of tribological properties of duplex treated specimens. The tested pair consists of case-hardened steel 14 220 and duplex treated steel 31CrMoV9. The pair of discs was lubricated. The regime of testing - rolling and rolling/sliding with constant rpm.

Load can be changed from 50 to 1500 N (line contact). The friction torque and loading were measured and stored continuously. The pitting was detected by the stereomicroscopy. The wear was measured by weighting.

Test parameters:

Revolutions	330 rpm
Velocity difference	0, 10% (others by a change of diameter)
Normal load	50 up to 1500 N
Temperature	room temperature
Movements	sliding/rolling
Contact	line contact

The fatigue life (pitting) was set by stereomicroscopy and weight loss. The specimens were completely immersed in a lubricant. Test conditions – loading from 100 to 1400 N and 330 rpm ring, giving maximum Hertzian stress on the line contact of 700 MPa. Pitting was detected by streomicroscopy and with automatically registered the coefficient friction.

The results of the experiments were presented in Figs. 1 and 2.

The combination of transfer of iron oxides and deterioration of thin PVD CrN coating (1 μm) and creation of wear debris are typical processes which proceeded on the functional surfaces of tested specimens. The thicker CrN coatings (3 μm) had bright surface during high load of bearing steel from opposite member of sliding pair.

Practically the same situation was in the case of PVD TiAlN coating – bright surface with local traces of transferred metal.

The local deterioration of the PVD (CrN-TiN)×3 coating and transfer of metal from the second member of sliding pair was the typical worn surface appearance.

The normal force 700 N was too high and practically all the duplex treated specimens were seriously worn-out and the PVD coatings were damaged with cracking of surface layers.

The highest fatigue life from tested duplex treated structural steels have plasma nitrided steels with PVD coatings CrN and (CrN-TiN)×3.

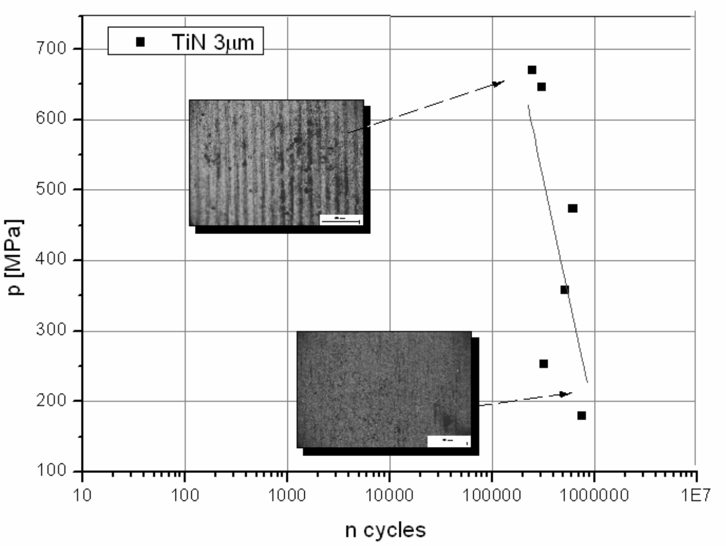


Fig. 1. Graphical presentation of adhesive wear tests of duplex treated steel 31CrMoV 9 plasma nitriding + TiN coating (3 μm).

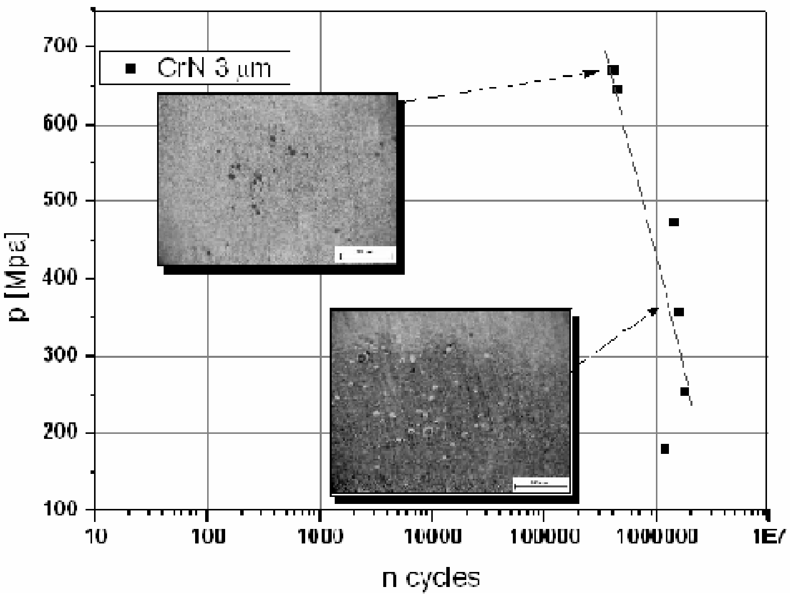


Fig. 2. Graphical trend of adhesive wear tests of duplex treated steel 31CrMoV 9 - plasma nitriding + CrN coating (3 μm).

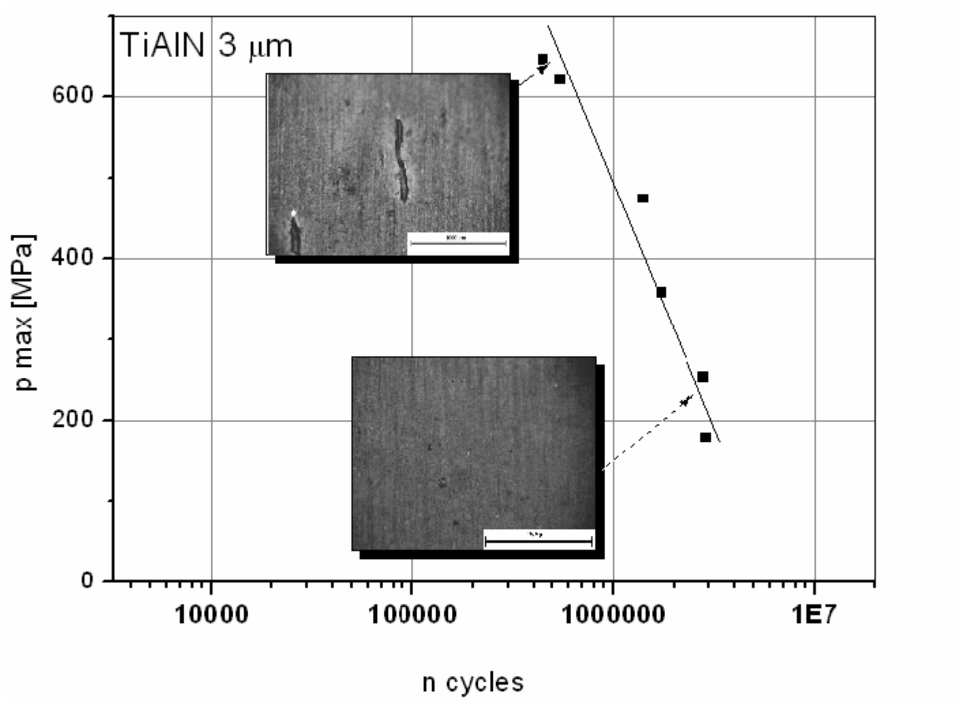


Fig. 3. Graphical presentation of adhesive wear tests of duplex treated steel 31CrMoV 9 plasma nitriding + TiAlN 3 μm.

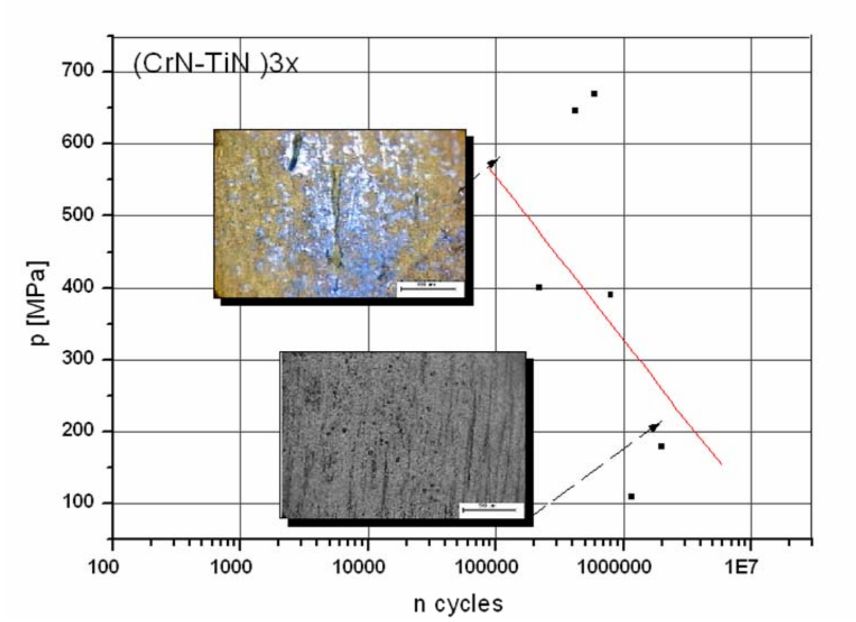
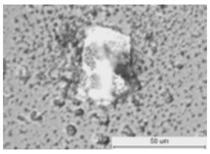
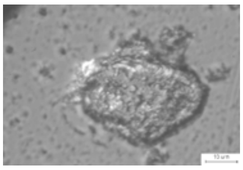


Fig. 4. Graphical output of adhesive wear tests of duplex treated steel 31CrMoV 9 plasma nitriding + PVD coating (CrN-TiN)3x 1μm.



The shape of debris from tested pair - hardened steel 14 220 -duplex treated steel (CrN-TiN) 3x µm (40 µm)



Cluster of debris with average diameter upto 25 0 µm

Fig.5.

The same situation was in the case of PVD TiAlN coating – bright surface with local traces of transferred metal. The degradation of thicker PVD coatings started in the friction contact by the influence of transferred particles from case-hardened counterbody and gradual contact fatigue of coatings. The progress of contact fatigue depends on the loading.

The damage of duplex coated rings with PVD (CrN-TiN)×3 was intensive during the contact fatigue tests. The tests were stopped after degradation of the first TiN layer. The damaged specimens were small micropitting in the conditions of low load. During the tests with higher loading (F= 1400 N) the surfaces degradation was too heavy. The tribological tests were finished after deterioration of the first layers TiN of PVD (CrN-TiN)×3 (see Fig.4).

Project co-operation

Mention the forms of co-operation used:

The co-operation is with ATG Ltd., Czech Republic- project TS-M5, Technical University -Liberec and and Institute of Terotechnology, Radom, Poland.
Exchange of results of experiments is carried out by e-mail contacts and researchers visits.
There were prepared several joint presentations in the scientific journals and on the national and international conferences.

Planned or achieved industrial improvements in commercial use

At this moment there are no industrial achievements.

Publications were project results are reported

1. Zdravecká, E.; Suchánek, J.; Gmiterko, A.; Tkáčová, J.; 2003;Vizualizácia morfologických zmien prostredníctvom Matlabu. MATLAB 2003. In: Sborník příspěvků 11. ročníku konference, díl. II, Praha, 2003
2. Zdravecká, E.; Tkáčová, J.; Solfronk, P.; Suchánek, J.; 2005, Influence of pulse plasma nitriding on surface and subsurface systems of 31CrMoV9 steel. Problemy Eksploatacji – Maintenance Problems, 2/2005, (57), pp. 161-170
3. Zdravecká, E.; Suchánek, J.; Tkáčová, J.; 2005; Influence of pulse plasma nitriding parameters on the nitriding layer creation of the 31CrMoV9 steel. In: Transtribo 2005, Sankt Petersburg 2005, pp. 105-110
4. Suchánek, J.; Jurči, P.; Zdravecká, E.; Hrubý, V.; 2005, Vliv parametrů pulzní plazmové nitridace ocelí 31CrMoV9 A 34CrAlNi7 na tvorbu nitridované vrstvy (Influence of pulse

plasma nitriding parameters of 31CrMoV9 and 34CrAlNi7 steels). In: VRSTVY A POVLAKY 2005 (COATINGS AND LAYERS 2005), Demänovská dolina, 23.-24.6.2005, pp. 193-198
5. Jurči, P.; Suchánek, J.; 2005, Development of optimal inter-layer on the medium carbon Cr-Al-Ni-alloyed steel for the duplex-coating. In: 10th conference „Přínos metalografie pro řešení výrobních problémů“, Lázně Libverda, 2005, pp. 303-306
6. Zdravecká, E.; Suchánek, J.; Fescu, Š.; Klamar, P.: Analýzy vybraných vlastností duplexných povlakov. Proc. INTERTRIBO 2006, Tribological Problems in Exposed Friction Systems, Stará Lesná, 11-13.10.2006, pp. 245-248
7. Zdravecká, E.; Suchánek, J.; Chomjaková, I.; Tkáčová, J.; Fecsu, Š.: Adhézné vlastnosti duplexných povlakov na konštrukčných nízkolegovaných oceliach (Adhesive properties of duplex coatings on structural low-alloyed steels). Acta Mechanica Slovaca, 2-B/2006, pp. 1-6

TS7 - EXPERIMENTAL INVESTIGATION OF WET CLUTCH FRICTION MATERIALS FOR LIFETIME AND CLUTCH SHUDDER

Co-ordinator and partners

Co-ordinator :

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Project status and schedule

Project finished. Starting and ending dates:
From April 2003 to April 2007.

Project aims

The aim of the study is twofold :

1. To develop a better friction model for boundary lubricated surfaces than available in literature, which could provide more insight in the occurrence of vibrations in wet friction clutches. This friction model, combined with a simple mechanical model off the test rig will be validated in small-scale tests for different friction material/ATF combinations. Once the friction model is validated for small scale tests, a number of SAE#II test will be undertaken to check if the model holds true for full scale clutches.
2. While the materials (friction materials and ATF) are available, small scale testing will be undertaken to rank them for wear resistance, which would render the selection of materials for friction clutches for transmissions in off-highway vehicles more easy

Project results

Firstly the mechanism which gives rise to torsional vibrations in clutches was studied on a small-scale test rig (see figure 1)

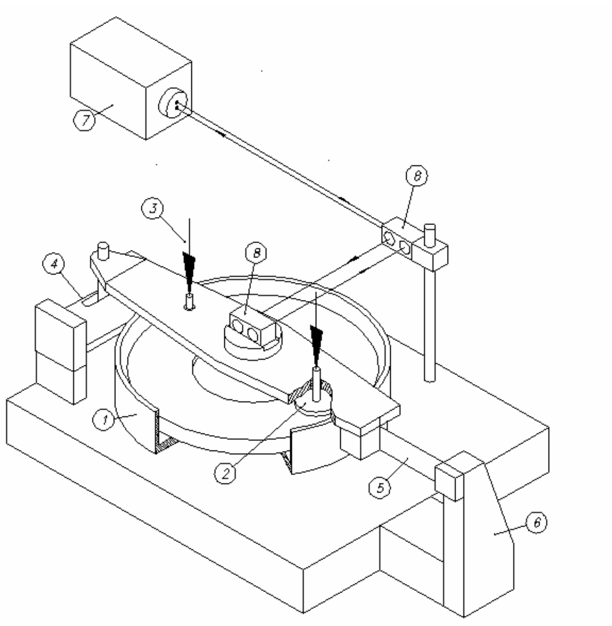

Fig. 1. Experimental test set-up.

Basically, this test-rig consists of a rotating ring placed in an oil bath (1), driven by an electric motor controlled by an inverter. The electric motor is coupled through an elastic claw coupling to a reduction gearbox (worm-wormwheel drive). The outgoing axle of the reduction gearbox drives a V-belt, for which three different pulleys are available, which allows to reduce velocity, increase it or provide a direct drive. The other pulley of the V-belt drive is connected to the ingoing axle of a switchable gearbox, which allows for either a direct drive or a reduction. The outgoing axle of the switchable gearbox is connected to the pinion of a set of gears, which drives the oil bath and rotating ring.

On the rotating ring two sliding shoes (2) are pressed by means of loading pins. The pins are placed in linear guides affixed to the rotating arm and are loaded by calibrated weights (3). The rotating arm is connected by either a leaf spring (5) or a torsion bar to the fixed frame of the test-rig (6). The angular displacement, velocity and acceleration of the sliding shoes are measured by laserinterferometry (7 and 8). The resolution of this measurement is 0.005 seconds of arc, the accuracy is ± 0.2%. This test-rig conforms to an elementary and well-known mechanical mass-spring-damper system, which is governed by equation (1).

$$m\ddot{x} + c\dot{x} + kx = F \qquad \text{Eq. 1}$$

During the course of this work a number of modifications were made to this test-rig (see reference [1] to make the test-rig more conforming to the model of equation 1.

Concerning the occurrence of torsional oscillations in wet friction clutches, the results obtained on the small-scale test-rig indicate that:

- The mechanism which gives rise to the torsional vibrations is of an oscillatory sliding nature: no stick episodes were detected, the oscillations abate for low imposed disk velocities and the frequency is independent of the imposed velocity and equal to the natural frequency.
- Adding damping inhibits the occurrence of oscillatory behaviour.
- Increasing the stiffness of the mechanical system lowers the amplitude of the observed oscillations.

- There is no clear effect of contact pressure on the occurrence of oscillatory sliding.
- Oscillations for which the minimum of the relative velocity ($v_{rel,min}$) is larger than zero could be observed.
- While for some values of the imposed velocity the slope of the $\mu(v_{rel})$ curve is sufficiently negative, the correlation between the slope of this relation and the occurrence of oscillations is far from perfect. For some values of the disk velocity oscillations do occur when the slope of $\mu(v_{rel})$ is insufficiently negative.

These experimental results have the following implications on the way in which the friction needs to be theoretically modelled to predict the occurrence of oscillatory sliding:

- A linear dependence of $\mu(v_{rel})$ would imply that the oscillation amplitude grows exponentially. It is shown that when the oscillation amplitude is sufficiently large ($v_{rel,min}=0$), this would entail a sign reversal of the friction force. Consequently the amplitude cannot grow further and a stable limit-cycle results with $v_{rel,min}=0$. This runs contrary to the experimental results, where oscillations with amplitude $v_{rel,min}>0$ were observed.
- It is shown that a non-linear friction model could produce stable oscillations with $v_{rel,min}>0$. Once the amplitude has grown sufficiently large, further growth of the oscillation amplitude is prevented by the non-linear terms of $\mu(v_{rel})$, producing a stable limit cycle. The slope of the $\mu(v_{rel})$ relation around $v_{rel}=v_{disk}$ however needs to be sufficiently negative for oscillations to occur. The experimental results show that this condition is not met for a number of values of the imposed velocity, where the slope of $\mu(v_{rel})$ is insufficient for oscillations to occur.
- A dynamic element can be added to the non-linear $\mu(v_{rel})$ relation. The dynamic element is necessary to create oscillations when the slope of $\mu(v_{rel})$ is insufficiently negative. The amplitude of the oscillations is then limited by the non-linearity of $\mu(v_{rel})$. Based on experimental data, a dynamic model of this type is proposed. The obtained fit between the data and the model is not accurate however. This does not as such invalidate the proposed dynamic friction model, as the discrepancy could also be due to the application of the perturbation theory that was used to fit the model to the available data.

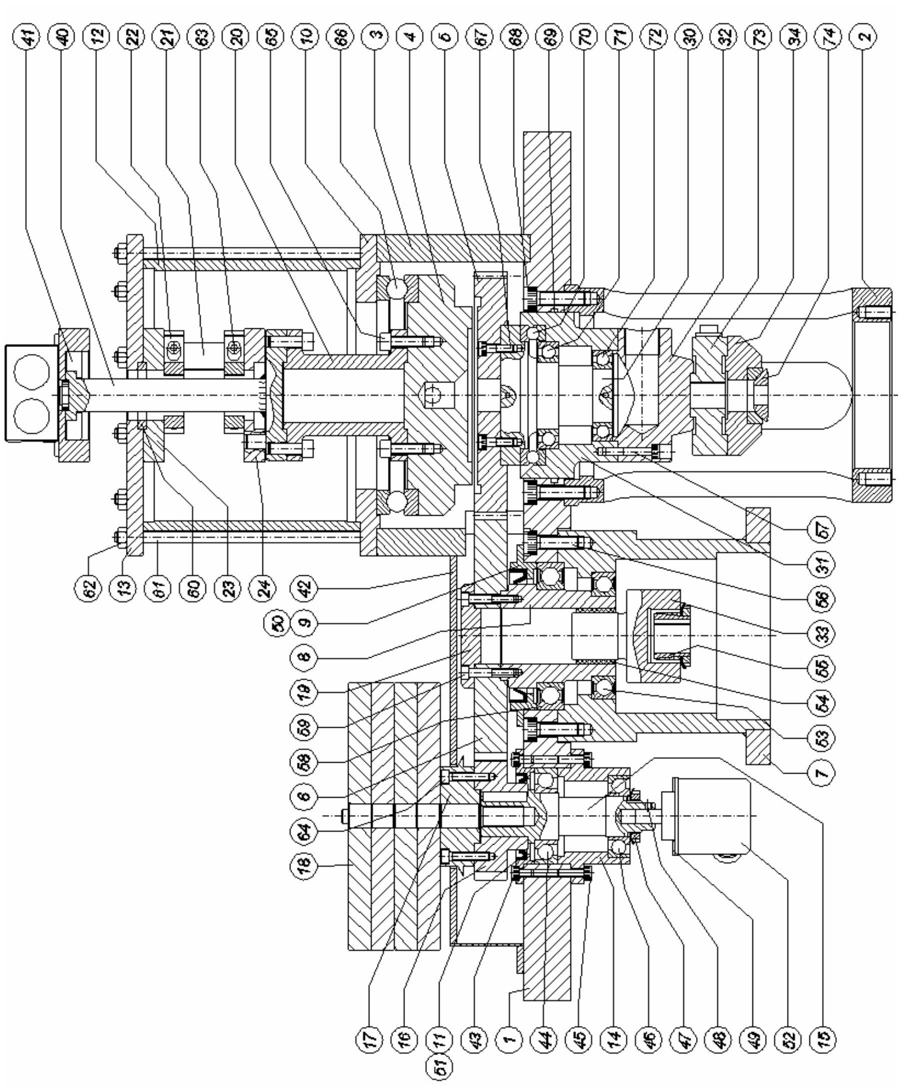

Fig. 2. Disk-on-disk apparatus.

As part of this work a new plate-on-plate test-rig has been developed (see figure 2). The basic design of the test-rig is inspired by the plate-on-plate test-rig described by Holgerson [2]. The test-rig is driven by a hydraulic motor through a one-way clutch (64), while the friction and separator plate are loaded by a hydraulic piston. Also a torsionally weak element (21) is added.

This test-rig combines certain traits of the SAE#II test-rig and certain traits of the test-rig described in chapter 5.

- The separator plate is either driven by a flywheel or a hydraulic motor. The motor can be used to directly drive the separator plate, so test comparable to the tests described in chapter 5 can be made. The hydraulic motor can also be used to bring a rotating inertia mass up to speed, which can then subsequently dissipate its energy in the clutch plates.
- The normal load on the plates is applied by a hydraulic piston, which allows to quickly vary the normal load and in a next stage to control the normal load.
- The frictional torque generated by the plates will be measured with a torque meter, but the test-rig will also contain a torsionally weak element. The angular displacement of this element will be measured with the same laser-interferometrical system used on the small-scale test-rig described in chapter 5. This will allow a dynamic measurement of the friction force, even when oscillations do take place.

The main differences between this test-rig and the one described by Holgerson [2] are threefold. Firstly it allows to easily vary the stiffness of the test-rig. Secondly the one-way clutch makes it possible to perform both tests in which the clutch is used to dissipate the energy of the flywheel and tests with constant velocity. Thirdly the coefficient of friction and the relative speed of the surfaces can be measured during oscillations using the interferometrical system.

This test-rig was used to evaluate the wear mechanisms of a number of commercially available friction materials for wet clutches, with conditions regarding velocity and normal load chose according to the real operating conditions of a wet friction clutch. Results of the wear testing will be described in an upcoming publication.

References

[1] Ost W., Tribology and Vibrations of wet clutches, PhD thesis, Ghent University, 2006, ISBN 90-8578-096-9

[2] Holgerson M., Apparatus for measurement of engagement characteristics of a wet clutch, Wear, Vol. 213, 1997.

Project co-operation

Mention the forms of co-operation used: e-mail contacts, meetings, seminars, researchers visits, joint publications, joint presentations etc

Publications were project results are reported

1. On the origin of torsional vibrations in automatic transmissions: small scale experimental results, OST, W ; DE BAETS, P, Proc. AITC 2004, 4th AIMETA International Tribology Conference / Ed. Bassani, R ; Belfiore, N ; Ciulli, E. - 2004 p. 243-250

2. Ost W., De Baets P., The frictional stability of wet clutch friction material investigated on a small scale test-rig, Proc.WTC2005, World Tribology Congress III, 2005, paper number WTC2005-63514

3. Ost W., Tribology and Vibrations of wet clutches, PhD thesis, Ghent University, 2006, ISBN 90-8578-096-9

Planned or achieved industrial improvements in commercial use

None so far

TS8 - ADHESIVE WEAR AND CONTACT FATIGUE OF DUPLEX TREATED LOW ALLOY STEELS

Co-ordinator and partners

Co-ordinator:

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Partners:

Ing. Peter Jurči, Ph.D., ECOSOND Ltd., K vodárně 531, Čerčany, Czech Republic, jurci@ecosond.cz

Ing. Ivan Fürbacher, CSc., SVÚM a.s., Podnikatelská, 190 11 Prague 9 – Bèchovice, Czech Republic, strength@svum.cz

Project status and schedule

Running with partial funding
Starting and ending dates: 9/2003-6/2007

Project aims

The scientific aim of the study is the degradation mechanisms of duplex treated low-alloyed steels in the conditions of contact fatigue and adhesive wear. The technological aim is to produce data for selected range of duplex treatment technologies applied to structural steels. The objective is to contribute to the design of duplex treated systems with optimized friction and minimized wear and thus to enable materials to be used in different applications.

Project results

In the first phase of the project there were prepared specimens for analysis of parameters pulse plasma nitridation, specimens for tribological tests (pin-on-disc, ring-on-plate) and specimens for twin disk tribometer and modified four-ball tester. All the specimens from the low-alloyed steels (31CrMoV9 and 34CrAlNi7) were heat treated (hardening 865-870°C/N_2 + tempering 600°C/2h), pulse plasma nitrided and PVD coated. The changes of chemical composition of duplex treated steel 31CrMoV 9 was studied by EDAX and GDOES.

Adhesive wear tests

In the second phase of the project the duplex treated specimens from the steel 31CrMoV 9 were tested with the ring-on-plate tribometer. The tested duplex treated specimens:

- plasma nitriding + PVD TiN (1 and 3 μm),
- plasma nitriding + PVD CrN (1 and 3 μm),
- plasma nitriding + PVD TiAlN (3 μm),
- plasma nitriding + PVD (CrN-TiN)×3 (3 μm)

After plasma nitriding the specimens had the thin surface layer of nitrides. Therefore, it was necessary to remove this layer by lapping before the deposition of PVD coatings.

The specimens from the steel 34CrAlNi 7 were plasma nitrided at the different parameters to eliminate the layer of the nitrides before the PVD coating. The two-step plasma nitriding produces surfaces without this layer of nitrides. The specimens were coated only with PVD CrN coating. The results of tribological tests both duplex treated steels with tribometer HEF are given in Tabs. 1 and 2.

Table 1. Results of adhesive wear tests of duplex treated steel 31CrMoV 9 .

Parameters of tests: tribometer HEF, sliding couple – duplex treated steel/hardened bearing steel, F_N– 50N and 150N, v – 0,916 ms^{-1}, L = 1; 2,5; 5; 10 km, without lubricant.

Type of duplex treatment	Load (N)	Weight loss (10^{-6} kg) at sliding path			
		1000 m	2500 m	5000 m	10000 m
PN+TiN (1 µm)	50	+ 0,93	0,37	3,47	10,24
	150	17,8	84,45	323,85	915,9
PN+TiN (3 µm)	50	+0,37	0,133	1,167	2,20
	150	0,45	3,35	13,1	44,4
PN+CrN (1 µm)	50	1,63	4,10	12,76	25,56
	150	63,9	165,7	485,1	1118,3
PN+CrN (3 µm)	50	+0,83	+0,53	+0,2	1,46
	150	29,6	111,15	216,1	416,8
PN+TiAlN (3 µm)	50	+1,2	+1,36	+0,6	1,0
	150	+1,75	+0,3	4,1	23,9
PN+(CrN-TiN)x3 (3 µm)	50	+0,67	+1,0	+0,83	+0,67
	150	8,1	20,33	39,2	103,27

Thin PVD TiN coatings (1 µm) were worn-out during the tribological tests. At the beginning of tests (F_N = 50 N) the surface of the PVD TiN coatings (3 µm) was coated by thin layer of iron and iron oxides transferred from the opposite member of sliding pair. After 10 km the coating TiN was partly deteriorated.

The combination of transfer of iron oxides and deterioration of thin PVD CrN coating (1 µm) are typical processes which proceeded on the functional surfaces of tested specimens. The thicker CrN coatings (3 µm) had bright surface with local transfer of bearing steel from opposite member of sliding pair.

Practically the same situation was in the case of PVD TiAlN coating – bright surface with local traces of transferred metal.

The local deterioration of the PVD (CrN-TiN)×3 coating and transfer of metal from the second member of sliding pair was the typical appearance of the worn surface.

The normal force 150 N was too high and practically all the duplex treated specimens were seriously worn-out and the PVD coatings were removed totally.

Tab. 2 Results of adhesive wear tests of duplex treated steel 34CrAlNi 7.

Parameters of tests: tribometer HEF, sliding couple – duplex treated steel/hardened bearing steel, F_N– 50N and 100N, v – 0,916 ms^{-1}, L = 1; 2,5; 5; 10 km, without lubricant.

treatment	Load (N)	Weight loss (10^{-6} kg) at sliding path			
		1000 m	2500 m	5000 m	10000 m
PN+TiN (1 µm)	50	1,2	0,8	0,2	1,3
	100	10,2	30,33	63,19	123,25
PN+TiN (3 µm)	50	+0,9	+1,0	+0,3	+0,3
	100	13,63	33,93	66,79	127,55

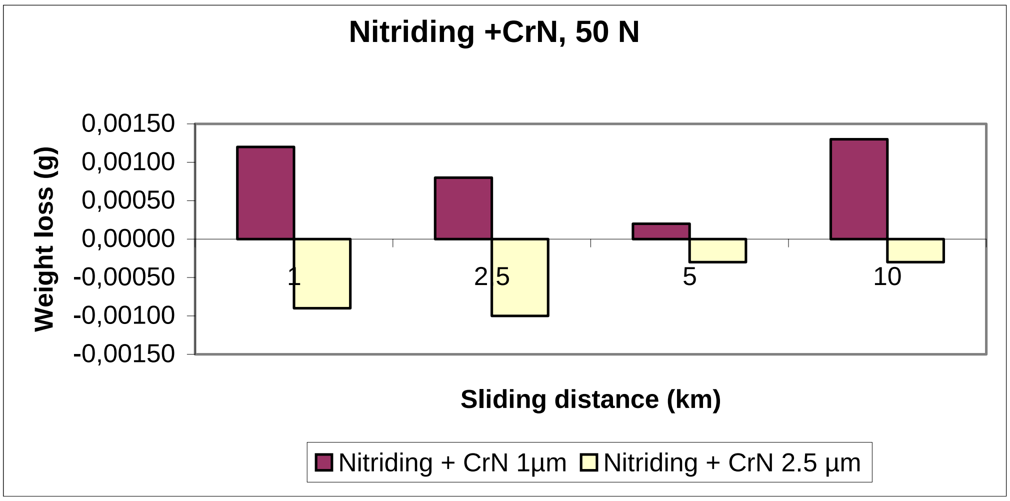

Fig. 1. Weight losses of duplex treated specimens (steel 34CrAlNi 7).

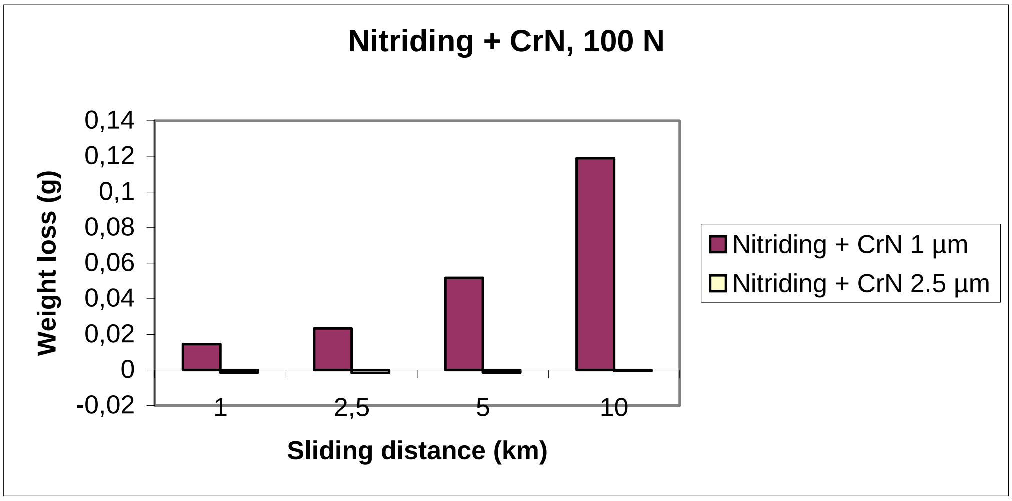

Fig. 2. Weight losses of duplex treated specimens (steel 34CrAlNi 7).

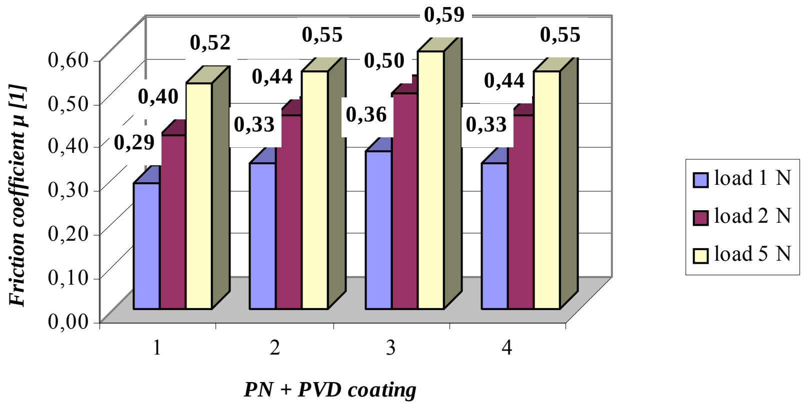

Fig. 3. Friction coeficients (1 – TiN, 2 – (Crn-TiN)×3, 3 – CrN, 4 – TiAlN).

The results of tribological tests of duplex treated steel 34CrAlNi 7 are given in Figs. 1 and 2. During the tests with load 150N the surface degradation was too heavy and therefore, the load was reduce to 100 N.

The ball-on-disc tribometer tests have shown that the friction coefficients grow with the applied load. The parameters of tests - load – 1,2 and 5 N, velocity – 0,1 ms^{-1}, path – 100 m, diameter of ball from hardened bearing steel – 7,94 mm, dry friction.

The minimum friction coefficient was measured on the TiN coating at 1 N and maximum friction coefficient on CrN at 5 N. But the differences among the PVD coatings are very small (see Fig. 3).

Contact fatigue tests

The fatigue life (pitting) was characterised by the 10% fatigue life L_{10}. The L_{10} life was determined using the T–03 tester (collaboration with IteE Radom). The tribosystem consists of three lower balls freely rotating in a special race, and driven by the top cone with the investigated coating.

The specimens were completely immersed in a lubricant. Test conditions were 3924 N (400 kg) load and 1450 rpm top ball speed, giving maximum Hertzian stress on the top cone of 7.32 GPa. The load and geometry of the tribosystem were modified in comparison with the IP standard. Pitting was detected by a special system with a vibration sensor, which automatically stopped the machine. The test balls are from bearing steel. The results of the experiments were presented in fig. 4. The highest fatigue life from tested duplex treated structural steels have plasma nitrided steels with PVD CrN and (CrN-TiN)×3.

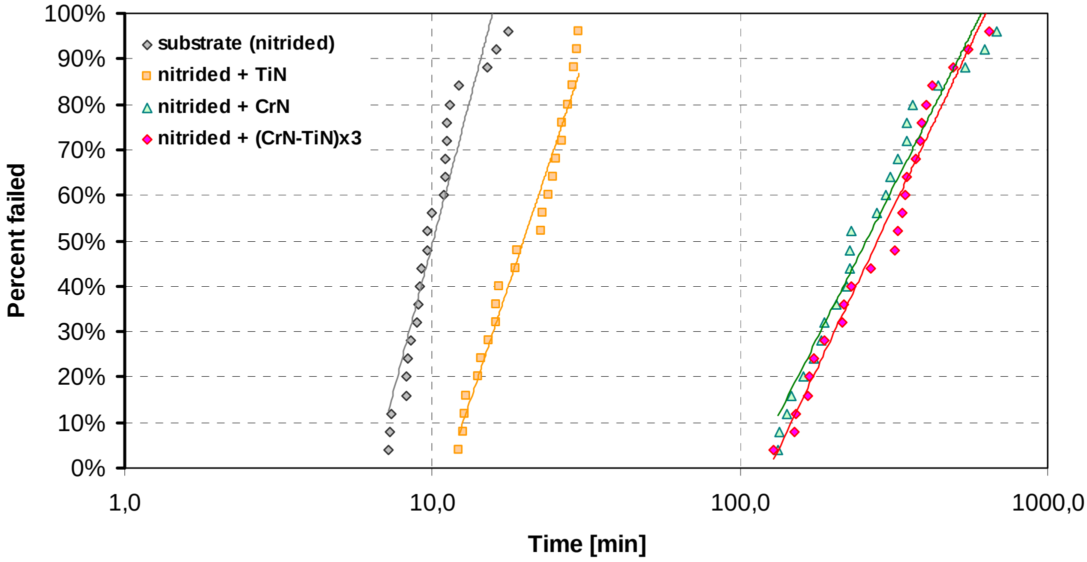

Fig. 4. Percentage of failed uncoated and coated elements (cones) lubricated with the mineral base oil.

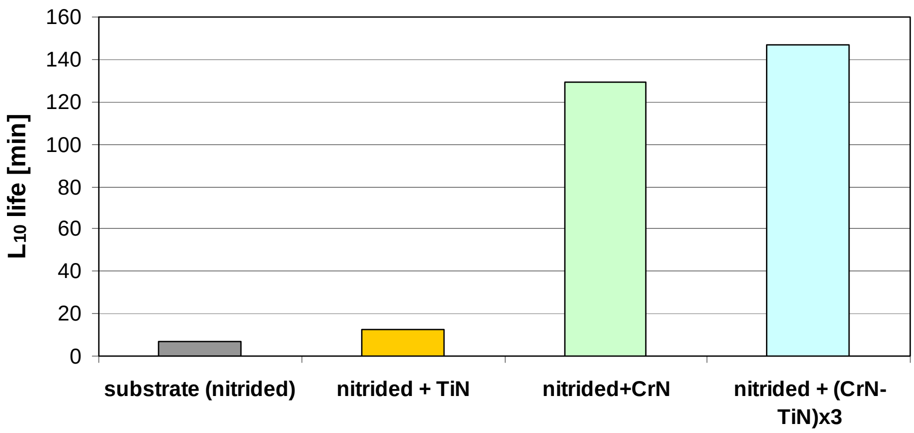

Fig. 5. L_{10} lives for uncoated and coated elements (cones) lubricated with the mineral base oil.

Very interesting results of contact fatigue tests on the duplex treated cone specimens need to check in revised set of experiments. The specimens were prepared in cooperation with ITeE Radom and the experimental results will be presented after finishing this repeating tests.

The results of contact fatigue tests were presented later.

Project co-operation

Mention the forms of co-operation used:
Co-operation with Technical University Košice, Slovakia (project M7) and Institute of Terotechnology, Radom, Poland.
Exchange of results of experiments is carried out by e-mail contacts and researchers visits.
There were prepared several joint presentations in the scientific journals and on the national and international conferences.

Planned or achieved industrial improvements in commercial use

At this moment there are no industrial achievements.

Publications were project results are reported

1. Zdravecká, E.; Suchánek, J.; Gmiterko, A.; Tkáčová, J.; 2003;Vizualizácia morfologických zmien prostredníctvom Matlabu. MATLAB 2003. In: Sborník příspěvků 11. ročníku konference, díl. II, Praha, 2003
2. Zdravecká, E.; Tkáčová, J.; Solfronk, P.; Suchánek, J.; 2005, Influence of pulse plasma nitriding on surface and subsurface systems of 31CrMoV9 steel. Problemy Eksploatacji – Maintenance Problems, 2/2005, (57), pp. 161-170
3. Zdravecká, E.; Suchánek, J.; Tkáčová, J.; 2005; Influence of pulse plasma nitriding parameters on the nitriding layer creation of the 31CrMoV9 steel. In: Transtribo 2005, Sankt Petersburg 2005, pp. 105-110
4. Suchánek, J.; Jurči, P.; Zdravecká, E.; Hrubý, V.; 2005, Vliv parametrů pulzní plazmové nitridace ocelí 31CrMoV9 A 34CrAlNi7 na tvorbu nitridované vrstvy (Influence of pulse plasma nitriding parameters of 31CrMoV9 and 34CrAlNi7 steels). In: VRSTVY A POVLAKY 2005 (COATINGS AND LAYERS 2005), Demänovská dolina, 23.-24.6.2005, pp. 193-198
5. Jurči, P.; Suchánek, J.; 2005, Development of optimal inter-layer on the medium carbon Cr-Al-Ni-alloyed steel for the duplex-coating. In: 10th conference „Přínos metalografie pro řešení výrobních problémů“, Lázně Libverda, 2005, pp. 303-306
6. Zdravecká, E.; Suchánek, J.; Fescu, Š.; Klamar, P.: Analýzy vybraných vlastností duplexných povlakov. Proc. INTERTRIBO 2006, Tribological Problems in Exposed Friction Systems, Stará Lesná, 11-13.10.2006, pp. 245-248
7. Zdravecká, E.; Suchánek, J.; Chomjaková, I.; Tkáčová, J.; Fecsu, Š.: Adhézné vlastnosti duplexných povlakov na konštrukčných nízkolegovaných oceliach (Adhesive properties of duplex coatings on structural low-alloyed steels). Acta Mechanica Slovaca, 2-B/2006, pp. 1-6

TS9 - ABRASIVE PARTICLES INFLUENCE ON DURABILITY OF TRIBOLOGICAL PAIRS IN MEANS OF TRANSPORT

Co-ordinator and partners

Co-ordinator:

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Prof. Kirill Voynov, Machine Building Institute, St Petersburg, Russia
Prof. Jerzy Dryzek, Institute of Nuclear Physics PAN, Poland, Jerzy.Dryzek
Ph.D. Eng. Bogdan Stolarski, INSTITUTE OF MACHINE DESIGN
Cracow University of Technology, Poland

Project results

First year (2004) of the project was focused on building of the basis for regular research. During this phase test stand was prepared and preliminary studies were done. Second year of the project was focused on the investigations of tribological processes in the friction pair with the presence of hard abrasive particles. This comprise test on the stand and investigations of the surface layer. Last year (2006) of the project was aimed to friction mechanism investigation and determination.

Character of this project is forcing focus on the test stands. Presence of hard particles is the reason why special design of test stands and measuring system has to be provided. As an additional feature, enhanced possibilities of observations have been included into design. Those assumptions were realized in the stage of test stands design process, which included: choice of kind of the tribological pair, choice of materials, operating parameters, measuring system. Operating parameters were chosen on the basis of earlier studies of automotive friction pairs. Results of those studies were obtained by series of in field tests and comparison with literature data. Special test stand: brake disc – brake pad was designed and built. In order to obtain the best possible information from test runs, special measuring system was prepared. System is built of two basic parts. First part is the measuring system and second – video system. Measuring of basic operation parameters are based on the solutions of Hottinger Baldwin Messtechnik. Force measurements are performed with strain gauge. Temperature is measured by thermocouple and additionally by infrared pyrometer. Sliding speed is adjusted by frequency inverter. All necessary data are acquisited with Spider 8 measuring amplifier, measurement process is governed by Catman software. Aside from basic operating parameters of the friction pair, which are: sliding speed, pressure and temperature, researchers decided to obtain visual information on the changes induced by friction processes and presence of hard particles. Test stand is equipped with video system and recording devices. The essential for system used in the project is fully controlled camera, which permits to adjust parameters for recording objects in the motion with poor lighting conditions. Used functions include inter alia: shooter adjustment, colour-BW switching, image enhancement functions, selective light regulation and motion detection. Special attention was put on the shooter and lighting conditions. Wide range of adjustment in the case of those two parameters is crucial for possibility of obtaining sharp and information worth images. In some cases, color to BW mode switching was used. The latter one mode is used in the conditions where color image can not be obtained due to poor lighting parameters. Output signal is in the VHS format with 25 frames per second and is transmitted to the Pinnacle video system installed in the PC computer. Film is stored on the PC HDD in the avi format for further edition. After edition procedure films are stored in DVD format. Video edition system gives possibility for use of special functions and fundamental are: observation in the slow motion and extraction of interesting frames in given time intervals. This is used in order to obtain information on particles movement in the friction zone and comparison between the stages of friction zone status.

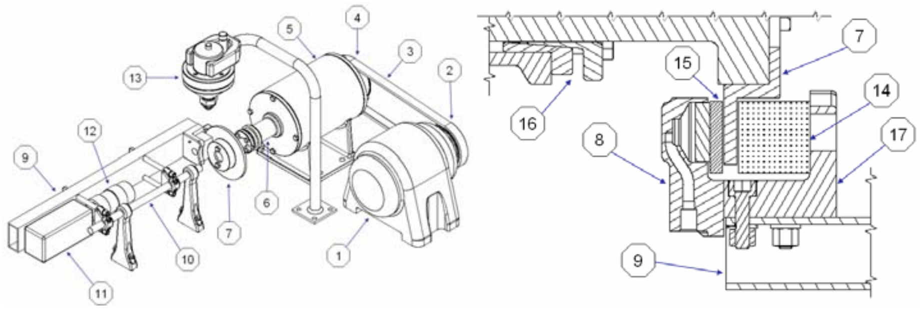

Fig.1. Schema of the test stand 1- electric motor, 2- drive wheel, 3- belt, 4- driven wheel, 5- housing of spindle, 6- spindle, 7- brake disk, 8- hydraulic caliper, 9- beam of caliper, 10- bar – linear bearing, 11- camera, 12- zoom lens, 13- particle feeder, 14- transparent pad, 15- passive pad, 16- self centering clutch, 17- passive caliper.

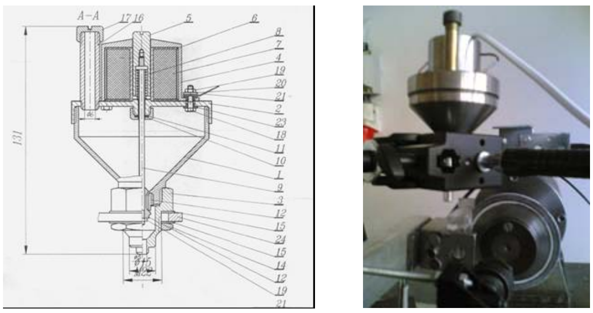

Fig.2. Hard particles delivery device.

With the use of test stand there were conducted tests and friction force and other operating parameters were recorded simultaneously with view of friction zone. After the tests obtained data and video sequences were analysed. To enable automatic operation of the stand, a controller of SR type fitted with calendar and clock was used. This allows automation of devices controlled by the SR controller. The controller enables repeatable cycles – time loop to be operated. The controller panel has a LCD display, four programmable pushbuttons and four function keys. The controller of SR type is programmable with the computer program SuperCad.

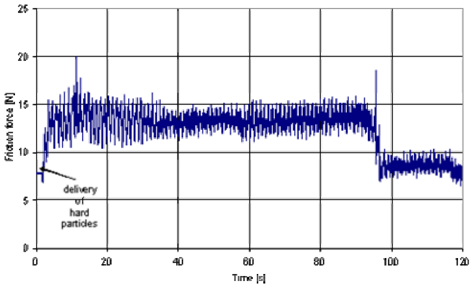

Fig.3. Test run with the presence of hard particles.

Fig.4. General changes in the friction zone from start to the end of the test run.

Usage of presented procedure allowed for obtaining information on the run tribological processes in the presence of hard particles. Hereafter are presented chosen results of investigation and analysis. As examination showed, presence of hard particles can cause both increase and decrease of friction force. Delivery of hard particles is usually connected with radical variations of the friction force. This is also connected with acoustic emission. Crucial for the behaviour of friction pair in the presence of hard particles is the possibility of entering friction zone by those particles. Main difference is observed for different moments of particles delivery, especially for the loaded and unloaded brake. With the brake unloaded, brake pads are positioned with clearance in relation to disc, so particles can penetrate the friction zone. After the loading of brake the clearance is reduced and big particles can not enter the friction zone. For the loaded brake, access to the friction zone is limited. In such case, during the test, after delivery of hard particles momentary decease of friction force was observed. Fluctuation of friction force is lower. Data obtained form video imaging gave information on the third body creation and destruction.

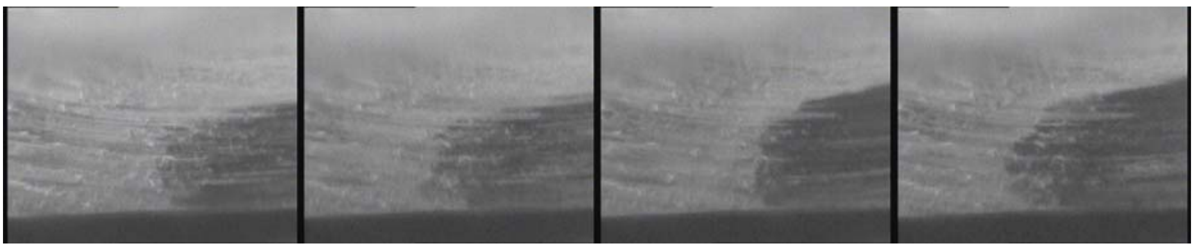

Fig. 5. Formation the third body during test run without delivery of hard particles.

Presence of big sized hard particles plays crucial role in the destruction of third body structures.

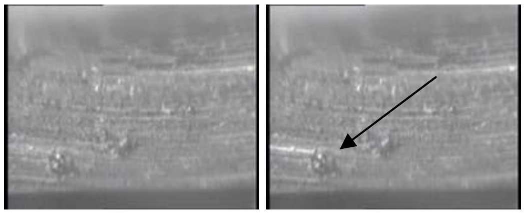

Fig. 6. Two extracted frames, second one with the presence of scratch create by hard particle.

Run of tribological processes is strongly influenced by particles embedded into soft pad and surface roughness. They influence the way that particles are moving across friction zone.

Samples after the test runs are treated by surface analysis. This analysis comprises various microscopy techniques (optical, metallographic, scanning electron microscopy), surface roughness measurements and as a basic research tool positron annihilation technique is used.

Crucial for realization of the project is to discover essential differences presence between processes taking place with and without hard particles presence. Those differences were confirmed in wide range of measurements and observations. As it was described in the methodology the substance was connection of measurements and observation with image analysis techniques. Test conducted with measurements and recording of operating parameters let us to get knowledge on the character of changes induced by hard particles. Essential changes concern friction force fluctuations, material transfer processes and temperature in the friction zone. Operation of brake disc without hard particles leads to increase of temperature and material transfer process (from pad to disc). Already after short time of operation, operating surface of the disc is covered by the transferred material. Further operation and increase of temperature are the reason of fast friction force increase caused by thermal changes in the pad. Operation without hard particles is connected with fast increase of temperature – especially for high rotational speeds. Presence of hard particles causes, in some operating conditions, limitation of temperature increase.

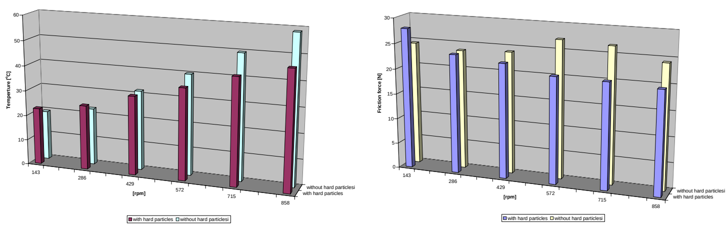

Fig. 7. Temperature and friction force comparison between the tests conducted with and without hard particles.

There were stated also significant differences in the value of friction force. In the case of hard particles presence, in spite of temperature increase, average value of friction force decreased. During the tests without hard particles value of friction force increased and after reaching of maximum value- decreased.

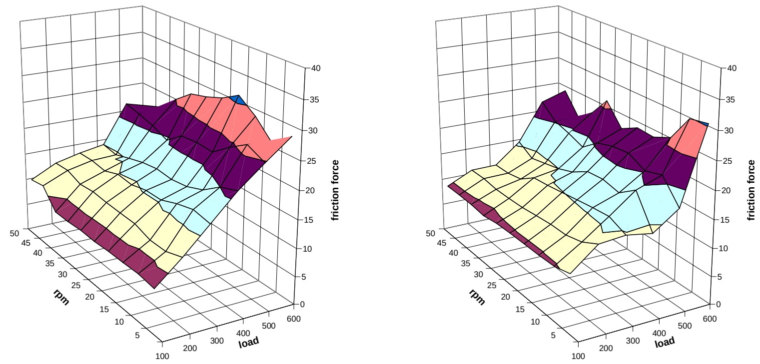

Fig.8. Friction force for the disc operating with and without hard particles (unsorted sand).

Crucial for the getting knowledge on the processes taking place in the friction zone is the analysis of video recording. According to the research methodology assumptions, video recording was performed for the individual test runs. Video data was analyzed and processed. Analyze of recorded data showed, that fundamental for the friction zone status is the possibility of hard particles getting into friction zone and their movement. This depends on the design of friction pair, state of operation (brake on – brake off) and size of particles. Among those factors, as a basic one, state of operation was chosen: during switching off the brake, brake pads are moved away the disc and possibility of easy delivery of hard particles into friction zone appears. Analysis of the video recording confirmed significance of the hard particles presence for the material transfer and third body creation phenomena. During the test conducted without hard particles relatively stable structure of surface is created and brake disc is covered with transferred material. Delivery of hard particles disturbs this situation. On the first sequence presented below, changes in the friction force are practically invisible (operation without hard particles). After the delivery of hard particles situation changes immediately and structure visible on the first sequence is now destroyed. After some period of time, material transferred on the disc is removed. Image analysis tools were used for the description of presented phenomena. Individual frames were graphically processed and level of black was analyzed. Chosen examples are presented below.

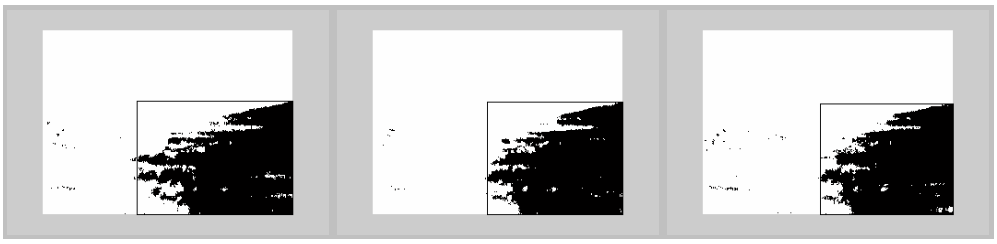

Fig.9. Results of the friction zone analysis in respect to the creation and destruction of the third body.

Special attention in the video data analysis was put on the creation of scratches. Scratches were identified by analysis of frame sequences and comparison of two adjoining frames: last without scratch and first with the scratch visible. Chosen results of analysis are presented below. Images obtained as a result of described procedure are the graphical differences between two frames. Proposed way of image analysis let us get clear view of the scratches. As it is visible, scratches are the sections of circle (with the center in brake disc axis). There is differentiation among their length and position of starting and ending points. After creation of the scratch, a set of phenomena leading to its disappearing. Analysis was done by sequence of graphical operations. First operation it was the selection of referring frame – the last frame before scratch appeared. It was the basis for further calculations and graphical operations. Next frames were compared to this frame – change of scratch images was obtained this way. After the conversion for 1-bit format, following point in time were ascribed to the values referring to the size of scratch (level of white). Chosen examples for this procedure and studies of scratch disappearance are presented below.

Fig.10. Process of scratch disappearance; images obtained by graphical operations; time interval between frames: 1 second.

Creation of the scratch is equivalent to the creation of the „channel”, which is the way for next particles movement. If size of the particles is bigger than size of the channel, process of secondary scratch creation appear.

Neural network was used for modeling of friction pair. Neural networks were chosen due to their features in relation to the character of tribological processes - especially the possibility of learning algorithms usage. Neural networks were used in the field of: Modeling of friction processes with and without hard particles as separate models; Modeling of friction processes with and without hard particles as coherent model; Creation of model for diagnostic (reverse model, used for detection of hard particles presence, on the basis of friction pair operating parameters). It is the substantial item for the creation of effective diagnostic tool used for detection of hard particles presence. Diagnostic is based on the model, where as inputs, measurable parameters of friction pair were chosen (especially friction force). Output it is the diagnostic answer: operation in the presence of hard particles or without them; Modeling of friction zone view (especially the presence of third body structures); Joining of measured and analyzed parameters (friction pair operating parameters, presence of hard particles, view of the friction zone and acoustic signal). Chosen example of modeling is presented below.

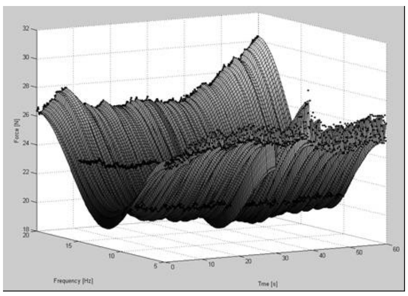

Fig.11. 3D model of friction force in dependence of inverter frequency (disc rotational speed) and time.

There was also acoustic analysis conducted. Test stand was modified, by add of acoustic chamber. Acoustical measurements were done with SVA 912 AE frequency analyzer. Program of the study assumed analysis of acoustic pressure for the following operating conditions: rotational speed of the disc: 140-1400 rpm, operation with hard particles, operation without hard particles, different load of the friction pair. Acoustic signal recorded during test runs, was treated by spectral analysis in the whole range of ear frequencies.

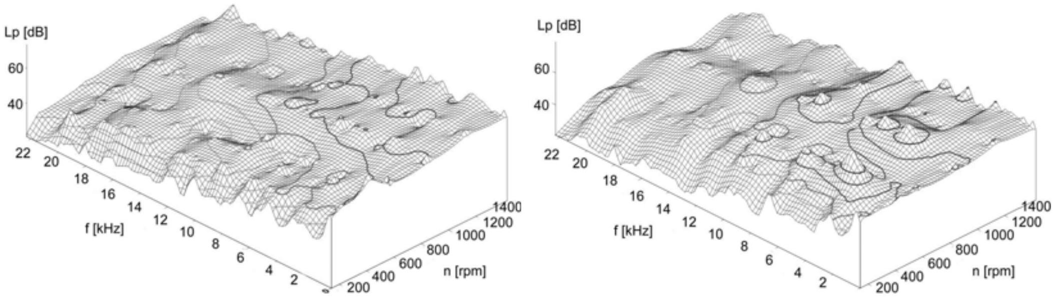

Fig.12. Variability of acoustic level pressure in relation to frequency for different rotation speeds of brake disc; operation with and without hard particles.

Recorded data were also FFT treated (for frequencies 0 to 22 kHz). Chosen spectrums are presented on figures below.

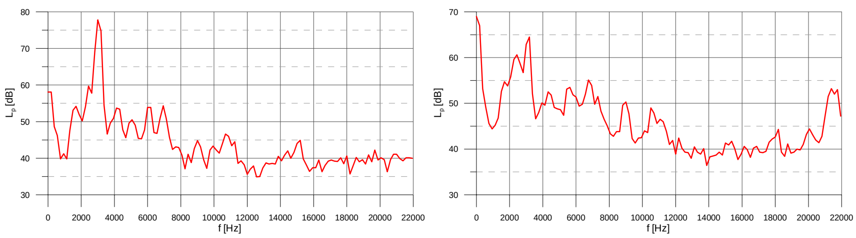

Fig.13. Acoustic pressure spectral analysis (disc rotational speed n = 85,5 rpm and n = 142,5 rpm).

Analysis of this study data, shows, that phenomena taking place in brake disc – brake pad friction pair find their acoustic response. Maximal acoustic energy is about 3000 Hz frequency and is almost independent on disc rotational speed. Next harmonicals of this signal (about f = 3000 Hz) occur after inclination of brake pad. In the ultrasound range, there are clearly elevated amplitudes (f=21 Hz) for chosen rotational speeds of brake disc.

Popularization of research results

Polak A., Grzybek J., The mechanism of changes in the surface layer of grey cast iron automotive brake disc, **59th ABM Congress**, Sao Paulo, Brasil, 2004
Polak A., Dryzek J., Grzych K., Changes in the surface layer of automotive sliding bearing investigated by positon annihilation technique, KONMOT 2004, September 2004, Zakopane, Poland
Polak A., Grzybek J., The mechanism of changes in the surface layer of grey cast iron automotive brake disc, **Materials Research**, Oct./Dec. 2005, vol. 8, no.4, p. 475-479, ISSN 1516-1439
Polak A., Grzybek J., Voinov K., Pytko S., Reuse of wear particles in automotive disc brakes, Proceedings of WTC2005:**World Tribology Congress III**, September 12-16, 2005, Washington, D.C., USA
Polak A. Grzybek. J., Thickness and distribution of the transfer film in journal bearing, Proceedings of WTC2005:**World Tribology Congress III**, September 12-16, 2005, Washington, D.C., USA
Paper: Reuse of wear particles in automotive disc brakes was submitted to the Tribology International and is under verification.
Polak A., Grzybek J., The method of friction mechanism investigation in the automotive disc brakes in the presence of hard particles, **Superior Friction and Wear Control in Engines and Transmissions**, Edit. K. Holmberg, COST, Porto 2005, pp. 231-239

Polak A., Grzybek J., Stolarski B., Noise, vibration and harshness in automotive disc brakes, **Austrib 2006**, 3-6 December 2006, Brisbane, Australia
Polak A., Grzybek J., Nabagło T., Neural networks application in modeling of the tribological processes, **Austrib 2006**, 3-6 December 2006, Brisbane, Australia
Two next papers are accepted for the year 2007:
Polak A., Grzybek.J, Oleksowicz S., Friction processes in automotive disc brakes in the presence of hard particles, ECOTRIB 2007, Lubljana, Slovenia
Polak A., Grzybek J., Oleksowicz S., Stand for automotive durability testing, Quality, Safety and Ecology in Vehicles, 18-19 June, Kraków, Poland

Conclusions

Study conducted in this project (2004-2006) proved earlier assumptions, basic for the project proposal. Planned work scope was realized and significance of hard particles presence for the tribological disc brakes behavior was proved.

Conclusions:

- Conducted investigations showed significant difference for brake disc operating with and without hard particles. This difference concerned friction force value, kind of wear processes and surface layer parameters. Presence of hard particles is essential for material transfer phenomena and for third body formation, thus influences processes basic for the brake disc operation.
- Basic mechanism of hard particles influence is based on the increase of the abrasive wear mode share in overall friction processes. This conclusion has a decisive meaning for the possibilities of technical improvements. This is connected with friction material composition and especially content of abrasive components.
- There are two possible mechanisms of hard particles influence. First case is three body abrasions, second – three body. Their occurrence depends on the friction material composition, size of the particles delivered and size of the gap between disc and pad.
- On the basis of obtained results stated, that for the operation in dusty environments friction material composition should be adjusted, by decrease of abrasive components and use of relatively soft matrix.
- From the design of brake mechanism it is essential to precisely control the gap between disc and pad in the not braking mode (brakes not applied).

Project co-operation

-

Planned or achieved industrial improvements in commercial use

-

Publications were project results are reported

1. *The mechanism of changes in the surface layer of grey cast iron automotive brake disc.* 58th AMB Congress, Brazylia, 2004
2. *Changes in the surface layer of automotive sliding bearing investigated by positon annihilation technique.* KONMOT 2004, Zakopane, Poland

3 *The mechanism of changes in the surface layer of grey cast iron automotive brake disc.* Materials Research, Oct./Dec. 2005, vol. 8, no.4

4 *Reuse of wear particles in automotive disc brakes.* World Tribology Congress III, USA, 2005

5 *Reuse of wear particles in automotive disc brakes.* Paper was submitted to the Tribology International and is under verification.

6 *Thickness and distribution of the transfer film in journal bearing.* World Tribology Congress III, USA, 2005

7 *The method of friction mechanism investigation in the automotive disc brakes in the presence of hard particles.* Superior Friction and Wear Control in Engines and Transmission, Portugalia, 2005

8 *Modeling of friction mechanism in automotive disc brakes.* Dubrovnik, 2005

9 *Neural networks application in modelling of the tribological processes.* Austrib 2006, Australia

10 *Noise, vibration and harshness in automotive disc brakes related to the presence of hard particles.* Austrib 2006, Australia

11 *Friction processes in automotive disc brakes in the presence of hard particles.* ECOTRIB 2007, Ljubljana, Slovenia

12 *Reliability improvement of automotive disc brakes operating in dusty environment.* Quality, Safety and Ecology in Vehicles, 18-19 June 2007, Kraków, Poland

TS10 - CONTROL OF FRICTION AND WEAR BY USE OF APPROPRIATE MATERIALS, COATINGS AND LUBRICANTS

Co-ordinator and partners

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Project status and schedule

Running with partial funding
Starting and ending dates 1st January 2003 - 1st January 2007

Project aims

The aim of the study is to find out optimal combinations of materials, coatings and lubricants for the critical tribosystems of engines and transmissions in order to achieve higher energy efficiency and prolonged component lifetimes. Applicability of different materials and surface modification and coating processes for engine and gearbox components will be examined. Important part of this research considers formulation of transmission lubricants that will improve gears efficiency in extreme operating conditions with extended working time. As transmission lubricants are applied in diverse application it is necessary to develop more lubricant types for automotive and industrial transmissions application.

Project results

One team in the project works on modification of tribological layers deposited by plasma spraying by use of sol-gel process. As a substrate we used Al_2O_3 coatings. The equipment for sol-gel process was designed and produced.

We used Zr - precursor $Zr(O\text{-}nC_4H_9)_4$ as a material for deposition by sol-gel process at Al_2O_3 substrate. The process parameters we changed are: velocity, viscosity and crystallization temperature. Tribology tests of specimens and materials characterization showed that Zr layer on Al_2O_3 substrate significantly reduce coefficient of friction.

Second team in project works on development of new oil formulations for application in industrial and car transmission.

For **industrial gear** oils we formulated two types of transmission oils:

- F1 SPS 680 - synthetic EP gear oil, polyalphaolefins and S-P additive
- F2 SPM 680 - mineral oil and molybdenum disulphide (CLPF)

Both types satisfy all requirements of specifications for industrial oils even those listed in US Steel 224.

For **application in automotive** we developed three new transmission oils:

- F1 HD 75W-80 is part synthetic multigrade type for application at high and low temperatures up to – 40^{o}C
- F2 LS 90 is mineral monograde transmission oil with especial additivation for limited slip
- F3 TDL 80W-90 is multigrade mineral oil based transmission fluid for total drive line-wide temp. range -26^{o}C (approved by MAN and ZF and included in several lists)

This second team already finish their work.

Project co-operation

We had a lot of contacts by email and phone with Dublin Institute of Technology, Dublin, Ireland and EMPA Switzerland. Partners from Ireland and Switzerland visited us several times. Substrate material for specimens has been prepared in Croatia and the different types of coatings were made in laboratories in Ireland and Switzerland.

Very good collaboration with Institute for Terotechnology in Radom, Poland and VITO, Mol, Belgium resulted with three COST Short term scientific missions. Researchers from Croatia were tested the specimen in Poland and Belgium and were introduced with the new methods for materials characterization.

Planned or achieved industrial improvements in commercial use

Planned industrial improvements in commercial use were new types of automotive and industrial gear oil lubricants and improvement of tribological properties of coatings. These improvements are not in commercial use yet.

Publications were project results are reported

PEER REVIEWED JOURNAL ARTICLES

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TS11 - GREASE FOR SLIDING SPRING

Co-ordinator and partners

Co-ordinator :

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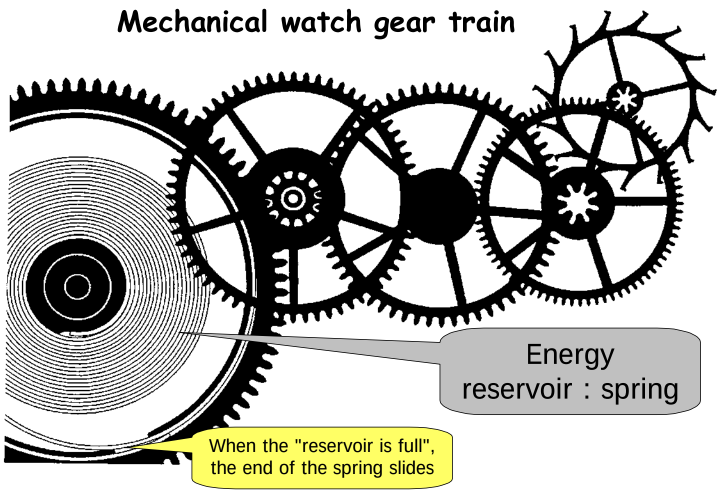
Industrial partners : 16.

Project status and schedule

Project is nearly finished.

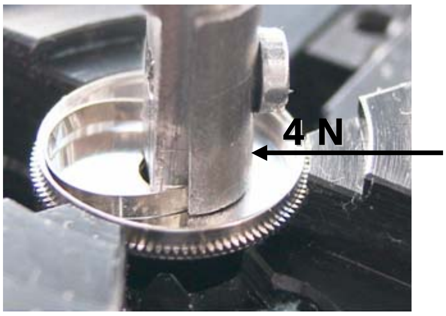
Project aims

The present project aims to obtain the best possible grease for the delicate lubrication of the sliding spring used in mechanical watches.
The mechanical watches avoid the use of batteries. For more convenient use, the mechanical watches have a self- winding system based on a eccentric mass oscillating when the arm moves. The obtained mechanical energy is stored by the compression of a spring. When this "reservoir" is full, the spring of the self-winding mechanism must slide to avoid damages. This sliding is helped by the use of very special greases. The actually used grease is not perfect and may be no longer available.

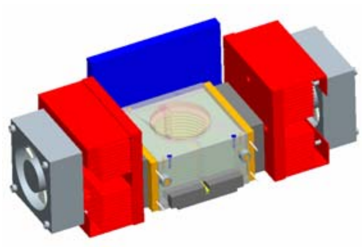


Project results

A pin-on-disk tribometer was modified to measure the friction directly between a portion of a spring and the barrel wall. The friction coefficient is measured as a function of sliding speed from 0.07 to 230 mm/s. The wear is evaluated after 15000 revolutions at 11 mm/s.

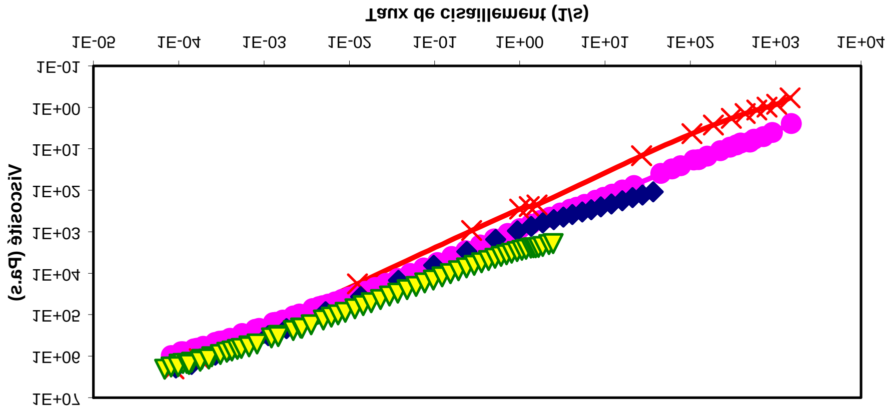


A micro-chamber was developed to evaluate the effect of the temperature on such mechanisms directly on the torque measurement device. The temperature can be easily stabilised between 8°C and 40°C.

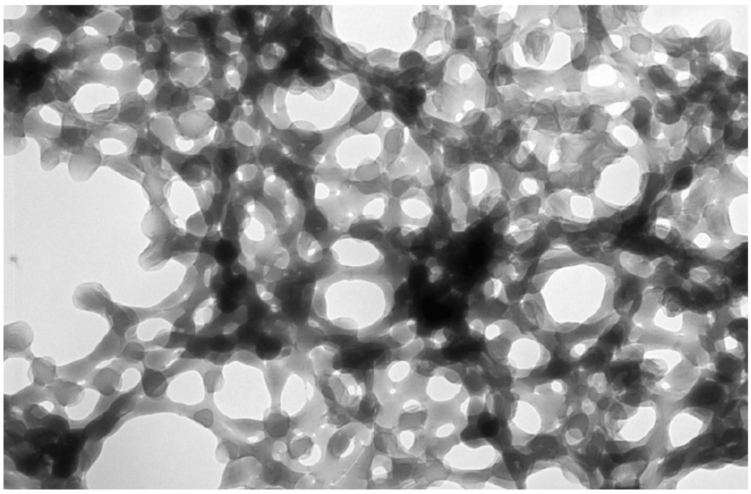


In a first step, the composition and behaviuor (ageing, tribology, rheology) of the actually used lubricants and of older lubricants was evaluated. The figures below show some examples of results.

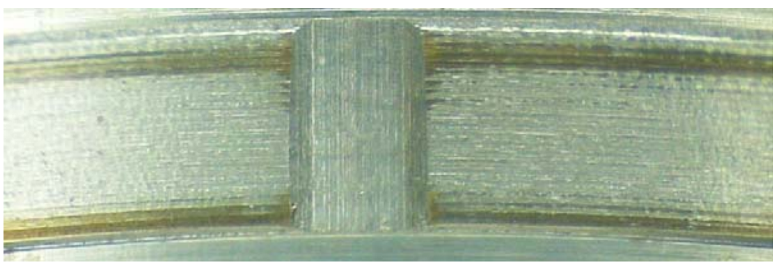
Rheology



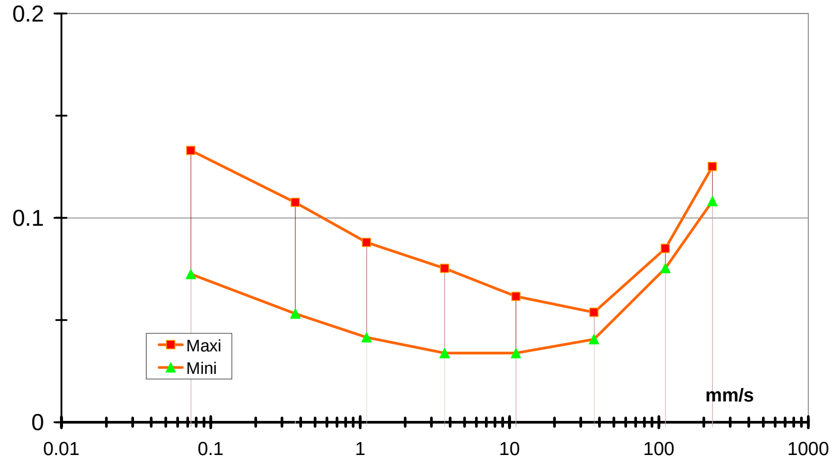
TEM image of one of the greases.
(Real size: 2.6 µm x 4 µm)



Wear damage after 15 000 revolutions on a Rhodium coating on brass



Friction coefficient as a function of sliding speed for one of the greases, tested on a gold alloy coating. (This behaviour produces stick-slip.)



The requirements needed are very special for such greases. The sliding is generally made between the spring alloy against a coating of Rh or gold alloy or against oxidised aluminium.

The grease must protect against wear during many years, therefore the grease properties must be stable. With this grease, the **friction must be high** at high speed as well as at low speed, without stick-slip. The grease must be applicable with automatic devices for calibrated and reproducible quantities. Therefore the grease must be bubble free. The grease must adhere to the surface, therefore showing high tackiness, but the grease flow should be easily cut without building "fondue like" filaments.

More than 30 different grease prototypes were prepared by a watch lubricant manufacturer and more than 30 other prototypes prepared by the Laboratoire Dubois with different bases. All these greases were evaluated by tribological tests and by torque measurements.

After different composition changes and modifications, two prototypes of good greases where selected. The practical tests in real watches are starting. After these long tests the final grease will be chosen. For each type of spring and barrel, the end part of the spring must be optimised according to the grease before practical use in corresponding watch mechanism.

Project co-operation

Co-operation used: e-mail contacts, periodic meetings with all the participants, researchers visits, joint presentations. Deliveries of reports in the form of CD containing all the documents explained during the meetings.

Publications where project results are reported

Confidential reports supplied to the participants only and following paper.
Greases for sliding springs, to be submitted to ECOTRIB 2007 Joint European Conference on Tribology and Final conference of COST 532 action : Triboscience and Tribotechnology, 12-15.6.2007 Ljubljana Slovenia, xp.

Planned or achieved industrial improvements in commercial use

Any new solution will need long testing before being applied in real mechanisms.

TS12 - STUDY OF SURFACE PROCESSES IN PLASMA NITRIDING OF STAINLESS STEEL AT ATMOSPHERIC AND REDUCED PRESSURE

Co-ordinator and partners

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Project status and schedule

Running with partial funding.
Starting and ending dates: 2005 01 01-2007 12 30

Project aims

The technological aim is realization of plasma nitriding process in producing of nitride layer on steel surfaces and optimization of plasma nitriding parameters to obtain layers with best mechanical, tribological and corrosion properties.

The scientific aim is development of relationship between atmospheric and reduced pressure plasma process, nitrided surface structure and their tribological properties.

Project results

Two DC plasma systems for plasma nitriding at atmospheric and reduced pressure were developed. Plasma nitriding process is illustrated in fig. 1. Electrical and thermal characteristics of the plasma generators were established. The plasma source characteristics and the main working parameters (plasma temperature, velocity, etc.) were estimated (Table 1).

It was found that the mean temperature of the nitrogen or hydrogen plasma leaving plasma torch may be estimated by (1) and (2) equations, respectively.

$$T_f = 13\left(\frac{I^2}{Gd}\right)^{0,28} \quad (1), \qquad T_f = 78\left(\frac{I^2}{Gd}\right)^{0,12} \quad (2).$$

Plasma nitriding of selected austenitic (AISI 304 Fe70Cr19Ni11) and high speed tool (P6M5 Fe70Cr4W6Mo5V2) steel surfaces employing atmospheric pressure plasma has been done. Various nitrogen and nitrogen/hydrogen mixture gas flow rates were used and different plasma torch regimes were selected. The plasma nitrogen treatment were realized using various condition and processes parameters (spray distance, arc current, voltage, substrate temperature, time).

Results of studying the influence of plasma nitriding parameters on microstructure and thickness of nitrided layers were evaluated and characterized using scanning electron microscopy (SEM) and glacing-angle X-ray diffraction (XRD). The surface morphology and cross section of steel samples were characterized using SEM. The phases formed near the surface were identified by XRD (Cu-K radiation).

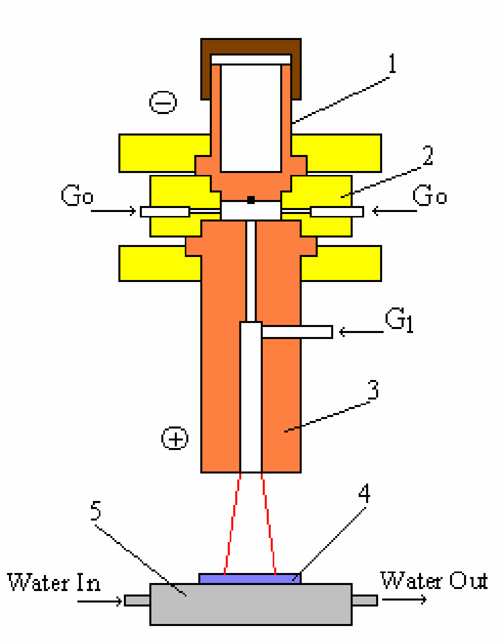

Fig. 1. Schematic diagram of the DC plasma torch: 1 – cathode, 2 – plasma forming (N_2) gas injecting ring, 3 – anode, 4 – sample, 5 – sample holder, G_0 – nitrogen gas injection places, G_1 – hydrogen gas injection place.

Table 1. Plasma torch parameters.

Parameters	Gases	
	Nitrogen	Hydrogen
Power, (kW)	1,2-4,7	2-3,2
Current (*I*), (A)	7-75	18-26
Voltage (*U*), (V)	65-170	90-140
Efficiency (η)	0,3-0,59	0,045-0,13
Flow rate of the working gas (*G*), 10^{-3} kg/s	0,1-0,4	0,0046-0,0157
Temperature of the gas leaving plasma torch, T_f (K)	3500-6200	1600-1870
Velocity of the plasma jet, W_f (m/s)	150-440	24-80

The surface layer of AISI 304 steel after nitrogen-hydrogen plasma treatment become rough and contains micrograins as can be seen from Fig. 2. A nitrided layer formed over the diffusion zone of austenitic stainless steel causes significant reduction in penetration depth of nitrogen and should be improving. Fig. 3 shows the presence of "white"layer up to 250 µm of thickness for the steel P6M5 treated employing two different ratios of N_2/H_2. Plasma nitriding in a N_2/H_2=25/1 gas mixture resulted the highest nitrogen penetration depth; however the homogeneity of the layer was significantly lower. The bigger amount of H_2 decreased the thickness of "white"layer up to 200 µm, increasing layer homogeneity. The existence of a nanocrystalline structure in the “white” layer seems to affect the nitrogen penetration mechanism significantly.

Table 2. Plasma nitriding conditions.

Sample No	Current, A	Voltage, V	N_2 flow rate, g/s	H_2 flow rate, g/s	Time, s
1	27,2	85	0,11	0,0045	300
2	27,8	81	0,11	0,0034	300
3	26,2	90	0,11	0,0048	300
4	28,6	52	0,11	0,0035	180
5	26,1	85	0,11	0,0048	600
6	26,4	83	0,11	0,0048	900

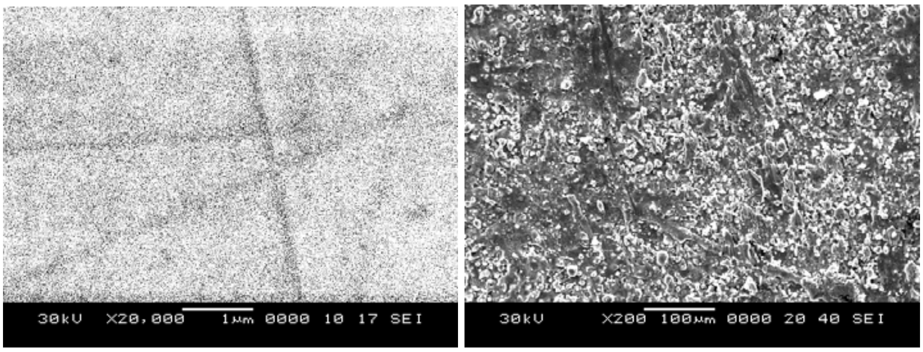

Fig. 2. SEM view of stainless steel surface: (left) before and (right) after plasma nitriding for 10 min at 450 °C.

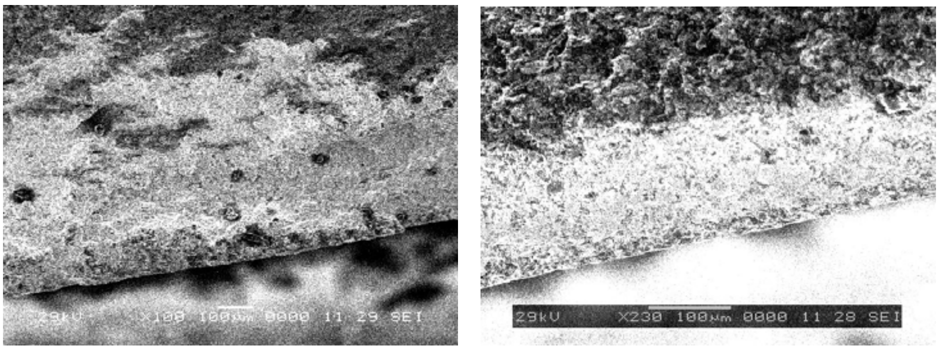

Fig. 3. SEM images of P6M5 steel surface zone after plasma nitriding in N_2-H_2 plasma in presence of additional cooling with nitrogen jet (left, sample No.2) and without additional cooling (right, sample No.1).

Increase of hydrogen gas flow rate during plasma nitriding influence formation of iron nitrides and carbides with alloying elements such as molybdenum (Fe_3Mo_3N) and wolfram (Fe_3W_3C). The highest intensity peak of specimen No.1 belongs to the untreated steel iron phase (fig. 4). Strong peaks of the hafnium oxide were found on a specimen No.2 surface layer nitrided at higher N_2/H_2 gas rate. X-ray diffraction pattern of the sample 2 also shows small intensity iron nitride (FeN) and iron molybdenum nitride (Fe_3Mo_3N) peaks.

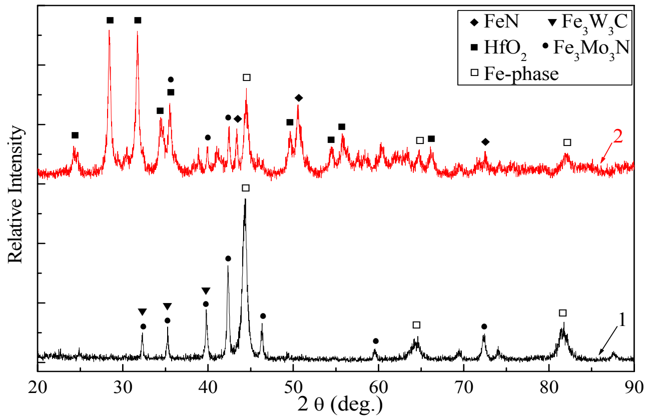

Fig. 4. XRD diffraction spectra of nitrided P6M5 steel.

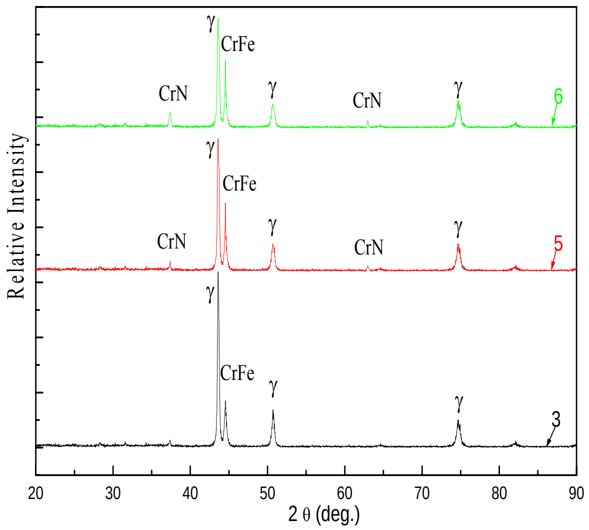

Fig. 5. XRD diffraction spectra of nitrided AISI 304 steel samples.

The XRD patterns of the surfaces modified the austenitic stainless steel using different nitriding times are shown in figure 5. The obtained diffraction pattern shows the presence of three peaks, the peaks at 43.6^o, 50.7^o and at 74.7^o witch clearly represent austenitic (γ) phase. However the exact same phase peaks were observed on untreated AISI 304 steel samples. All samples show CrFe phase on surface. Small intensity peaks of CrN were found on samples No. 5 and No. 6. The intensity of these peaks increases increasing nitriding time. Increase of CrFe phase and appearance of CrN phase in the surface layer, is due to introduction of nitrogen in surface layer. Formation of CrN probably related with increase of surface temperature during the longer nitriding process. At high temperature more Cr can bond with iron and with incoming nitrogen. Formation of CrN on surfaces layer is undesirable phenomenon, because decreasing the corrosion properties of stainless steel.

The influence of the nitriding temperature on steel samples during plasma nitriding operation is still under the investigation. Experiments were done at various plasma torch powers; due to variation of plasma temperature. The main process parameters are given in table 3. The coatings surface phase conversation will be investigated by XRD. The surface hardness measurement of the nitrided samples will be done to find relationship between nitriding temperatures and steel layer hardness. These results intend to be presented at the ECOTRIB 2007 conference.

Table 3. Process parameters.

Sample No	Current, A	Voltage, V	N_2 flow rate, g/s	Distance, m	Temperature, ^oC	Time, s
7	15	98	0,11	0,03	350	900
8	29	78	0,11	0,03	450	900
9	36	80	0,11	0,03	700	900
10*	15	98	0,11	0,03	400	900

*-nitriding was done without cooling of the sample.

It's well known that nitriding temperature plays a major role in the nitriding process. In this response the nitrogen plasma temperatures at various distances from plasma torch – substrate were measured. The measurements were done employing X-A thermocouples. Profiles of the substrate temperatures obtained at different distances and various plasma troche powers showed a very large temperature gradient in vertical direction which strongly results nitriding process.

Appearance of the micrograins on the surface of the samples after plasma nitriding can be seen from fig. 6. It is visible that after plasma treatment at various substrate temperatures (from 350 ^oC to 700 ^oC), the formation of micrograins on the surfaces originated. It may be noted that surfaces are rougher compared to an untreated steel sample. SEM micrographs indicate existence of the white zone, which may be associated with formation of the iron nitrides on the surface layer.

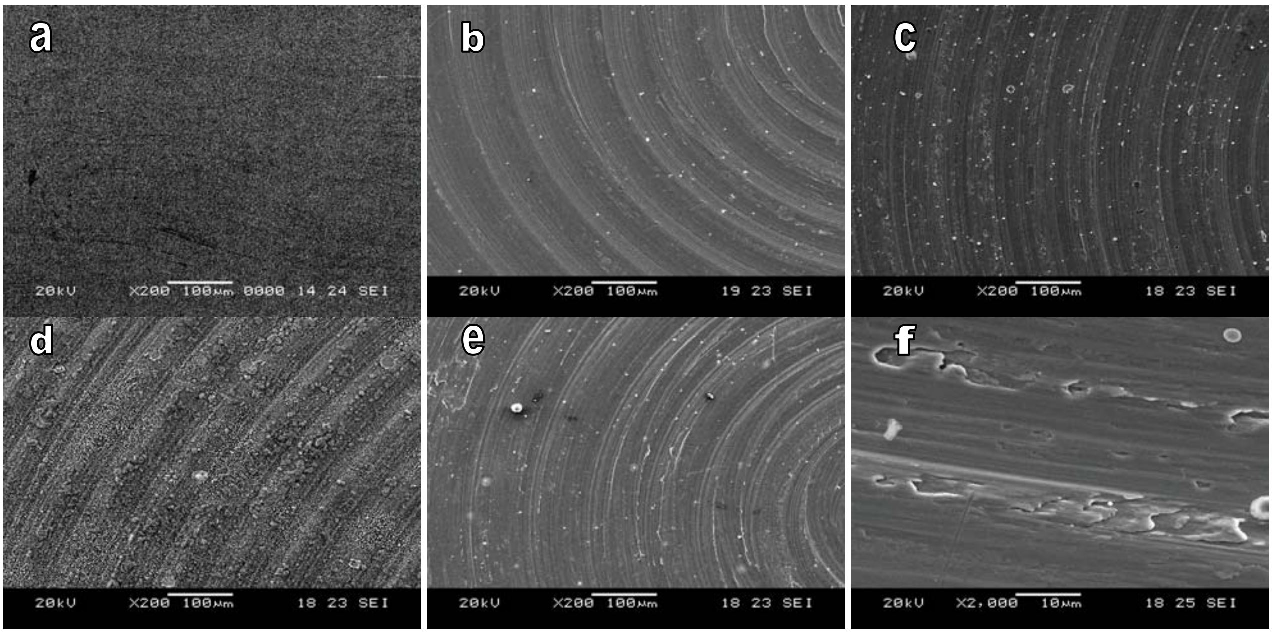

Fig. 6. SEM images of AISI 304 steel surfaces after plasma nitriding in N_2 plasma, a) before plasma nitriding, b) No. 7, c) No. 8, d) No. 9, e) and f) No. 10.

Project co-operation

Mention the forms of co-operation used: e-mail contacts, meetings, seminars, researchers visits, joint publications, joint presentations, COST Short Term Scientific Missions etc

Industrial improvements in commercial use

1) Development of new technology for the surface nitriding of austenitic steels based on plasma method.
2) Reduction of friction face between the sliding surfaces of machine parts.
3) Improving of hardness and wear resistance of metals and alloys.

Publications were project results are reported

1. Marcinauskas L., 2004, Operating characteristics of the DC plasma source at atmospheric and low pressure conditions, Thermal Engineering and Technologies. Proceed. of the Conf., Kaunas, p. 209-212. (In Lithuanian).
2. Valincius V., Krusinskaitė V., Valatkevicius P., Valinciutė V., Marcinauskas L., 2004, Electric and thermal characteristics of the linear, sectional DC plasma generator, Plasma sources science and technology, Vol.13, No.2, p. 199-206.
3. Marcinauskas L., 2005, Surfaces modification processes employing plasma, Thermal Engineering and Technologies. Proceed. of the Conf., Kaunas, p. 128-131. (In Lithuanian).
4. Valincius V., Marcinauskas L., Valatkevicius P. The nitriding of steel alloys employing atmospheric pressure plasma // COST 532 Conference: Triboscience and Tribotechnology Superior friction and wear control in engines and transmissions, integrated with NIST Conference: Integrated engineered surface technology to reduce friction and increase durability. FEUP/ISEP, Porto, Portugal, 2005. P. 243-248.
5. Marcinauskas L., 2006, Influence of plasma flow parameters on modification of material surfaces, Thermal Engineering and Technologies. Proceed. of the Conf., Kaunas. (In press, in Lithuanian).
6. Marcinauskas L., Valincius V., Valatkevicius P., Grigonis A., 2006, Investigation of single-chamber linear plasma torch characteristics heating monatomic and diatomic gases. Power Engineering. Vol.1 P.36-41.
7. Valatkevičius P., Marcinauskas L., Valinius V. Surface modification of steel alloys by nitrogen-hydrogen plasma // International Conference Plasma Physics and Plasma Technology PPPT-5, Minsk. Belarus, September 18-22, 2006 contributed papers. Volume II (section 4-6). P. 471-474.
8. Kavaliauskas Z, Marcinauskas L, 2007, Variation of the surface temperature during the plasma nitriding, Thermal Engineering and Technologies. Proceed. of the Conf., Kaunas, p. (In Lithuanian).(In press).
9. Marcinauskas L., Valatkevicius P., Valinčius V., The nitriding of steels by nitrogen-hydrogen plasma using plasma torch. "submitted to ECOTRIB 2007 Joint European Conference on Tribology and Final conference of COST 532 action: Triboscience and Tribotechnology, 12-15.6.2007, Ljubljana, Slovenia, x p.".

TS13 - WET CLUTCH TRIBOLOGY

Co-ordinator and partners

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Partners:
Haldex Traction AB, Sweden, http://www.haldex-traction.com/default.htm
Statoil Lubricants R&D, Sweden, http://www.statoillubricants.com

Project status and schedule

Start date: 1 January 2001
End date: 31 December 2005

Project aims

The aim of this project is to gain knowledge about the frictional performance and lubrication regimes in these types of applications, and thereby be able to optimise the lubricant and the clutch control software to minimize variations in transferred torque.

Project results

A test apparatus, which is able to monitor friction and temperature as a function of applied force, sliding velocity and oil flow have been developed and is operational at Luleå University of Technology. A cooling system is also installed in order to enable low temperature investigations of friction. The designed test equipment has shown good repeatability and data quality, as well as good agreement with other equipments.

The friction-temperature behaviour of the clutch has been investigated under high clutch disc pressure conditions. The results obtained show that increase in the surface temperature lowers the friction by as much as 40% under typical operation conditions, Figure 1. Further investigations will evaluate means of reducing this influence in the coupling. The influence of clutch disc pressure on friction is quite moderate compared to the influence of temperature and sliding velocity. The influence of velocity on friction is governed by the transmission fluid and friction material used in the clutch.

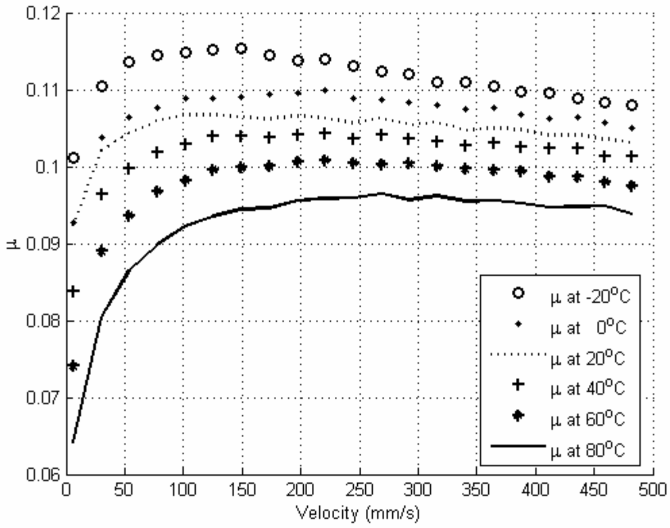

Fig. 1. Friction-velocity characteristics measured at different initial temperatures.

The friction-velocity relationship is a good indicator of the fluid's ability to suppress friction induced vibrations. It is, however, important to measure the friction-velocity relationship at constant temperature, or to compensate the relationship for temperature effects.

A method for measuring and presenting anti-shudder properties has been developed. The friction is presented as a discrete function of velocity at a constant temperature. By using this method it is possible to compare anti-shudder properties obtained under different conditions, since the data are not influenced by the chosen test conditions, Figure 2.

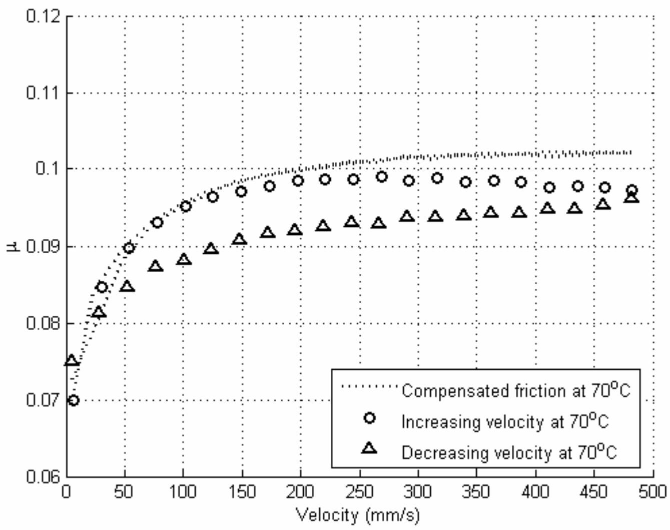

Fig. 2. Friction characteristics measured during speed increase and speed decrease, and the same two curves compensated for the different conditions during measurements.

Base oil type and viscosity have been found not to significantly influence friction characteristics of a wet-plate clutch, indicating that the torque is primarily transmitted by asperity contacts rather than fluid films. Oil additives, on the other hand, have a considerable influence on friction, again leading to the conclusion that tribolayers on contacting asperities rather than fluid films govern friction. From these observations it can be concluded that the lubrication regime under the conditions studied are boundary lubrication, moving into mixed lubrication at high velocities and low temperatures.

A successful method to develop transmission fluids has been developed. Formulated fluids allow good anti-shudder properties to be combined with good lubrication performance for other machine elements present in the transmission. Interactions between different additives must be considered which can, in many cases, completely alter the friction characteristics since additives compete for the same adsorption surface. Extreme pressure additives have been found to be particularly troublesome when used in combination with other additives as far as their ability to maintain good anti-shudder properties is concerned.

A study of the influence of porosity and wear of the sintered friction material on friction characteristics have been carried out. The results from this study shows that the friction discs in a wet clutch play an important part in the anti-shudder performance of the clutch, and that it is possible, by characterizing the topography and calculating the parameters S_{sc} and S_{dq}, to predict the remaining lifetime of a sintered friction material in a wet clutch.

Based on the knowledge of clutch performance obtained from the research presented in this thesis, a model to predict transmitted clutch torque has been developed. This accurately determines the transferred torque from the current operating conditions and the thermal history of the clutch, Figure 3. It can be concluded that thermal effects have a significant influence on the torque transferred by the clutch, and it is therefore necessary to have a thermal model of the clutch combined with a temperature dependant boundary friction model based on empirical friction data for the friction material/transmission fluid combination of interest.

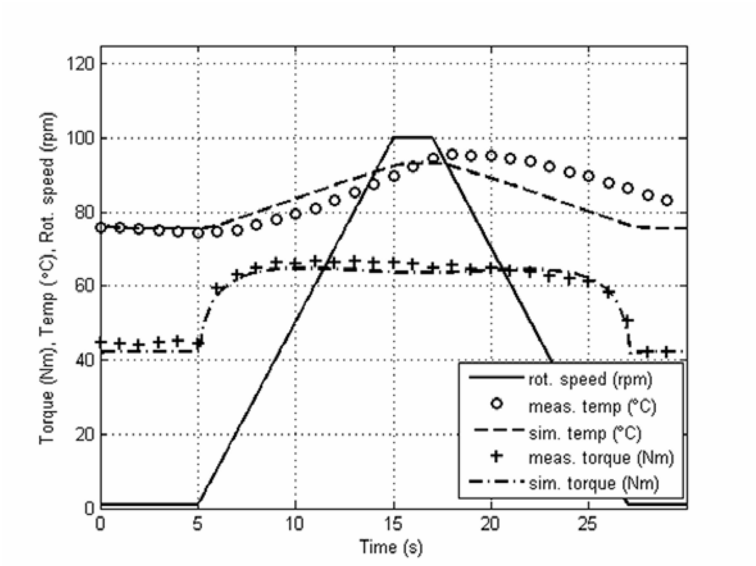

Fig. 3. Comparison between measurements and simulation with an axial force of 25.3kN.

Project co-operation

All work in this project is carried out in close cooperation with Haldex Traction Systems AB and Statoil Lubricants R&D.

Project meetings twice a year, e-mail contacts, informal meetings, seminars, researchers' visits, joint publications and joint presentations have been used to discuss results and future work.

Planned or achieved industrial improvements in commercial use

The aim of this project is to gain knowledge about the frictional performance and lubrication regimes in these types of applications, and thereby be able to optimise the lubricant and the clutch control software to minimize variations in transferred torque.

A test apparatus, which is able to monitor friction and temperature as a function of applied force, sliding velocity and oil flow have been developed and is operational.

The friction-temperature behaviour of the clutch has been investigated under high clutch disc pressure conditions. The results obtained show that increase in the surface temperature lowers the friction by as much as 40% under typical operation conditions, Figure 1.

A method for measuring and presenting anti-shudder properties has been developed. The friction is presented as a discrete function of velocity at a constant temperature. By using this method it is possible to compare anti-shudder properties obtained under different conditions, since the data are not influenced by the chosen test conditions, Figure 2.

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Thus, the project has led to both new design of wet clutches for use in four-wheel drive cars and to new fill-for-life lubricants formulated to give improved traction.

Publications were project results are reported

Journal Articles:

1. Ganemi B., Mäki R., Ekholm K., Olsson R., and Lundström B., 2003, "Limited Slip Wet Clutch Transmission Fluid for AWD Differentials; Part 2: Fluid Development and Verification", SAE Technical Papers, Paper number: SAE 2003-01-1981 / JSAE 20030121.
2. Mäki R., Ganemi B., Olsson R., and Lundström B., 2003, "Limited Slip Wet Clutch Transmission Fluid for AWD Differentials; Part 1: System Requirements and Evaluation Methods", SAE Technical Papers, Paper number: SAE 2003-01-1980 / JSAE 20030119.
3. Mäki R., 2003, "Wet Clutch Tribology – Friction Characteristics in All-Wheel Drive Differentials", TRIBOLOGIA – Finnish Journal of Tribology, vol. 22, pp. 5-16.

4. Mäki R., Nyman P., Olsson R. and Ganemi B., "Measurement and Characterization of Anti-Shudder Properties in Wet Clutch Applications", SAE Technical Papers, Paper number: SAE 2005-01-0878, 2005.
5. Mäki R., "New Demands Driving New Technology; A literature Review of Research into the Behaviour and Performance of Wet Clutches". Submitted for publication

Conference Articles:

1. Mäki R., "Apparatus for Measurement of Friction Surface Temperature in a Wet Clutch." Proc 2nd World Tribology Congress, Vienna, 2001.
2. Mäki R., Ganemi B., and Olsson R., 2002, "Wet Clutch Transmission Fluid, Development Method", presented at NordTrib 2002, Stockholm, Sweden.
3. Mäki R., Ganemi B., and Olsson R., 2004, "Wet Clutch Transmission Fluid for AWD Differentials; Base Fluid Influence on Friction Characteristics", presented at Tribology and Lubrication Engineering, Esslingen, Germany.
4. Mäki R., Ganemi B., Trivino, F. R. and Olsson R., 2004, "Wet Clutch Transmission Fluid for AWD Differentials; Influence of Lubricant Additives on Friction Characteristics", presented at Tribology and Lubrication Engineering, Esslingen, Germany.
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Thesis Reports:

1. Mäki R., 2003, "Wet Clutch Tribology – Friction Characteristics in All-Wheel Drive Differentials", Licentiate Thesis, ISSN: 1402-1757, Luleå University of Technology.
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3. Nyman P., 2004, "Utredning av friktionsmaterialets topografi och sammansättnings inverkan på våta kopplingars tribologi", Master Thesis MMK 2004:20, KTH, Royal Institute of Technology.
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5. Mäki R., 2005, "Wet Clutch Tribology – Friction Characteristics in Limited Slip Differentials", Doctoral Thesis, ISSN: 1402-1544, Luleå University of Technology.

TS14 - TRIBOLOGICAL AND MECHANICAL CHARACTERISTICS OF SHOT PEENED AUSTEMPERED DUCTILE IRON GEARS

Co-ordinator and partners

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Project status and schedule

Running with partial funding
Starting and ending dates

Project aims

Many gears are first machined from steel blanks and then carburised. This method of manufacture though costly, offers the combined advantage of a tough core and hard skin.

The aim of the project is to replace steel gears in automotive industry by the less costly austempered ductile iron (ADI) while maintaining the tribological performance of steel counterparts. The study seeks to achieve this by applying surface treatments such as shotpeening and surface coatings / modification to ADI.

Project results

Introduction

The purpose of this study is to improve the fatigue and wear properties of Austempered Ductile Iron (ADI) gears, by shot peening. These properties should be comparable to case-carburized gears, commonly used in industry.

The properties of ductile iron can be improved by an austempering heat treatment cycle. The iron is first austenitized at temperatures and for periods depending on the chemistry, section thickness and final structure and properties required and then quenched in the austempering bath and held for a predetermined period. The resulting iron is called austempered ductile iron, ADI.

Project Results

As – cast material

Keel blocks of ductile iron were cast having the composition as shown in Table 1, and having nodularity greater or equal to 90%, and a nodule count of around 200/mm^2.

Table 1. Composition of cast material.

C	Si	Mn	P	S	Ni	Cu	Mg	Fe
3.32	2.32	0.22	0.034	0.008	1.56	1.61	0.06	Bal

As - austempered iron

Some samples were austempered in the higher temperature region thus producing grade 1 iron with high toughness and ductility. This resulted in properties similar to those required by the bulk material but did not yield desired surface properties such as fatigue. The fatigue strength was then improved by inducing surface compressive stresses by shot peening. Lower ausferritic iron samples (grade 2 irons) were also manufactured in order to compare properties with those austempered at higher temperatures.

An austenitizing temperature and time of 900°C and 2 hours were selected based on previous studies [1], while an austempering temperature and time of 240°C and 3 hours were chosen to obtain a Grade 1 iron, while 360°C and 1 hour were chosen to obtain a Grade 2 iron.

Figure 2 is a summary of the impact energy values of ductile iron samples for two different grades of ADI. It can be seen that the impact energy of the as-cast nodular iron is rather low even though the nodularity of the iron is better then 90 per cent. In this case, the major factor determining the toughness of the iron is the matrix structure.

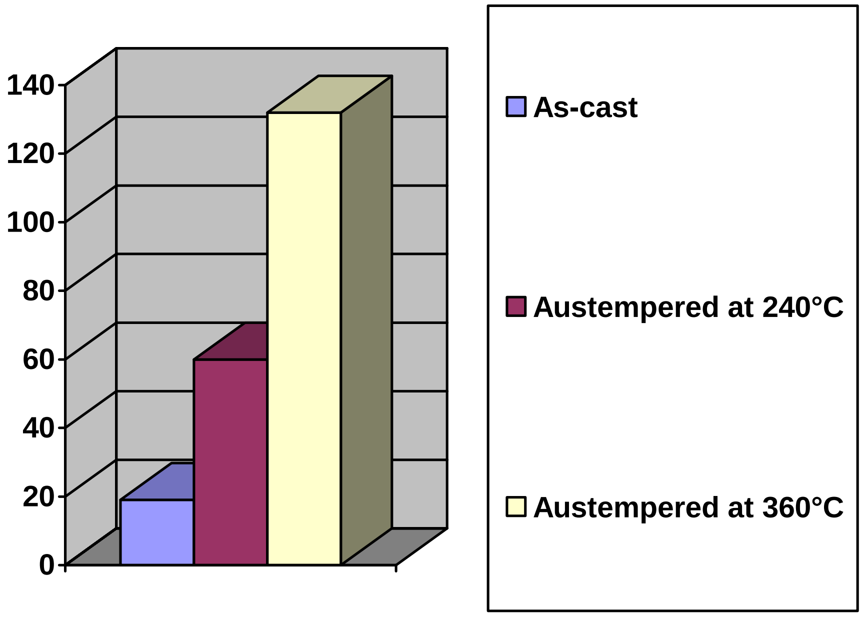


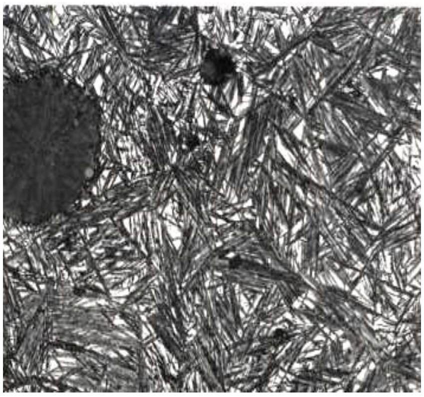
Fig. 1. Impact energy of nodular cast iron samples treated at different conditions.

Microstructure

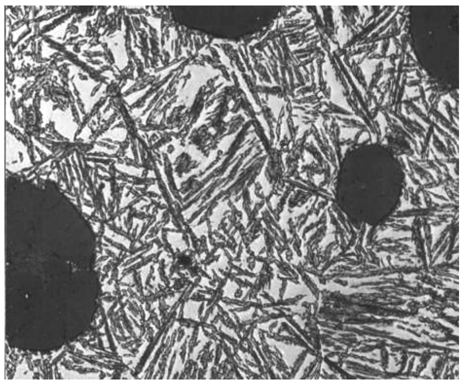
Figure 2(a) and (b) show the microstructure of samples austempered at 240°C and 360°C respectively. The specimen austempered at 240°C has an acicular structure characteristic of martensite in steel. Image analysis and XRD measurement showed that these structures contain 10.5% carbon and 16% austenite. At this temperature, the austenite occurs mainly in the form of slivers between adjacent ferrite plates. In comparison, structures austempered at 360°C have a coarser structure. In this case, the ferrite needles are short and have a smaller aspect ratio. The austenite content increases to 40% and is in a more equiaxed form. Neither of the two structures showed signs of martensite.

Table 2. Percentage microconstituents in austempered samples.

Condition	**Graphite (% vol.)**	**Retained austenite (% vol)**	**Martensite (% vol.)**
Austempered at 240°C	10	17	None
Austempered at 375°C	10	40	None



(a)



(b)

Fig. 2. Microstructures of samples austempered at (a) 240°C and (b) 360°C (X 500).

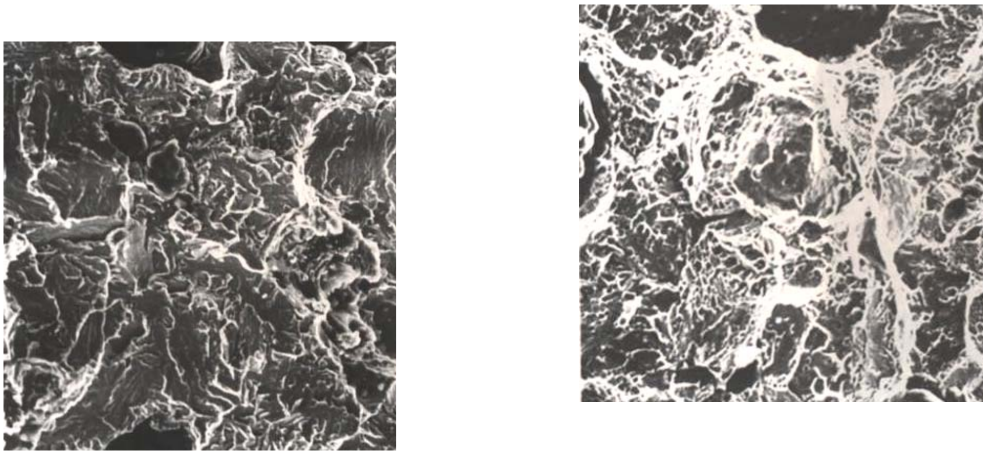
Impact energy, fracture toughness and hardness

Impact Energy

Figure 1 shows the difference in impact energy between samples treated at 240°C and samples treated at 360°C. The presence of large quantities of retained austenite is considered to be responsible for the high level of impact energy of the sample austempered at the higher temperature.

Fracture Toughness

Fractographs of samples austempered at 240°C and 360°C are shown in Figure 3. Samples austempered at the lower temperature show very few microvoids, in fact the fracture is mainly intergranular in nature. In comparison, surfaces of samples austempered at 360°C show extensive microductility. The high fracture toughness of the latter can again be explained in terms of the large content of stable high carbon austenite. The brittle fracture of the sample treated at 240°C is related to the lower austenite content and aggregate of carbides which form around the ferrite/austenite grain boundaries at temperatures higher then 350°C.



(a) **(b)**

Fig. 3. Fractographs of samples austenised at (a) 240°C and (b) 360°C.

Hardness

Figure 4 shows the difference in hardness between samples treated at 240°C and samples treated at 360°C. The high hardness of samples austempered at 240°C can be attributed to the closely packed highly acicular ferrite needles. The slow carbon diffusion is responsible for carbon being trapped inside the fast nucleating ferrite sheaves. On cooling to room temperature carbides form within the ferrite needles. It is also possible that the low carbon austenite transforms to martensite during the application of the hardness test. This would increase the stresses within the structure and consequently increasing the hardness still further.

The large quantity of stable high carbon austenite and coarse ferrite with practically no trapped carbon content is responsible for the low hardness of samples austempered at the higher temperature.

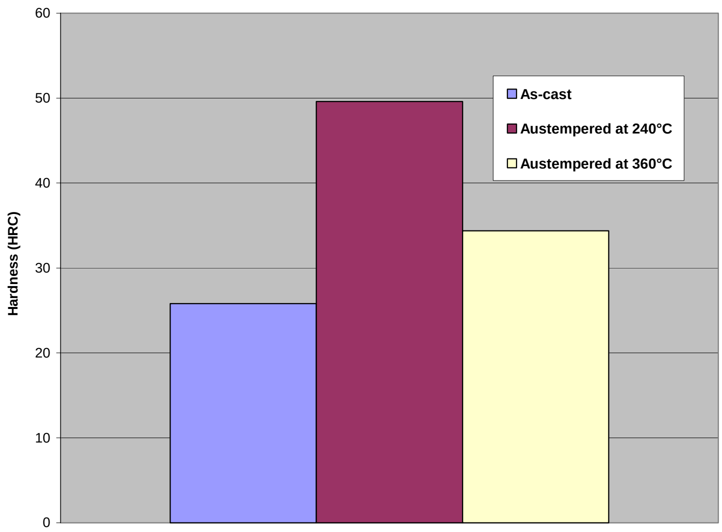


Fig. 4. Bulk hardness values of nodular cast iron samples treated at different conditions.

Austempered and peened samples

Samples were shot peened at the Dublin Institute of Technology and the University of Malta. Different shot peening process parameters such as shot coverage, and velocity of shot were studied. Breakdown of shot was controlled to avoid sharp-edged broken media. Angle of impingement was kept at 90°.

Shot peening is generally known to induce surface stresses. In particular to austempered ductile iron, the transformation of austenite to martensite caused by shot peening, results in a net volume increase leading to additional compressive stresses in the surface. These stresses help combat modes of failures such as fatigue, stress corrosion cracking and pitting.

Preliminary results show that shot peening increases the hardness of the surface. Figure 5 shows a typical hardness profile of a section of a shot peened sample.

Work in progress will also investigate different peening parameters such as shot size, shot hardness and nozzle stand-off distance.

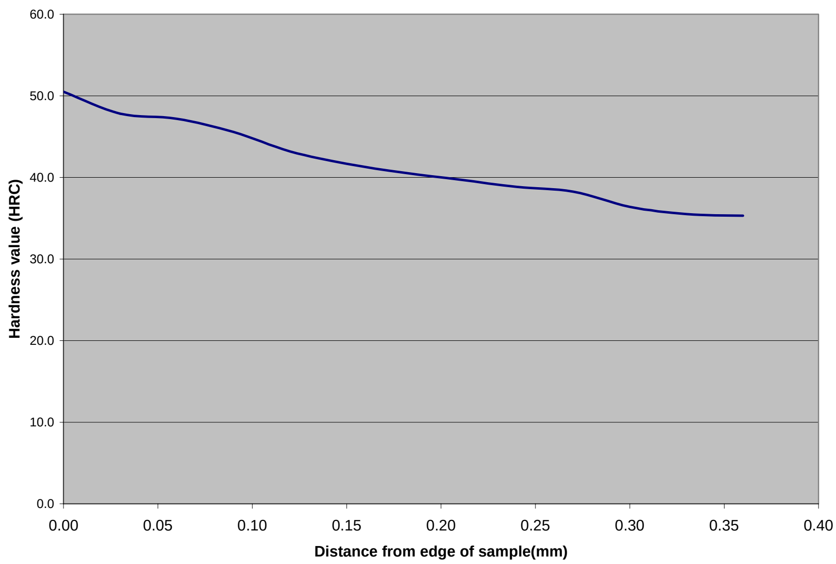


Fig. 5. Hardness profile of shot peened Grade 2 iron using S170 shots at a peening pressure of 6.5 bar.

Tribological Testing

Erosion Testing

Erosion tests were carried out at the University of Zagreb using the Whirling-Arm type rig. The test specimen was placed at the end of the arm and rotated at fixed speed in a closed chamber for a fixed time. Grit, also of controlled size and composition, was poured inside the chamber at a constant flow rate. The difference in mass of the test specimen before and after the test was calculated. Results for as-cast ductile iron, ADI, and shot-peened ADI samples were compared.

It is believed that Grade 2 irons are more erosion resistant than Grade 1 counterparts. Strain-induced martensitic transformation of retained austenite should also show superior erosion resistance [2].

Results obtained in this study and shown in Table 3 were however inconclusive. Further testing will therefore be carried out.

Table 3. Results of the erosion test.

Condition	**Sample**	**Initial Mass/g**	**Final Mass/g**	**Mass loss/g**
As-cast	1	41.3489	41.3451	0.0038
	2	41.3581	41.3543	0.0038
	3	41.3640	41.3613	0.0027
	4	41.4039	41.4006	0.0033
240°C	A	41.0558	41.0519	0.0039
	B	41.0932	41.0897	0.0035
	C	41.0808	41.0753	0.0055
	D	41.0775	41.0720	0.0055
240°C SP	E	41.0799	41.0757	0.0042
	F	40.9925	40.9909	0.0016
	G	41.1171	41.1125	0.0046
	H	41.6075	41.6050	0.0025
360°C	I	41.8258	41.8214	0.0044
	J	41.8627	41.8600	0.0027
	K	41.8200	41.8173	0.0027
	L	41.8075	41.8037	0.0038
360°C SP	M	41.8196	41.8156	0.0040
	N	41.8159	41.8128	0.0031
	O	41.7733	41.7701	0.0032
	P	41.8069	41.8037	0.0032

Abrasion Testing

The wear resistance in three-body abrasive tests is expressed by the term ß, the ratio of weight loss in a standard specimen of normalized steel to that of test sample [3].

$$\beta = \frac{\text{weight loss of the standard specimen (g)}}{\text{weight loss of the test specimen (g)}} \qquad (1)$$

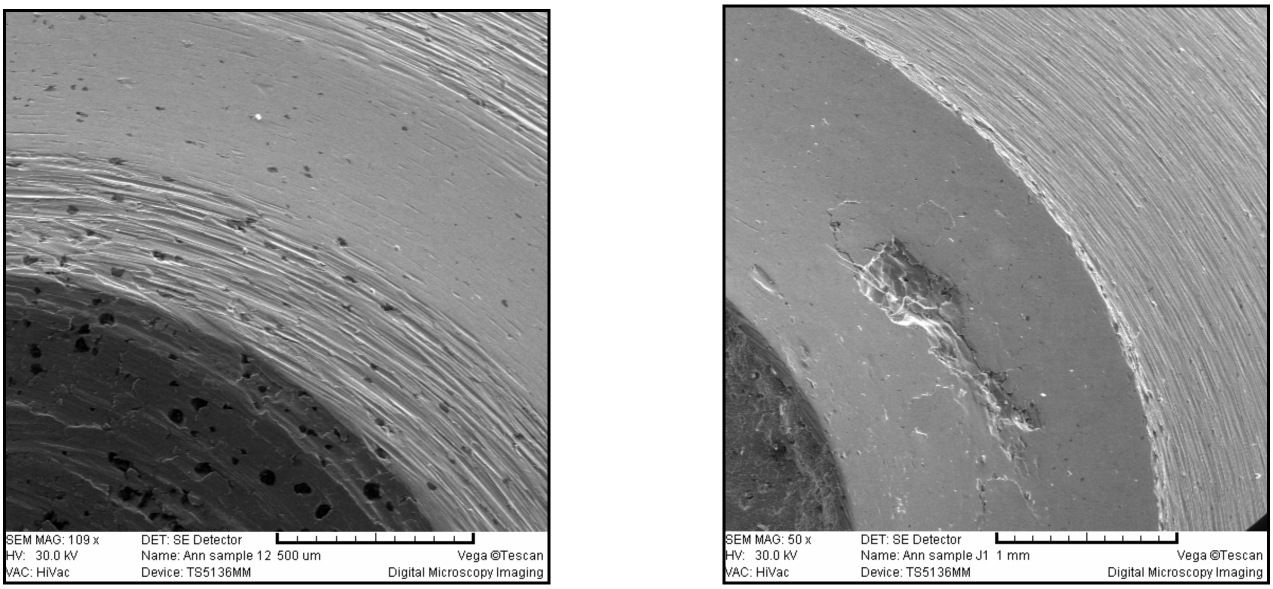
Abrasion tests involved the abrading of the test specimen with a grit of controlled size and composition. These tests were carried out at the University of Zagreb and were performed on the Dry Sand/Rubber Wheel apparatus.

Testing was carried out according to two different procedures Procedure 1 and 2. Abrasion testing was first carried out using a load of 130N and at a rotation of 2000 revolutions (Procedure 1). Procedure 2 was performed using a lower load and a lower number of revolutions namely 45N and 100 revolutions respectively. The results of these tests still need to be analysed.

Pitting Tests

Pitting tests using the Cone-Three Ball Pitting Test method were performed at ‘INA-Maziva’, in Zagreb, on as cast ductile iron specimens and shot peened ADI specimens. This test was carried out using a rotating cone made of the material under test, loaded against three steel balls which are allowed to rotate freely.

Preliminary results show that the best condition which withstands pitting is the shot peened iron austempered at 360°C and the time for pitting was much greater than the other samples which were treated at different conditions. This is thought to be due to compressive stresses created at the surface during shot peening which in turn prevent crack propagation. Further testing is required to assess the exact time when pitting starts under various test condition.



(a) (b)

Fig. 6. SEM micrographs of samples tested for pitting where(a) shows the wear track seen after testing and (b) shows pitting on one of the specimens.

Fatigue Tests

Fatigue tests will be carried out on a Rotating Bending testing system, to find the number of cycles to failure at a certain applied stress. As-cast ductile iron, as-austempered ductile iron, and shot peened austempered ductile iron will be tested and compared.

Construction of a Gear test rig

The construction of gear rig is currently in process. Case-carburized steel gears, together with austempered ductile iron gears and shot peened ADI gears will be tested on the gear-rig.

Conclusions

The low impact energy of the as-cast nodular iron can be improved by austempering.

Samples austempered at 360^{o}C exhibit high impact energy. This can be attributed to the high percentage of stable high carbon austenite. Fractured surfaces show extensive microductility.

The low impact energy of samples austempered at 240^{o}C can be attributed to the closely packed highly acicular structure and low austenite content. Fractures of these samples show very few microvoids and are in fact mainly intergranular in nature.

The high hardness of samples austempered at 240°C can be attributed to the closely packed highly acicular ferrite needles.

The increase in hardness of ADI samples following shot peening is attributed to residual compressive stresses induced in the surface and the stress induced transformation of the retained austenite to martensite.

Preliminary tests show that shot peened samples of irons austempered at 360°C exhibit best pitting resistance. This is thought to be due to surface induced compressive stresses which prevent crack propagation.

References

[1] M. Grech, P. Bowen, J.M. Young, Effect of austempering temperature on the fracture toughness and tensile properties of an ADI alloyed with Cu and Ni, University of Malta & University of Birmingham
[2]K. Shimizu, T. Noguchi, T. Yamaguchi, T. Kamada, AFS Trans, 63-94 (1994) 258-289
[3] Zhen-Lin Lu, Yong-Xin Zhou, Qi-Chang Rao, Zhi-Hao Jin, An investigation of the abrasive wear behaviour of ductile cast iron, Journal of Materials Processing Technology 116 (2001) 176-181

Acknowledgements

Our thanks go to all the staff at INA Masiva in Zagreb, for all their help and availability in assisting us to carry out the pitting tests.

Project co-operation

Mention the forms of co-operation used:
The three partners, mentioned above are in contact by emails and phone calls.
Ductile Ion Castings were purchased from **Castings Technology International, United Kingdom.**
Machining carried out at the **University of Malta, Malta.**

Heat treatment was carried out at **Surface Engineering Ltd., Malta.**

Shots used for shot peening were purchased from **Trelleborg Sealing Solutions, Malta**, and **Campbell Machinery, Dublin**.

Shot Peening carried out at the University of Malta, Malta & Dublin Institute of Technology, Ireland.

COST Short Term Scientific Mission: Researcher Ms. Ann Tedesco Triccas from the University of Malta, visited the **University of Zagreb** to carry out abrasion and erosion testing, and **INA Masiva**, also in Zagreb to carry out pitting tests.

<u>Publications were project results are reported</u>

M. Grech, D. Kennedy, Z. Schauperl, Integrated Engineering Engineering Surface Technology To Reduce Friction and Increase Durability Program Of US Department Of Energy, 2005, "An Investigation On The Suitability Of Surface Engineered Austempered Ductile Iron As A Gear Material".

TS15 - TRIBOLOGICAL CHARACTERIZATION OF DUPLEX COATINGS WITH ADDITIONAL ION BOMBARDMENT

Co-ordinator and partners

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Project status and schedule

Running with full funding

Project aims

The aim of this study is determining optimal microstructure, mechanical and.tribological characteristics with several examples of advanced coating systems in order to increase the life of machine parts, prevent the hazards and to be used in new applications and on differnt type of steels, like heat sensitive steels.

Project results

A duplex surface treatment involves the sequential application of two surface technologies to produce a surface composition with combined properties. A typical duplex process involves plasma nitriding and the coating treatment of steels. In the paper are presented characteristics of hard coatings, type TiN, produced by classic technology PVD (physical vapour deposition) and IBAD (ion beam assisted deposition). The synthesis of the TiN film by IBAD has been performed by irradiation of Ar ions. The evolution of the microstructure from porous and columnar grains to densel packed grains is accompanied by changes in mechanical and physical properties. Subsequent ion implantation was provided with N ions. Wear tests were carried out using a pin-on-ring geometry with no lubrication. Varieties of analytic techniques were used for characterization, such as scratch test, calo test, SEM, XRD and EDAX. X-ray diffraction studies were undertaken in an attempt to determine the phases present, and perhaps an estimate of grain size from line broadening. The results were correlated with properties determined from mechanical and tribological characterisation. The substrate material used was high speed steel, type S 6-5-2. Prior to deposition the substrate was mechanically polished to a surface roughnes of 0.12 In order to produce good adhesion of the coating, the substrates were plasma nitrided at low pressure. The PVD treatment was performed in a Balzers Sputron installation with rotating specimen. The other samples were produced with IBAD technology in DANFYSIK chamber. After deposition, the samples were irradiated with 22 keV, N^{2+} ions at room temperature (RT). N^{2+} ions were supplied by an electron cyclotron resonance (ECR) ion source. The implanted fluences were in the range from 0.6×10^{17} to 1×10^{17} ions/cm^2. Scratch adhesion testing was performed using commercially available equipment (REVETEST CSEM). X-ray diffraction studies were undertaken in an attempt to determine the phases present, and perhaps an estimate of grain size from line broadening. The surface roughness was measured using stylus type (Talysurf Taylor Hobson) instruments. The tribological behaviour of the coatings was studied by means of pin-on-ring contact configuration in dry sliding conditions. The friction coefficient of sample with duplex coating with additional ion implantation, is presented in Fig. 1

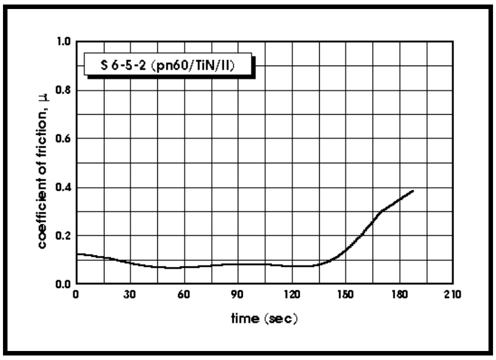


Fig. 1. Friction Coefficient of pn/TiN/II.

The curves of friction coefficient are clearly reproducible and distinctively show a lower rise in friction coefficient for the composite (pn/TiN) coated specimens and much more for sample with additional ion imlantation (under 0.1). The three basic points that are considered fundamental to studies of friction are the surface area and nature of the intimate asperity contacts, the surface adhesion and shear strength, and the nature of deformation and energy dissipation occurring at the asperity junctions. The wear resistance of the TiN coating was obviously improved by the presence of a nitride interlayer. Such an improvements is probably due to the adequate bonding between the nitrided layer and substrate (3). Energy depressive analyze with X-ray (EDAX), of the transfer layer showed that the transfer layer consists of small amount of counter material (adhesive wear), Fig.2.

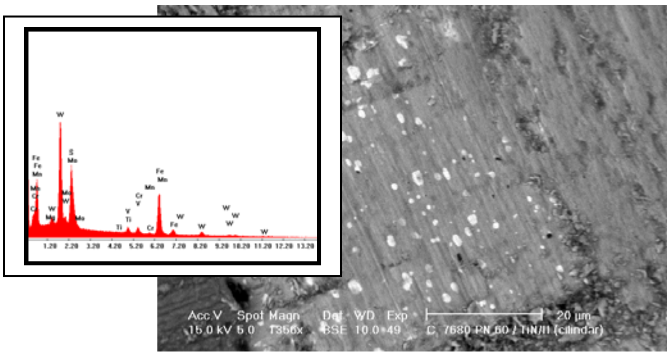


Fig. 2. SEM micrograph of wear track (BSE), with wear debrise and EDAX image of wear debrise.

The hardness values are also shown to demonstrate the increase in surface hardness due to nitriding at low pressure and coating, Tab.1

Table 1.Surface microhardness ($HV_{0.03}$).

Steel	Unco	TiN-PVD	Pn/TiN-PVD
S 6-5-2	850	2895	3480

The material under study is TiN coating with a thickness of approximately 1μm deposited by IBAD. With smaller load indentation, 5g, TiN(IBAD) coating show, irrespective of the coating thickness, the greatest increase in hardness ($5200HV_{0.005}$). The result from scanning electron microscopy shows a columnar structure reaching from the substrate to the coating surface. The films are very dense. The interface indicates very good coating to substrate adhesion. The values for critical load L_c are in general smaller for coatings deposited by PVD. It was found that the plasma-nitriding process enhanced the coating to substrates adhesion. In some places of hard coatings cohesive failure of the coating and the delamination of the coating was observed (Fig. 3).

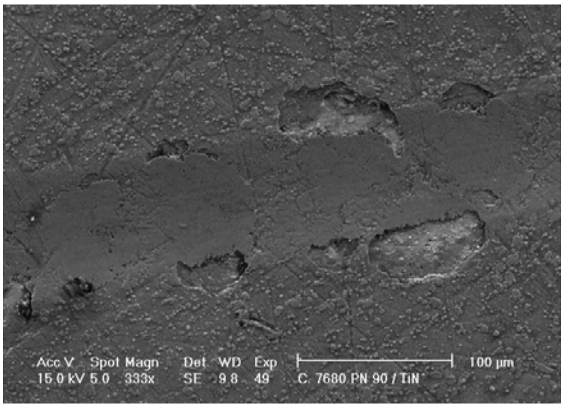


Fig. 3. SEM morphology of scratch test: pn/TiN(PVD).

TiN film grown under ion beam assisted deposition has a (200)) preferred orientation and TiN deposited by PVD has a (111) preferred orintation, according to JSPDS index card. XRD analysis revealed the presence of only one phase, δ-TiN, and there are no evidence for other phases, such as Ti_2N, could be found. The ε-Ti_2N do not lead to an improvement in the tribological behavior. The grain size is derived from the width of the diffraction peaks. The width of column is derived from the width of the diffraction peaks (λ=0.154nm, θ=62.5^o i β=0.056rad), and it is 70 nm. The tribological properties, preferred orientation, the microhardness, the coating to substrate adhesion and morphology of the hard TiN (IBAD) coating obtained on steel substrates offer the better performance the former coatings. It was concluded that the formation of a plasma nitrided layer at low pressure, beneath a hard coating, is important in determining the use of hard coating

NEW PROJECT RESULTS

The mechanical properties on coated samples were characterised using a Nanohardness Tester (NHT) developed by CSM Instruments, Switzerland. Nanoindentation testing was carried out with applied loads in the range of 10 to 20 mN. The nanohardness tester was calibrated by using fused silica samples for a range of operating conditions. A Berkovich diamond indenter was used for all the measurements. The tip radius of the indenter was approximately 50 nm and the displacement resolutions of the machine was 0.03 nm. The data was processed using proprietary software to produce load–displacement curves and the mechanical properties were calculated using the Oliver and Pharr method. At least ten measurements were made at each load on the coated sample. Measurement of hardness was also carried out using a conventional Vickers microhardness tester.

The Nano-Hardness tester uses an already established method where an Berkovich indenter tip with a known geometry is driven into a specific site of the material to be tested, by applying an increasing normal load. For each loading/unloading cycle, the applied load value is plotted with respect to the corresponding position of the indenter. The resulting load/displacement curves provide data specific to the mechanical nature of the material under examination. Established models are used to calculate quantitative hardness and modulus values for such data. The NHT is especially suited to load and penetration depth measurements at nanometer length scales. The maximum indentation depth for measuring H and E was fixed at one tenth of the coating thickness. The depth of nanopenetration provide an indirect measure of the area of contact at full load and thus hardness is obtained by dividing the maximum applied load with the contact area. Microhardness testing, Vickers microhardness, is dependent on visual resolution of the residual indent for accurate measurement. The diagonal of the indent, which is the key for hardness determination, is sometimes very hard to resolve if the load is low enough to avoid cracking and again this would be much more difficult if cracking occurs at high load within the indent site.

In the nanoindentation technique, hardness and Young's modulus can be determined by the Oliver and Pharr method (4), where hardness (H) can be defined as: $H = \frac{P_{\max}}{A}$, where P_{max} is maximum applied load, and A is contact area at maximum load.

Fig. 1 shows the typical load–displacement curve, showing the values used in the Oliver and Pharr method and cross section of an indent during indentation.

In nanoindentation, the Young's Modulus, E, can be obtained from: $\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}$, where v_i=Poisson ratio of the diamond indenter (0.07) and Ei=Young's modulus of the diamond indenter.

All the results of nanohardness are obtained with the Oliver & Pharr method and using a supposed sample Poisson's ratio of 0.3 for modulus calculation (Figure 4).

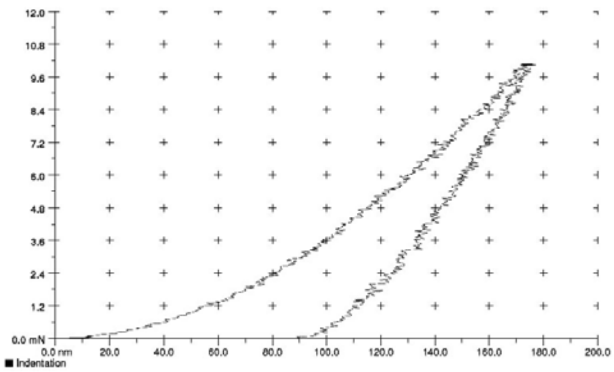
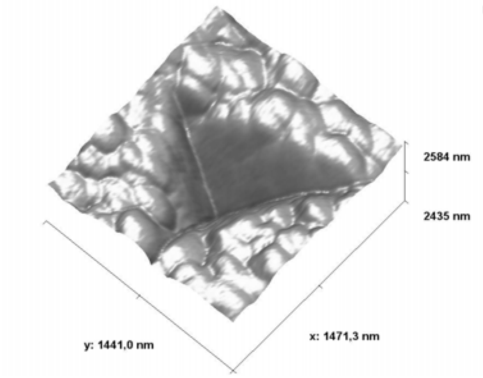
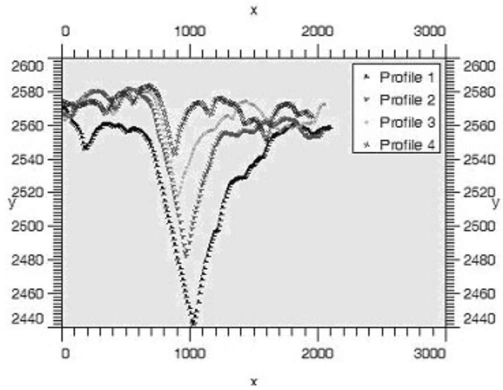


Fig. 4. Load–displacement curve, Oliver and Pharr method.

The analysis of the indents was performed by Atomic Force Microscope (Figure 5a).It can be seen that the indents are regularly shaped with the slightly concave edges tipically seen where is significant degree of elastic recovery.(Figure 5).





2a 2b

Figure 5. a) AFM image of a indentation made in the TiN coating b) Cross-section of the indentation

The nanohardness values are also shown in table 2, and Young's modulus in Table 3.

Table 2. Surface nanohardness.

	Unit	pn/IBAD	PVD	pn/PVD/II	Fused Silica
Average	**GPa**	**21,6**	**32,6**	**42,4**	**10,1**
StDev	GPa	2,0	4,4	1,7	4,3

Table 3. Young's modulus for coated samples.

	Unit	pn/IBAD	PVD	pn/PVD/II	Fused Silica
Average	**GPa**	**276,8**	**467,6**	**514,2**	**74,5**
StDev	GPa	32,4	103,7	20,4	1,1

Acoustic Emission (AE) is an important tool for the detection and characterisation of failures in the framework of non-destructive testing. The analysed AE signal was obtained by a scratching test designed for adherence evaluation. Scratch tests were performed under controlled conditions with a device that consisted of a loaded probe with a diamond indenter moving linearly along the sample with a constant speed and continuously increasing force.The steadily increasing contact load causes tensile stress behind the indenter tip and compressive stress ahead of the cutting tip. Detection of elastic waves generated as a result of the formation and propagation of microcracks. The AE sensor is insensitive to mechanical vibration frequencies of the instrument. This enables the force fluctuations along the scratch length to be followed, and the friction coefficient to be measured. The scratch tester equipment with an acoustic sensor (CSM-REVETEST) was used.

For each measurement, the penetration (Pd), the residual penetration (Rd), the acoustic emisssion (AE) and the frictional force are recorded versus the normal load. The breakdown of the coatings was determined both by AE signal analysis and optical and scanning electron microscopy. AE permits an earlier detection, because the shear stress is a maximum at certain depth beneath the surface, where a subsurface crack starts. Critical loads are presemts in Figure 6.

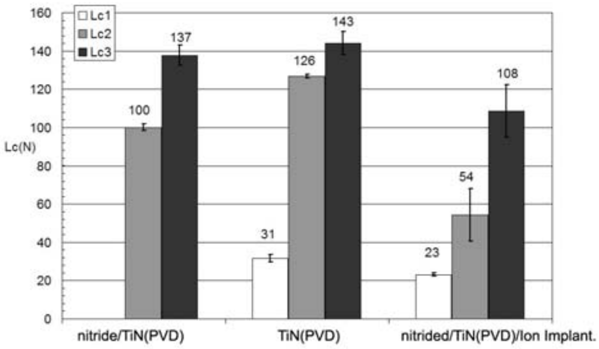


Fig. 6. Critical loads for diferent type of coatings.

The critical load Lc1 corresponds to the load inducing the first crack on the coating. No cracks were observed on sample 1.The critical load Lc2 corresponds to the load inducing the partial delamination of the coating. The critical load Lc3 corresponds to the load inducing the full delamination of the coating. AE permits an earlier detection, because the shear stress is a maximum at certain depth beneath the surface, where a subsurface crack starts (PVD). Figure 7.

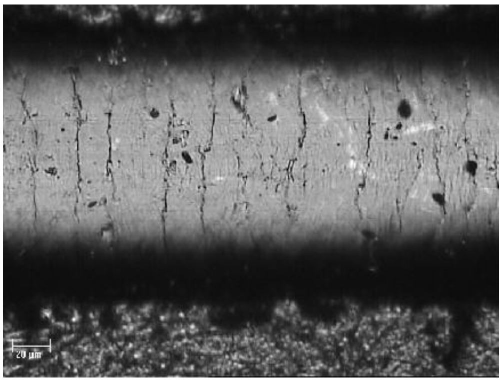


Fig. 7. SEM micrograph of scratch test of TiN(PVD) coating.

The stress determination, follows the conventional $\sin^2\psi$ method. Stress determination was pereformed using a PHILIPS XPert diffractometer. The (422) diffraction peak was recorded in a 2θ interval between 118° and 130°, with tilting angle: ψ_o^1=0°, ψ_o^2=18.75°, ψ_o^3=27.03°, ψ_o^4=33.83°, ψ_o^5=40°. A typical result for compact film, figure 8, with residual stresses σ = -4.28Gpa, has TiN(PVD).

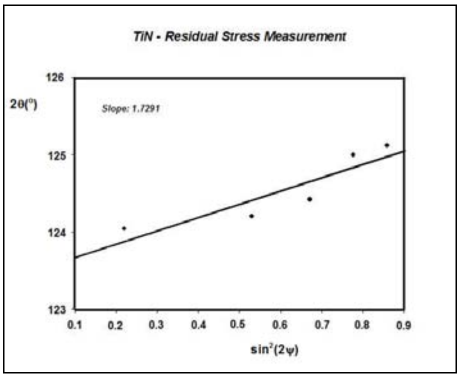


Fig. 8. $\sin^2\psi$ curves for the (422) reflection.

NEW PROJECT RESULTS

The composition of the films (nitrogen to metal ratio) was determined by energy-dispersive X-ray analysis (EDAX).

The analyzed nitrogen-to-metal ratio of the deposited films, with EDAX, is given in the Table 4.

Table 4. Atomic ratio N/Ti in coating.

	Coating	Ratio N/Ti (atomic)
1	IBAD	1.00
2	PVD	0.98
3	pn/PVD/II	0.89

For each measurement, the penetration (Pd), the residual penetration (Rd), the acoustic emission (AE) and the frictional force are recorded versus the normal load. The breakdown of the coatings was determined both by AE signal analysis and optical and scanning electron microscopy. AE permits an earlier detection, because the shear stress is a maximum at certain depth beneath the surface, where a subsurface crack starts.

The values for critical loads L_c are in general smaller for coatings deposited by PVD. Figure 10 presents the SEM photograph of a scratch channel of sample with film TiN(PVD) and Figure 11 with TiN(IBAD).

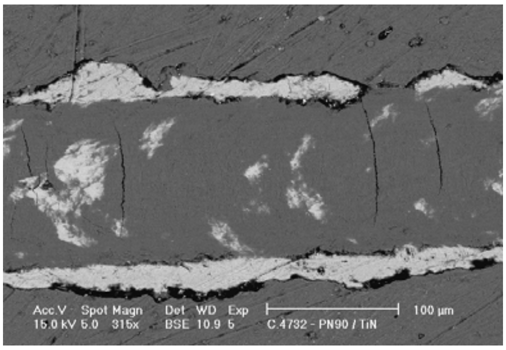


Fig. 10. Delamination of TiN(PVD) coating observed by SEM (BSE).

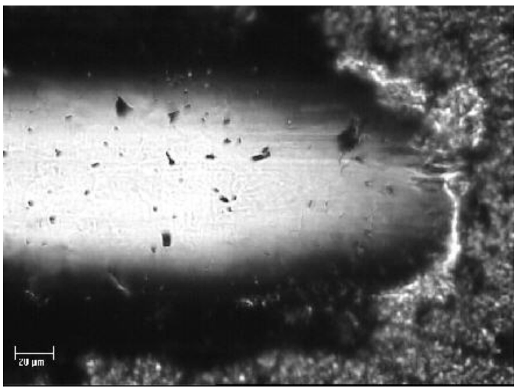


Fig. 11. SEM photograph showing the sctrach channel of TiN(IBAD).

The determination of phases was realized by X-ray diffraction using PHILIPS APD 1700 X-ray diffractometer. The X-ray sources were from CuKα with wavelength of 15.443 nm (40kV, 40mA) at speed 0.9^o min^{-1}.X-ray diffractogram for the coating is shown in Fig 12.

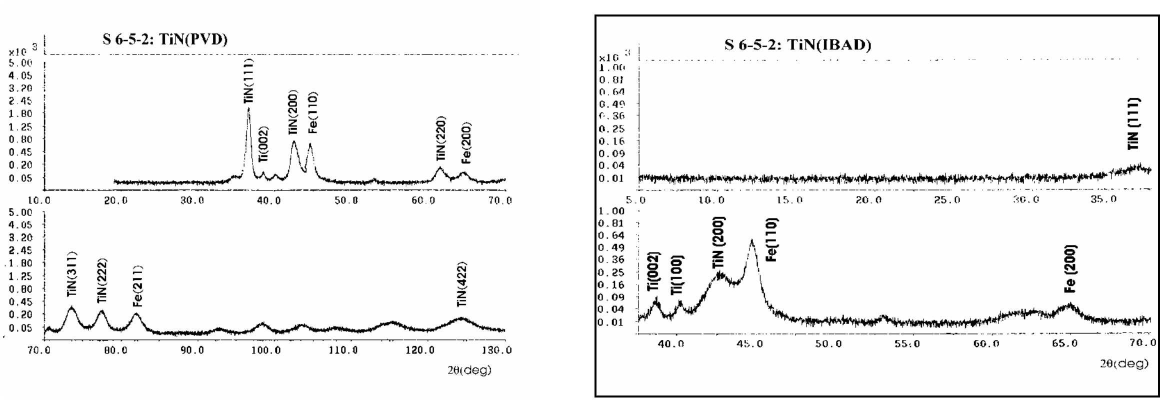


Fig. 12. X-ray diffraction spectrums of a)TiN(PVD) and b)TiN(IBAD).

Compared with the corresponding XRD patterns shown in Figs 12, TiN film grown under ion beam assisted deposition has a (200) preferred orientation and TiN deposited by PVD has a (111) preferred orientation. During TiN film growth, titanium atoms are firstly piled, as compact as possible, depending on the local conditions. The nitrogen atoms occupy the octahedric sites in varying number according to the energy that these atoms possess to cross the potential barriers created by the surrounding titanium anions. The formation of (111) preferred orientation has its origin in a kinetically controlled growth. The (111) plane is the most closely packed and exhibits the lowest surface energy.

XRD analysis revealed the presence of only one phase, δ-TiN, and there are no evidence for other phases, such as Ti_2N, could be found. The ε-Ti_2N do not lead to a improvement in the tribological behaviour , It is observed an increase in microhardness with the (200) orientation degree. These results are in agreement with those obtained in other paper.

CONCLUSIONS

- Deposition of TiN on plasma nitrided steel by IBAD process was successfully used to produce a hard and wear-resistant surface.
- It is shown that TiN (IBAD) coatings have a high wear resistance and low friction coefficient. The IBAD process reduces significantly the friction coefficients and improves the wear resistance.
- The microhardness, the coating to substrate adhesion and morphology of the hard plasma nitrided with deposited TiN(IBAD) coating and additional ion bombardment obtained offer the better wear resistance of the former coatings.
- The above findings show that deposition process and the resulting coating properties depend strongly on the additional ion bombardment.

<u>Project co-operation</u>

The co-operation starts with CSM Instruments SA. The samples for micro and nano characterization are in CSM Instruments, Switzerland. Further measurements of nanohardness as a function of depth will be performed together with CSM Instruments. Characterization of TiN, duplex coatings and coatings with additional ion implantation with nano wear tester and atomic force microscopy will be done.

Planned or achieved industrial improvements in commercial use

At this moment is proceed the agreement with FKL – Temerin Factory for bearings, cooperation with SKF, and we achieved an industrial application and economic benefit after realisation this project.

Still in negotiation.

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TS16 - INFLUENCE OF LUBRICANTS ON TRIBOLOGICAL CHARACTERISTICS OF CONTACT SURFACES AND WORKING LIFE OF GEARS BY POWER TRANSMISSION AND ELEMENTS OF SYNCHRONIZATION SYSTEM OF MOTOR VEHICLES

Co-ordinator and partners

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Project status and schedule

Running with partial funding / Running with full funding / Finished
Starting and ending dates
01.05.2004.-01.05.2007.

Project aims

The aim of this project is to define a connection between properties of contact surfaces and lubricant oil characteristics as well as to recognize their effect to tribological characteristics of contacts at various lubricating conditions. Thus, model test results of various material variants of contact pairs and the lubricant should enable to make choice of optimal combinations which are to be tested on real parts in the transmission of power.

Project results

Experimental

Four different types of steel were investigated, where is changed the heat treatment (carburizing and carbonitriding) (see Tab.1). These materials are selected because their characteristics are appropriate for production of vehicle transmitter gears. Steel 100Cr6 is accepted as referential, because the standard SRV test plates are made of it.

Table 1. Test materials.

Nº	Material	JUS	DIN	Heat treatment
1.	Standard material	Č.4144-4146	100 Cr6	
2.	A	Č.4321	20MnCr5	carburizing
3.	B	Č.4321	20MnCr5	carbonitriding
4.	C	Č.4721	20CrMo5	carburizing
5.	D	Č.4721	20CrMo5	carbonitriding
6.	E	Č.4732	42CrMo4	carburizing
7.	F	Č.4732	42CrMo4	carbonitriding
8.	G	Č.7422	21NiCrMo2	carburizing
9.	H	Č.7422	21NiCrMo2	carbonitriding

Seven different formulations of gearbox oil of different basis (mineral, synthetic, semi synthetic) are used in the investigation (see Tab.2).

Table 2. Test oils.

Nº	Oil	SAE	API	Base oil
1.	EP-A	75W-90	API GL-4	mineral
2.	S4	75W-90	API GL-4	synthetic
3.	GL-3	80W-90	API GL-3	semisynthetic
4.	oil 1	75W-90	API GL-4	mineral
5.	oil 2	75W-90	API GL-4	mineral
6.	oil 3	75W-90	API GL-4	mineral
7.	oil 4	75W-90	API GL-4	mineral

The tribological property has been analyzed using an oscillatory SRV tribometer. Measuring of the friction coefficient is according to the DIN 51834 standard conditions: frequency of 50Hz, the sliding path of 1000μm, temperature of 50^{o}C, load of 300N, test time of 120min. The ball of 10mm diameter is made of steel 100Cr6. The plate is made of materials which were investigated.

For the investigation of pitting, wear and scuffing a standardized FZG test rig with a pitch line velocity of 8,3m/s is used. Two different standard types of gears are used: C-type gear and A-type gear. The C type gears are used in the investigation of the influence of oil supply conditions on wear and pitting. The A type gears have a gear tooth form with uneven sliding conditions which is specially designed for a high scuffing risk. A high sliding speed simultaneously with a high Hertzian stress causes the gear failure mode scuffing. Both types gears are made of materials which was the most optimal (material "H" - 21NiCrMo2 -carbonitriding).

The scuffing test was used test conditions following to DIN51354.

For all pitting tests oil 2 was used. The test gears were run at a constant load (stepwise LS 9), with a constant oil temperature of 90^{o}C until the pitting damage occurs (max test time of 300h).

Finally to ensure that the model test results are correct some test of real systems have been carried out with the select oil and material and selected optimal gear tooth contact material along with lubricant characteristics at certain work regime and loading conditions.

Testing of real system will be investigated on a laboratory device having closed power circuit which was developed in the R&D Centre Automobile Institute "Zastava".

Testing of the complete gearbox is following to the conditions: cycle number of 100.000, max temperature of 100°C, speed of shaft 6000o/min and torque of 95Nm.

Determining the effect of oil kind on gears implemented in Zastava vehicles' gearboxes under real exploitation conditions was conducted after the research, which had ECE R83 regulations, annex VIII as its starting point. Considering the regulator allows any other similar testing having the same middle speed, speed arrangements and number of stops per kilometre, number of acceleration and braking we defined the paths.

Analyzing the traffic infrastructure around the city of Kragujevac and because we are out of own paths, based on a line of tests we chose a test consisted of 6 sections with the following characteristics:

- city drive to the length of 14.4 km (with 30 stops),
- main road to the length of 36.8 km (with 2 stops),
- city drive to the length of 4.8 km (with 5 stops),
- motorway of 22.4 km (with 2 stops),
    - main road to the length of 25,6 km (with 2 stops),
    - city drive to the length of 4.8 km (with 5 stops).

Namely, our driving cycle had the following structure:

- city drive 22%,
- main road drive 57% and
- motorway drive 21%.

Results

The SRV tests were the most comprehensive because they included research of many material-oil combinations and were of elimination character.

The same of SRV tests are presented in previous COST 532 project results reports. Those results are showed the effect of the different plate materials on the value of the friction coefficient and wear volume of the plate and the ball.

The surface topologies of the plates samples in tests with mineral gearbox oil API GL-4 and synthetic gearbox oil S4 were illustrated in Figures 1-2.

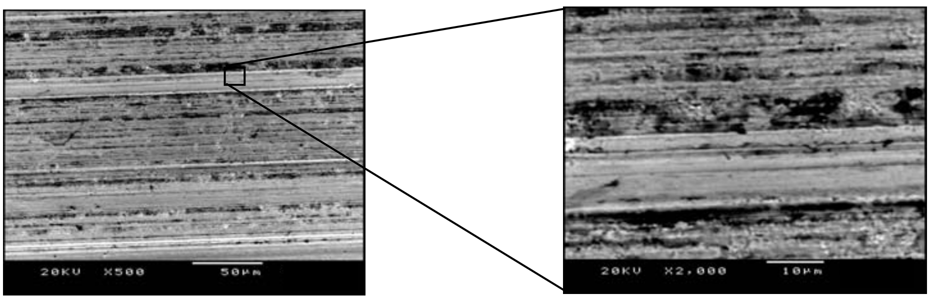

Fig. 1. The SEM surface topologies of the plate sample in test with mineral gearbox oil.

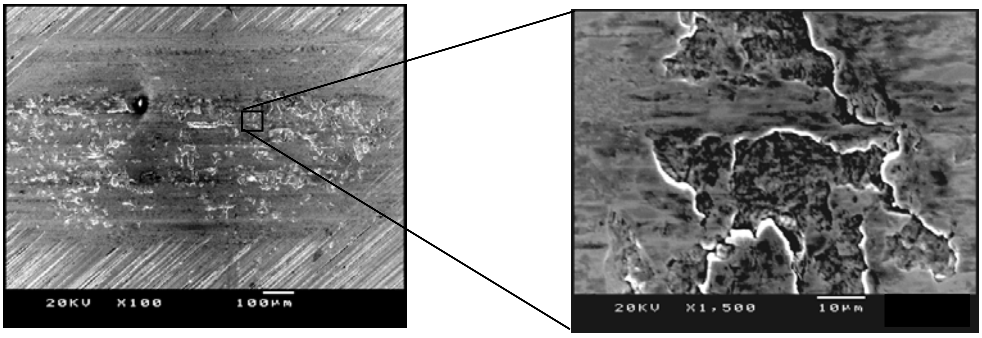

Fig. 2. The SEM surface topologies of the plate sample in test with synthetic gearbox oil.

From Fig. 1, it can be seen that there were only normal sliding scratches on the wear scar of the plate. It was smooth in the contact area of the plate sample.

Fig. 2 has clearly shown the significant distinction of the surface topologies of the tested samples with mineral oil. There was a number of pitting in the wear scar of the contact area of the plate. An oxidation film on which there were several holes covered the surface contact area of the plate.

In the Figure 3 shows the morphology of damage on gears after the pitting (FZG) test. It is visible the presence of large cracks featured by a very tortuous path.

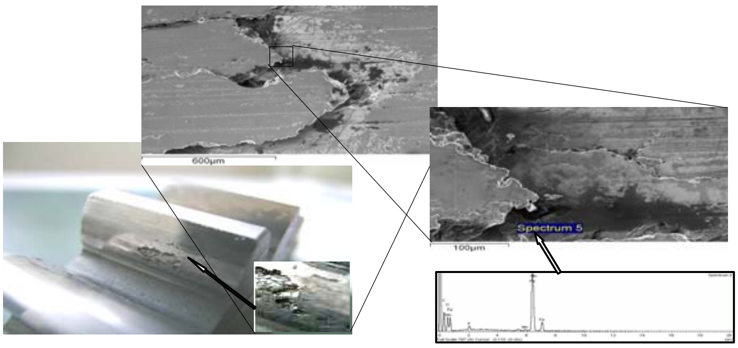

Fig. 3. Pitting damage on gear with SEM micrograph and EDS analysis.

Summary

In order to reduce the losses, i.e. to increase work life of gears as vital parts of many transmission of power it is very important to choose appropriate type of transmission oil and material. Demands to reduce the transmission of power dimensions and weight for passenger cars caused use of new formulation of transmission oils emphasizing a need for minimization of necessary lubricating oil quantity.

Methodology of testing developed within this testing should evaluate worthiness and applicability of certain lubricating oil formulation for the transmission of power as well as diagnostic for state of the transmission of power as a tribo-mechanical system. The test methodology being developed simultaneously may be applied to any problem or testing of a similar character.

The first faze of model tests is terminated.

In the moment, the tests on real system run. The results of these investigations will present in Conference in Ljubljana.

Project co-operation

e-mails: "Zastava automobili" – Serbia (www.institutzastava.com)
FAM – Serbia (www.fam.co.yu)
NIS Oil Refinery Belgrad - Serbia (galaxrnb@bitsyu.net)
Oil Refinery Modrica – Bosnia and Herzegovina

Meetings:
BALKANTRIB 05 – 15.- 18. June 2005, Kragujevac, Serbia
COST 532 – 12.-14. October 2005, Porto, Portugal
POWER TRANSMISSION - 25.-26. April 2006, Novi Sad, Serbia
AITC-AIT 2006 – 20.-22. September 2006, Parma, Italy
COST 532 – 02.-03. November 2006, Uppsala, Sweden
SLOTRIB 06 – 14. November 2006, Ljubljana, Slovenia

Industrial improvements in commercial use

The obtained results would be applied to the transmission of power of Zastava's vehicles. They would reach the following:

- Optimization of material of gears and synchronization system elements regarding wearing, strain and increase of hardness
- Choice of optimal heat treatment;
- Choice of the most optimal type of oil regarding its physical-chemical characteristics and tribological characteristics of contact

Publications were project results are reported

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17. Vukadinović Z., Josifović D., Vižintin J., 2007, Effects of oil kind on tribological characteristic of automotive gears, European Conference on Tribology and Final Conference of COST 532 action: Triboscience and Tribotechnology, Ljubljana, Slovenia, (paper in press)

TS17 - NANOSTRUCTURED COATING SYSTEMS AMORPHOUS CARBON-SILICON WITH LOW INTERNAL STRESS, HIGH HARDNESS AND CONTACT FATIGUE RESISTANCE

Co-ordinator and partners

Co-ordinator:

Dr. Petr Boháč, Institute of Physics of Academy of Academy of Science of the Czech Republic, Na Slovance 2, 18221 Prague 8, Czech Republic, bohac@fzu.cz

Partner:

Ass. Prof. Eva Zdravecká, Technical University Košice, Slovakia, eva.zdravecka@tuke.sk

Project status and schedule

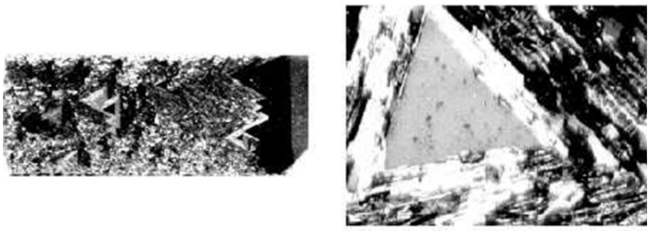
Running with partial funding
Starting and ending dates 01/2006 – 07/2007

Project aims

To suppress of high internal stresses through incorporation of Si into a-C films together with preservation of sufficiently high hardness and with improved adhesion to substrates as steel, or Si. Finding of optimal deposition parameters is one of the essential tasks arising from the theme. The other are finding of correlations between structure modification of these films (amorphous, nanocrystalline and or monocrystalline material) and mechanical and tribological properties.

Project results

The key factor preventing applications of wear resistant coatings with low coefficient of friction is high internal stress accountable for insufficient adhesion to substrate materials. The film structure is metastable because all methods for deposition are non-equilibrium processes based on thermal quenching of energetic ions on a cold surface. Presence of intrinsic stress (bringing often delamination of the film from a substrate) is then a consequence of the condensing non-balanced structure and, moreover, in a joint with different material of substrate. The stress can be as high as it can sometimes destroy even the substrate surface:



a) b)

Fig. 1 The a-C film deposited on Si substrate annihilated due to high compressive stress: (a) remainders of the film are shaped as triangles; (b) triangle shaped film rounded by furrowed Si surface which was torn away by delamination of the film [1].

Thus, it is desirable to find an element whose incorporation into amorphous structure of carbon brings lowering the internal stress together with preservation of good properties of coating. Si appears to be such element, for example. The deposition technique based on magnetron sputtering permits to realize films with various compounds practically from pure carbon to pure silicon. Thus, it is desirable to investigate influence of film composition on intrinsic stress, hardness and other properties at least in surrounding of stoichiometric SiC.

The hydrogen-free a-C:Si films with gradually varied Si concentration were prepared by DC magnetron sputtering using a Leybold Z 550M vacuum sputtering plant. The thin Si (111) plate with a diameter of 50 mm was glued to the carbon target (150 mm diameter, 99.5% purity) across the erosion zone. This combined target was sputtered in argon (purity 99.999%) at a pressure of 0.15 Pa. The discharge power was typically 300W. Some depositions at high temperature were performed with 150 W to decrease the deposition rate. The target–substrate distance was 50 mm. The substrates were placed parallel to the target diameter at different distances from the Si plate. This configuration and increased size of stuck Si plate (with respect to that in [2]) enabled us to obtain during one deposition cycle up to 7 a-C:Si films with different Si concentration from 3 to 70 at.% on unheated Si (111) substrates. A bias voltage has been applied to the substrates using a 13.56 MHz power source. Films with Si content from 35 to 55 at.% were deposited on grounded Si (111) substrates, pre-heated at 400, 600 and 800 °C.

Mechanical properties (hardness, intrinsic stress), film composition (EPMA and XPS) and film structure (electron diffraction, Raman spectra) were investigated in dependence on Si concentration, substrate bias and deposition temperature. Fig. 2 shows the hardness and intrinsic stress of the a-C:Si films as a function of Si concentration in the range of 3–70 at.%. When deposition occurs at optimal bias (it depends on the power used) the hardness initially decreases with increasing Si concentration. A sharp hardness increase then starts from ~25 at.% of Si, reaching its maximum at ~32–50 at.% of Si. This hardness is close to the maximum value characteristic for hard a-C films obtained under the same conditions at optimal substrate bias [1, 3]. The film hardness decreases sharply when Si concentration exceeds 50 at.%. The curve of the film hardness is asymmetric with respect to the stoichiometric SiC composition. The maximum is reached for slight excess of carbon in the film. The intrinsic stress of a-C:Si films obtained at ion bombardment decreases sharply from 4.0 to 2.3 GPa with Si concentration increase up to ~20 at.%. It remains almost constant at further Si content increase up to approximately 50 at.% and reduces again when Si concentration exceeds 50 at.%. When deposition occurs on grounded substrate, the increase of silicon concentration in the film leads to an increase in the hardness, which then goes through a wide maximum in the range of

Si concentrations from 25 to 55 at.%. This maximum is lower than that for biased films and also asymmetric with respect to the stoichiometric SiC composition. The intrinsic stress of these films grows only slightly starting from ~25 at.% of Si and then remains constant and it is considerably lower than that for biased a-C:Si films.

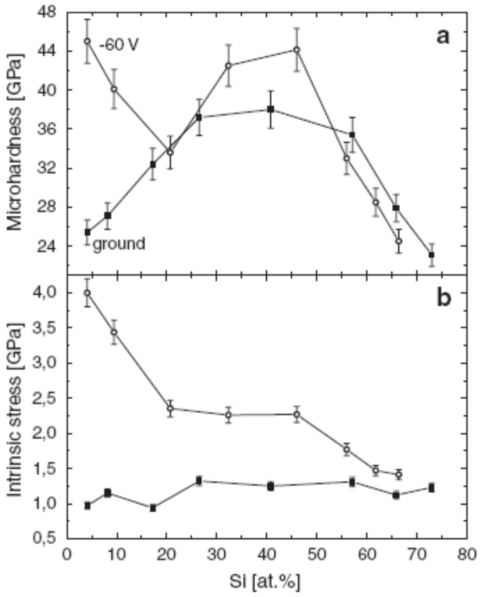


Fig. 2. squares – grounded substrates open circles – substrate bias – 60V.

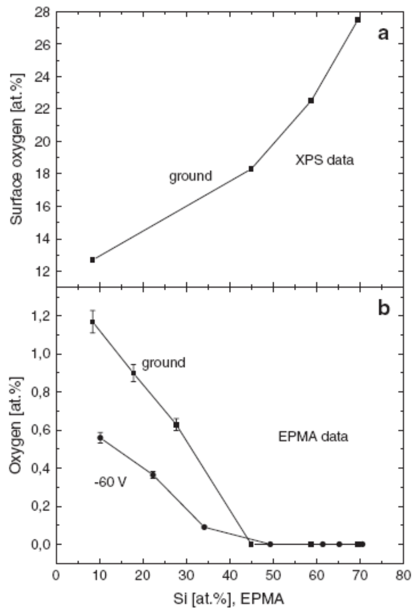


Fig. 3. Oxygen content for films deposited at room temperature onto grounded and biased (- 60V) substrates.

The concentration of oxygen impurity may indicate a decrease of the film density which influences the hardness. Fig. 3b shows the oxygen content determined by EPMA in the volume of a-C:Si films on biased and grounded substrates as a function of Si concentration. This content is practically zero for films with Si concentration above 50 at.%, no matter whether biased or grounded substrates were used. The lower the Si concentration, the higher the oxygen content in the film volume. The oxygen content in the films deposited on grounded substrates is considerably higher than that in films deposited on biased substrates. In contrast to the latter films, the structure of the former is more open and porous, containing clusters with graphite-like ordering with large interlayer space allowing the oxygen atoms to penetrate into the film [4]. On the other hand, XPS investigation of the sample surface showed that increasing Si content in the films is accompanied by a higher oxygen contamination, owing to the higher affinity of silicon to oxygen (Fig. 3a). This fact can explain some discrepancies in film composition determined by EPMA and XPS methods.

The film hardness was maximal for ~ 45 at.% of Si and slightly grew with increasing deposition temperatures to 600 and up to 800 °C. Reflection electron diffraction indicated an amorphous structure of all the films.

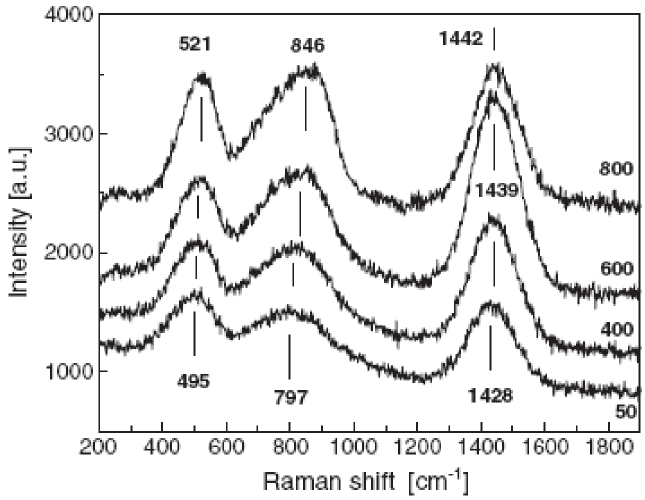


Fig. 4. Raman spectra of a-C:Si films with ~ 42 at.% of Si deposited at different temp. (right hand side), discharge power 300 W.

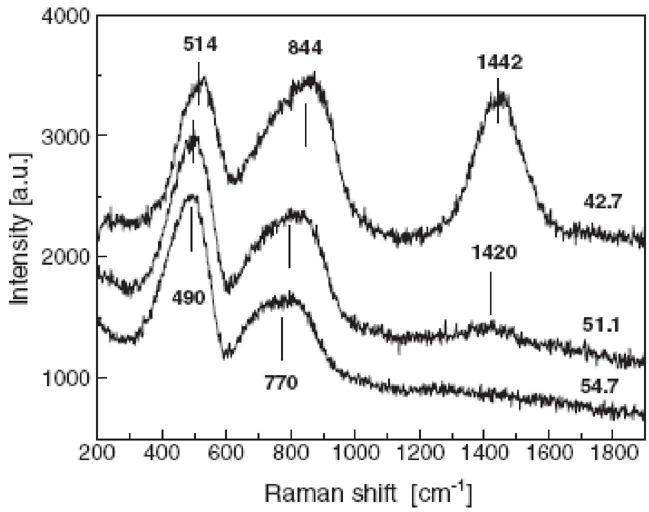


Fig. 5 Raman spectra of a-C:Si films with different at.% of Si deposited at 800 ^{o}C (right hand side), discharge power 150 W.

The Raman spectra of the films with Si content from 40 to 65 at.% show the three bands characteristic for carbon (1440–1360 cm−1), silicon (480–560 cm−1) and SiC (740–870 cm−1) vibrational modes (Figs. 4 and 5). It means that carbon, and silicon, as well as SiC clusters co-exist, even in the films deposited at 800 °C. The intensity and position of these bands can change with film composition, substrate bias, and temperature. It should be noted that the band assigned to the Si–Si vibration starts to be seen in the films already from 40 at.% of Si. Thus, these films may be qualified as nanocomposites a-SiC/a-C/a-Si. All these bands were observed also in the films sputtered from a SiC target [5] and also in a-SiC alloys prepared by ion implantation of carbon into the silicon matrix [6].

Raman spectra showed that the films in the range of 35–70 at.% of Si always contain three bands corresponding to the Si, SiC and C clusters. Photoelectron spectra showed dependency of Si–C bond formation on preparation conditions.

During film growth, part of C atoms can form sp^3 hybridized C–C bonds, especially at high temperature deposition and for compositions close to stoichiometric SiC. Such sp^3 bonds can arise partly due to substituting some Si atoms in disordered lattice of SiC clusters by C atoms. Similarly substituting C by Si in SiC lattice is more difficult because the Si atom is larger than the C one. It results in some excess of Si cluster number with enlarged size in comparison with that for C clusters in the case when Si and C atoms are arriving at the substrate in equal quantity. For this reason the maximum film hardness in such inhomogeneous films appears at small excess of C atoms with respect to stoichiometric SiC composition.

a-C:Si films (35–55 at.% of Si) deposited at all substrate temperatures up to 800 °C always were nanocomposites and consisted of carbon, silicon and silicon carbide clusters. The film hardness and intrinsic stress decreased quickly if Si content exceeded 50 at.%.

These results were published mainly in [7]. Besides, the deposition and investigation of hardness and elastic modulus through nano-indentation and abrasive wear testing on carbon, SiC and Ti-C:H films sputtered on steel were realized. Publication of results is prepared for conference **ECOTRIB 2007.**

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7. **V. Kulikovsky**, P. Bohac, J. Zemek, et al. ***Hardness of Nanocomposite a-C:Si Films Deposited by Magnetron Sputtering.*** Diamond Relat. Mater. 16 (2007) 167-173

<u>Project co-operation</u>

Mention the forms of co-operation used: e-mail contacts

Planned or achieved industrial improvements in commercial use

none

Publications where project results are reported

1. P. Boháč, V. Kulikovsky, R. Čtvrtlík, M. Stranyánek, J. Suchánek, ***Nanostructured Coating Systems Based on Amorphous Carbon with Low Internal Stress, and Good Tribological Properties.*** ECOTRIB 2007 – to be published
2. P. Boháč, R. Picek, V. Kulikovsky, ***Elastic constants of thin films based on amorphous carbon obtained by LAW method.*** ECOTRIB 2007 – to be published
3. V. Kulikovsky, V. Vorlicek, P. Bohac, M. Stranyanek, R. Ctvrtlik, A. Kurdyumov, L. Jastrabik. ***Hardness and elastic modulus of amorphous and nanocrystalline SiC and Si films.*** Surface and Coatings Technology (2007) – in press
4. V. Kulikovsky, P. Bohac, J. Zemek, V. Vorlicek, A. Kurdyumov, L. Jastrabik. ***Hardness of Nanocomposite a-C:Si Films Deposited by Magnetron Sputtering.*** Diamond and Related Materials 16 (2007) 167-173
5. R. Picek, P. Bohac. ***Princip měření elastických konstant metodou LAW (in Czech).*** JMO 52 (2007) 4 - 6
6. M. Stranyanek, R. Ctvrtlik, P. Bohac, L. Jastrabik. ***Nano-mechanical properties of carbon and silicon films.*** Materials Structure, ISSN 1211 – 5894, 13 (2006) 94
7. P. Bohac, K. Rusnak, O. Blahova, V. Kulikovsky, M. Sosnova. ***Mechanical Properties of the Hard Amorphous Carbon Films Sputtered on Steel Substrates.*** Proc. of abstracts, International Conference on Superhard Coatings, European Community DESHNAF project: “Super-hard nanocomposite films by plasma processing”, Ein-Gedi, Israel, 27 Feb. - 1 March 2006, p. 47

CHAPTER 5 IMPROVEMENTS IN COMMERCIAL USE, IM

5.1 Summary

The results from the COST532 Action are benefited in new industrial products and improvements in production methods in the 103 companies directly involved in the research work. The 42 projects carried out have already by now when the 5 year Action comes to an end resulted in 32 industrial improvements in commercial use.

The following industrial improvements in commercial use been reported:

- Duplex coatings for tools and implant , Inst. Terotechnol., Poland – ES3
- HVOF coatings, Tech. Univ. Kosice, Slovakia – ES7
- Oil-free powertrain, Tech. Univ. München (Coord), Germany – TS1
- Low friction coated machine parts, Inst. Terotechnology, Poland – TS2
- Coating modelling, VTT, Finland – TS3
- DLC for transmission systems, Univ. Ljubljana, Slovenia – TS4
- Nanogrease, Inst. Materials Sciences, Ukraine – TS5
- Wet clutch design, Luleå, Univ. Sweden – TS13
- Lubricant for car gear box, Univ. Kragujevac, Serbia & Mont. – TS16
- Self-lubricated coatings, Univ. Coimbra, Portugal – CH1
- DLC for diesel injection system, Univ. Ljublana, Slovenia – CH5
- Engine simulation tests, Tekniker, Spain – CH6
- Lubrication optimised coatings, Uppsala Univ., Sweden – CH7
- Coating selection for machine parts, Faunhofer Inst., Germany – CH8
- Composite for machine tool guides, Inst. Terotechnology, Poland – CH9
- Molecular structure of lubricants, Luleå Univ., Sweden – CH11
- Environmentally adapted lubricants, Luleå Univ., Sweden – CH12
- Selflubricating nano-coating, Univ. Targu-Mores, Romania – CH13

Most of them are described more in detail below.

5.2 Improvement descriptions

<u>CH1 – Self-lubricated coatings</u>

1. Name of improvement: New enterprise as spin off from action
2. Name of company: To be decided
3. COST 532 project code: CH1 (M6)
4. Name of project manager and organisation: Albano Cavaleiro, University of Coimbra
5. Description of the improvement in commercial use by the company mentioned above:

The action was proposed in 2005 by the innovation office of the University of Coimbra. Three students from the University of Coimbra, pick up the idea and propose the formation of an enterprise for exploring the results achieved in the aim of the project. Their proposal was analysed and accepted as a potential business. Last year the enterprise was proposed for financial aid to national authorities at the same time that a demand of funds was done to a Bank. The proponents are now waiting for the results of their demand for starting the activities of their enterprise.

CH5 – DLC for diesel injection system

1. Name of improvement: Optimized DLC coating for common-rail diesel injection systems
2. Name of company: Balzers Coating AG, Liechtenstein (O. Massler)
3. COST 532 project code: CH5
4. Name of project manager and organisation: Bojan Podgornik, University of Ljubljana, CTD
5. Description of the improvement in commercial use by the company mentioned above:

Optimized DLC coating for common-rail diesel injection systems, including high-pressure pump parts and injectors. Coating optimized in terms of composition, multilayer structure and thickness.

CH8 – Coating selection for machine parts

1. Name of improvement: Coating selection for machine parts
2. Name of the companies: KVT Kurlbaum GmbH, Osterholz-Scharmbeck, Germany
   Pallas GmbH & Co. KG, Würselen, Germany
   Rybak+Höschele RHV Technik GmbH & Co. KG, Waiblingen, Germany
3. COST 532 project code: CH 8 (M13)
4. Name of project manager and organisation:
   Dr. Berger, Lutz-Michael
   Fraunhofer Institute for Material and Beam Technology
5. Description of the improvement in commercial use by the company mentioned above:

With the project a systematic study of the oxidation and sliding wear performance (0.1-3 m/s and up to 800°C) of state-of-the-art thermally (HVOF-) sprayed hardmetal coatings was performed. The coatings were produced at the companies. These companies are typical thermal spray service-SME (job shops) without own R&D departments. The product profile includes individual machine parts and components, small series and repair. The systematic study of oxidation and sliding wear is permanently used at the companies for coating selection of such parts in different applications. As an example a coated part of a ball valve of company KVT is shown in the Figure.

CH9 – Composite for machine tool guides

1. Name of company: PONAR REMO Kępno, Poland

2. Description of the improvement in commercial use by the company mentioned above:

The elaborated chemical-setting metal-resinous composite were applied for the regeneration of flat guides in cutting machine tools. The places of regeneration are indicated in Fig. 1.

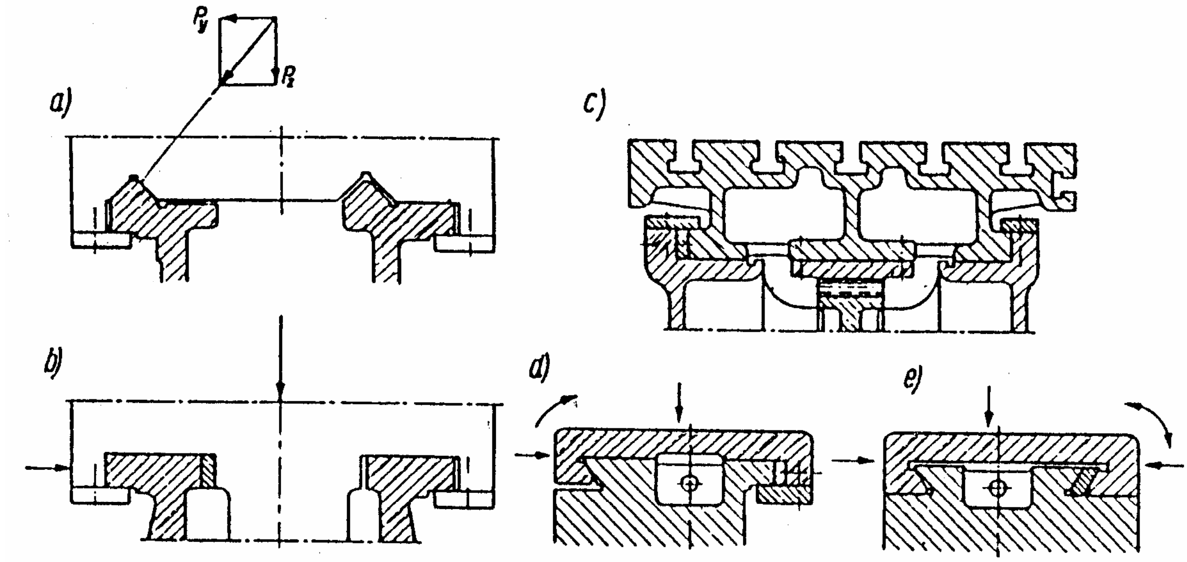


Fig. 1. The system of guides in the cutting machine tools to be subjected to regeneration.

CH12 – Environmentally adapted lubricants

1. Name of company: Statoil Lubricants AB
2. Description of the improvement in commercial use by the company mentioned above:

The synthetic lubricants examined in the experiments carried out under the scope of this study have been shown to continue to perform as intended even when severely aged / oxidised (i.e. with an acid number greater than 2). This provides evidence for the statement that these lubricants are suitable for long-term use in hydro-electric power generation plant and, given results from testing in other studies, can improve the efficiency of such machinery with associated commercial gains through providing a viable alternative to the currently employed mineral oils (also tested in this study).

CH13 – Selflubricating nano-coating

1. Name of improvement: Performance increase of sewing machine components by development of self-lubricated coatings
2. Name of company: Dürkopp-Adler Ltd.
3. COST 532 project code: CH13
4. Name of project manager and organisation:
   Associate Professor Dr. Dominic Biró,
   "Petru Maior" University of Targu-Mures, Romania
5. Description of the improvement in commercial use by the company mentioned above:

A versatile semi-industrial batch coating multi-cathode *UM* magnetron sputtering system was designed and constructed in co-operation with the *SME* industrial end-user partner. The newly constructed state of the art *UM* magnetron sputtering system housed in an octagonal vacuum chamber was evacuated to a base pressure of $p = 2 \cdot 10^{-4}\ Pa$.

Fig. 1. Overview picture on the newly constructed UM magnetron sputtering system.

Mass flow gas controllers were used for the reactive gas admission, which were operated in conjunction with a dynamic controlled pressure adjusting unit and plasma emission monitoring of process parameters.

The substrates were rotated in planetary motion by the external driven supporting table and were heated by *IR* radiation. The mounted components could be biased to a highly negative voltage during of surface cleaning by ion etching in argon gas, respectively for deposition of the adhesive seed-layer. Process parameters were continuously saved to a *PC* buffer and used in view of forward estimation of the reactive gas partial pressure. Optical emission spectral intensity of sputtered target atoms were excited in plasma environment while the characteristic radiation served as plasma state parameter. Discharge current intensity and reactive gas flow rate were selected as control parameters of the process. A sophisticate fuzzy-logic controlling software has been developed for adaptive process control of the reactive gas mass flow and of discharge power intensity.

The performance of the system was tested in dedicated experiments for sample preparation of compound phases of *TiAlN*C/MoS_2, and the obtained results indicated a very efficient control means in microstructure evolution of the multi-component multilayer coatings (Fig.2 and Fig. 3).

Co-deposited nanocomposite thin film coatings were processed by reactive magnetron co-sputtering of *TiAl*, MoS_2, and graphite targets performed in mixture of $Ar+N_2$ controlled atmosphere. Thin film architecture of self-lubricated wear-resistant coatings was designed according to some industrial needs for wear protection of sewing machine components exposed to an abrasive sliding wear. For model deposition of tribological coatings, substrates of polycrystalline hard metals and monocrystalline silicon substrates were used. Coatings of *TiAlCN* doped with MoS_2 phase, performed on *Si*(100) substrate were prepared in cross section thinning by ion milling technique for microstructure investigation in a transmission electron microscope.

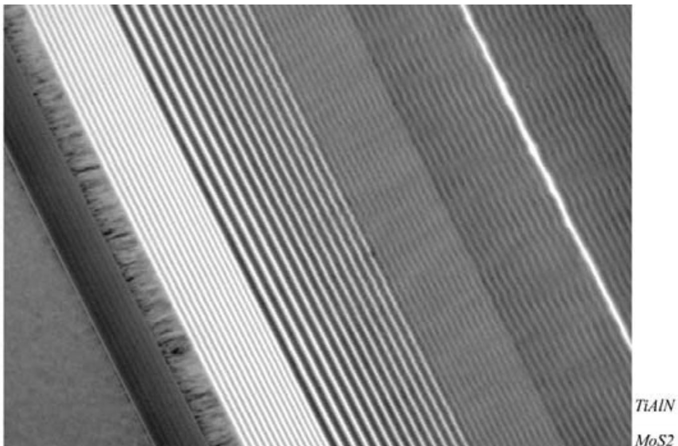


Fig. 2. Bright-field transmission electron micrograph showing the cross section image of self-lubricated MoS_2 doped TiAlCN coating developed in nano-scale multi-layer structure.

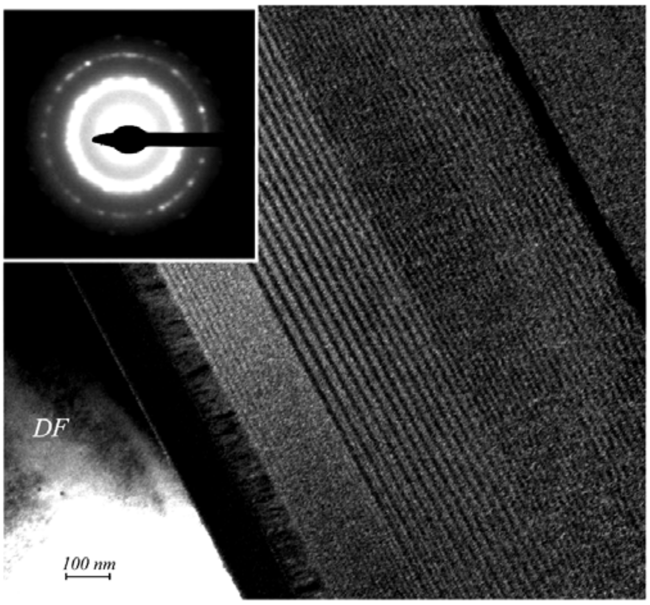


Fig. 3. Dark-field transmission electron micrograph with SAED electron diffraction pattern of the MoS_2 doped TiAlCN self-lubricating coating. The XTEM cross-section image of the as-deposited film shows a nano-grain structure (transmission electron microscope image was performed by prof. P.B. Barna in MFA-Budapest, using a 200 kV CM 20 Philips TEM microscope).

Crystal structure evaluation and determination of elemental composition of the coatings were performed by *XRD*, *EDX*, and *EDS* analysis, respectively. The hardness of 5 *µm* thick coatings has been evaluated by micro-Vickers tests performed on *HSS and WC-Co* hard metal substrates. Structure evolution and mechanical behavior of multilayered coatings processed on planetary rotated subtrates revealed the versatility of computer controlled deposition process. Crystal structure, preferred orientation and microstructure evolution of multilayered nanocrystalline *fcc-TiAlCN* phase coatings are sensitively influenced by plasma and process parameters. Experimental research performed in frame of this project indicates that self-lubricated tribological wear-resistant hard thin film coatings could be prepared with high reproducibility in well-controlled depostion conditions.

The research activity was extended also for architecture design of MoS_2 doped *TiAlCrN* coatings. Processing and investigation of TiAlN/CrN/MoS_2 multilayer system prepared by unbalanced magnetron reactive co-sputtering from alloyed Ti/Al: 50/50 at.%, pure chromium and MoS_2 sputter sources were performed too. The sputter sources were arranged side by side on an arc segment, therefore a broad interface of the processed multilayer thin film structures was produced. By this technique the morphology and structure of interfaces could enhance the hardness of multilayer thin films and release the strain energy due to the lattice mismatch of the sequencialy stacked layers. The thickness of the layers could be changed both by the oscillation frequency and by the discharge power applied for the targets. The deposition was performed in Ar-N_2 mixture atmosphere of 0.22 Pa working pressure.

The sputtering power of TiAl source was feed-back adjusted in fuzzy-logic mode in order to avoid the fluctuation of the TiAl target sputter rate due to the poisoning of the target surface. The 4-5 *µm* thick TiAlN/CrN/MoS_2 multilayer films were deposited on high speed steel substrates for tribological measurements. The structure characterization was performed on films deposited on <100> Si wafers covered by thermally grown SiO_2. Cross sectional transmission electron microscopy and XRD were used for structure characterization. A 200 *nm* thick Cr seed-layer was deposited at first on the substrate to improve the adhesion, which was followed by a CrN transition layer. The CrN transition layer was followed by a 200 *nm* thick TiAlN/CrN multilayer system. The TiAlN/CrN/MoS_2 multilayer system was deposited on the surface of this underlayer system. The Cr, the CrN and TiAlN/CrN underlayer system was crystalline with columnar structure according to the morphology of Zone *T* of the structure zone models. The column boundaries contained segregated phase showing up in the underfocussed TEM images. The surface of the underlayer system was wavy due to the dome-shaped columns. The nanometer-scale TiAlN/CrN/MoS_2 multilayer system followed this waviness (Fig. 4).

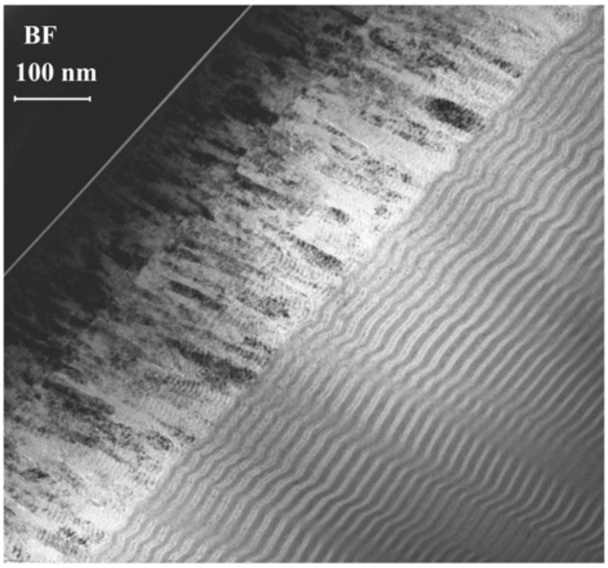


Fig. 4. The nano-scale multilayer structure of TiAlN/CrN/MoS_2 coating shown on BF XTEM-image.

The self-lubricated TiAlN/CrN/MoS_2 multilayers were characterized in 50 % humid atmosphere for sliding friction coefficients which ranged from 0.08 to 0.12. The micro-Vickers hardness values were evaluated betweeen $HV_{0.025}$=850 and $HV_{0.025}$=2500, the values were sensitive influenced by the MoS_2 crystalline phase amount and its distribution in the nanostructured coatings.

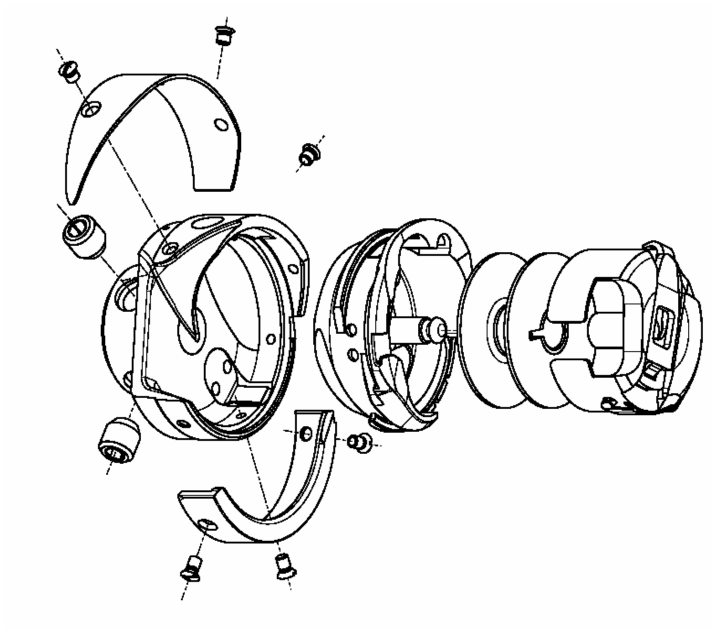


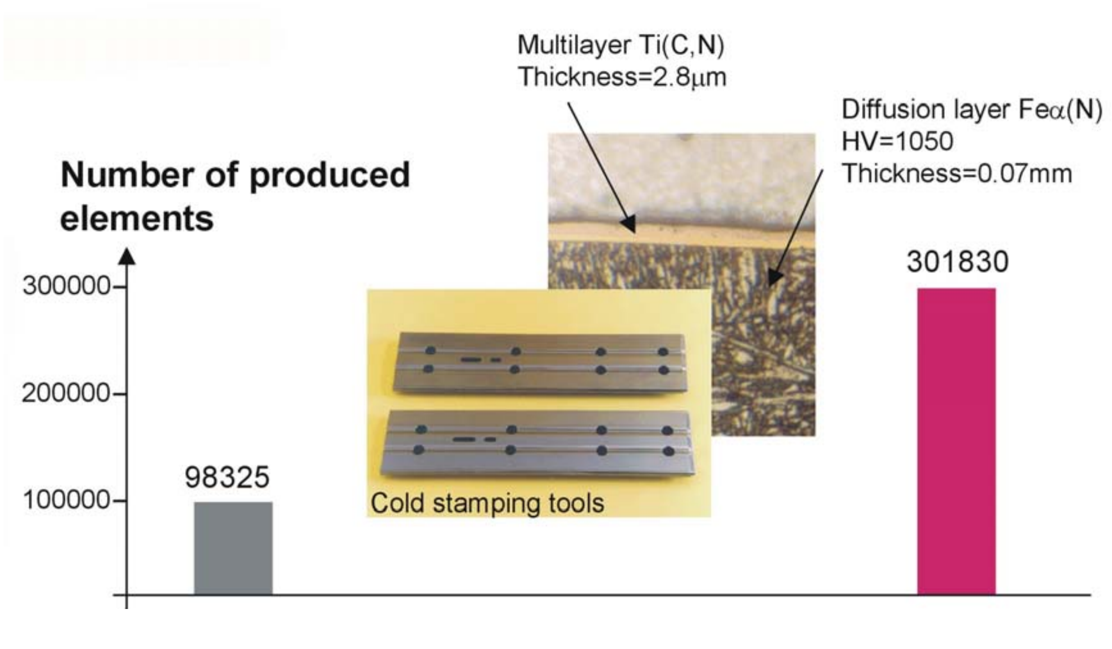
Fig. 5. Sewing machine components selected for deposition of self-lubricated TiAlN/CrN/MoS_2 coatings.

ES3a – The duplex treatment technology for increase of durability of cold stamping tools

1. Name of improvement: The duplex treatment technology for increase of durability of cold stamping tools [(*)]
2. Name of company: Institute for Sustainable Technologies – National Research Institute 26-600 Radom, Pułaskiego 6/10, Poland
3. COST 532 project code: ES3 (M12)
4. Name of project manager and organisation: Jan Walkowicz, Institute for Sustainable Technologies – National Research Institute, 26-600 Radom, Pułaskiego 6/10, Poland
5. Description of the improvement in commercial use by the company mentioned above:

Research and implementation work on duplex treatment technology of tools' life increasing was carried out in the Department of Surface Engineering. The composite structure "nitrided layer / multilayer coating $TiN\text{-}TiCN_{gradient}$" was obtained by duplex treatment technology realized by discontinuoues method (*nitriding process and PAPVD process were realized at the two different devices*). The nitriding process was carried out by the gas nitriding method and the PAPVD coating of a complex structure and composition was obtained by vacuum arc method with the help of the multi-source vacuum stand.

[(*)] The additional projects used for technology development:
"*Development of new generation of the cold stamping tools*"
Targeted Project nr 10 T08 033 2000 C/5264

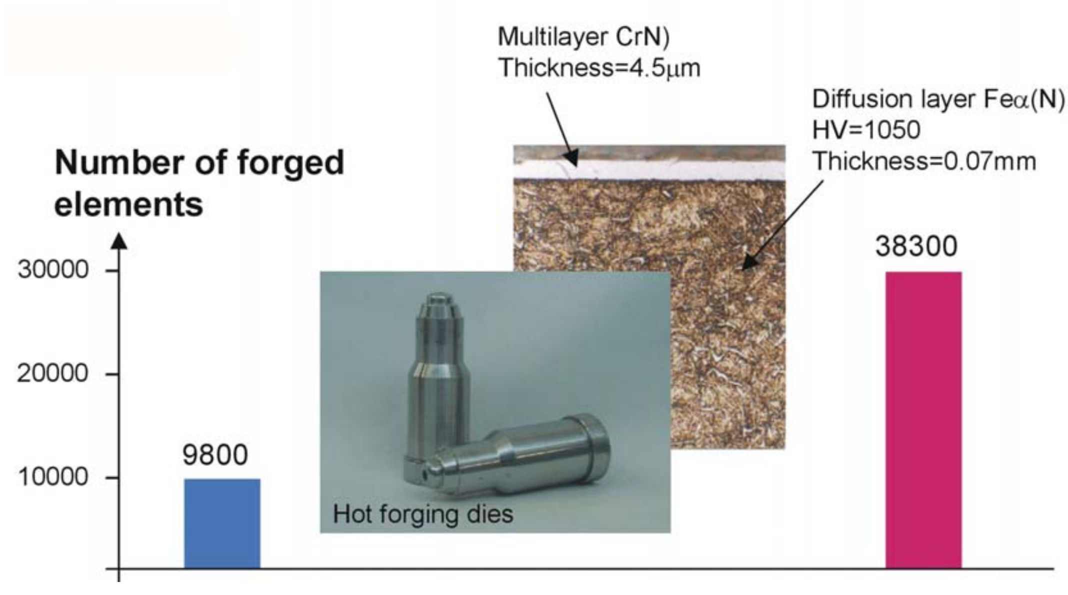


ES3b - The duplex treatment technology for increase of durability of hot forging dies [(*)]

1. Name of improvement: The duplex treatment technology for increase of durability of hot forging dies [(*)]
2. Name of company: Institute for Sustainable Technologies – National Research Institute, 26-600 Radom, Pułaskiego 6/10, Poland
3. COST 532 project code: M12
4. Name of project manager and organisation: Jan Walkowicz, Institute for Sustainable Technologies – National Research Institute, 26-600 Radom, Pułaskiego 6/10, Poland
5. Description of the improvement in commercial use by the company mentioned above:

Research and implementation work on duplex treatment technology of tools' life increasing was carried out in the Department of Surface Engineering. The composite structure "nitrided layer / coating CrN" was obtained by duplex treatment technology realized by continuoues method (*nitriding process and PAPVD process were realized at the same device in continuous technological process*). The nitriding process was carried out by the ion nitriding method and the PAPVD coating of a complex structure and composition was obtained by vacuum arc method with the help of the multi-source vacuum stand.

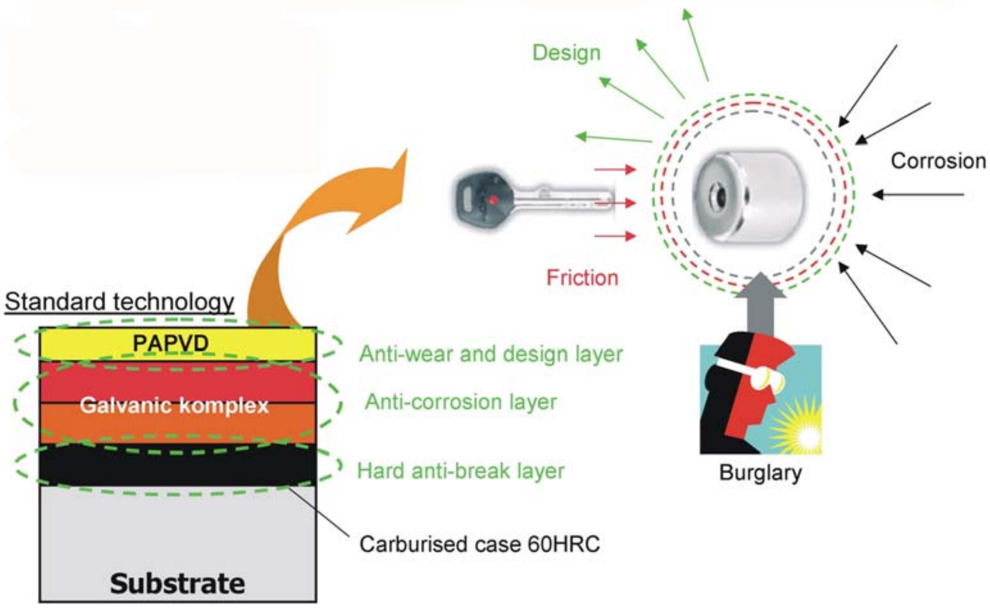
[(*)] The additional projects used for technology development:
"Elaboration of technology and equipment for continuous duplex treatment of hot forging tools"
Project No: GRD1-2001-40217, Fifth Framework Programme of the European Community



ES3c - The duplex treatment technology for increase of wear resistance, corrosion resistant and design of lock accessories

1. Name of improvement: The duplex treatment technology for increase of wear resistance, corrosion resistant and design of lock accessories.
2. Name of company: Institute for Sustainable Technologies – National Research Institute, 26-600 Radom, Pułaskiego 6/10, Poland
3. COST 532 project code: M12
4. Name of project manager and organisation: Jan Walkowicz, Institute for Sustainable Technologies – National Research Institute, 26-600 Radom, Pułaskiego 6/10, Poland
5. Description of the improvement in commercial use by the company mentioned above:

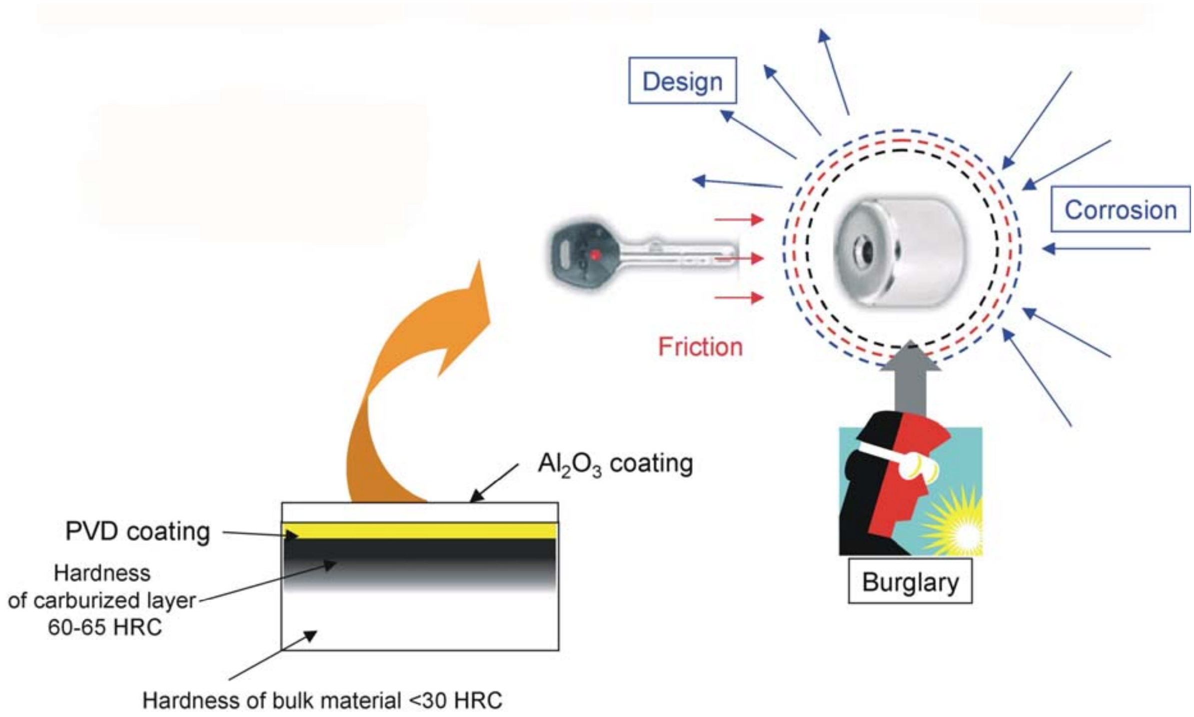
Research and implementation work on duplex treatment technology of lock accessories was carried out in the Department of Surface Engineering. The composite structure "carburised case / galvanic complex / coating TiN" was obtained by hybrid technology realized using three different surface treatment technologies: vacuum carburising for creation of carburized case, electrochemical deposition for creation of anti-corrosion galvanic complex and vacuum-arc deposition for creation of hard anti-wear PAPVD coating.



ES3d - The duplex treatment technology for increase of wear resistance, corrosion resistant and design of lock accessories.

1. Name of improvement: The duplex treatment technology for increase of wear resistance, corrosion resistant and design of lock accessories.
2. Name of company: Institute for Sustainable Technologies – National Research Institute, 26-600 Radom, Pułaskiego 6/10, Poland
3. COST 532 project code: M12
4. Name of project manager and organisation: Jan Walkowicz, Institute for Sustainable Technologies – National Research Institute, 26-600 Radom, Pułaskiego 6/10, Poland
5. Description of the improvement in commercial use by the company mentioned above:

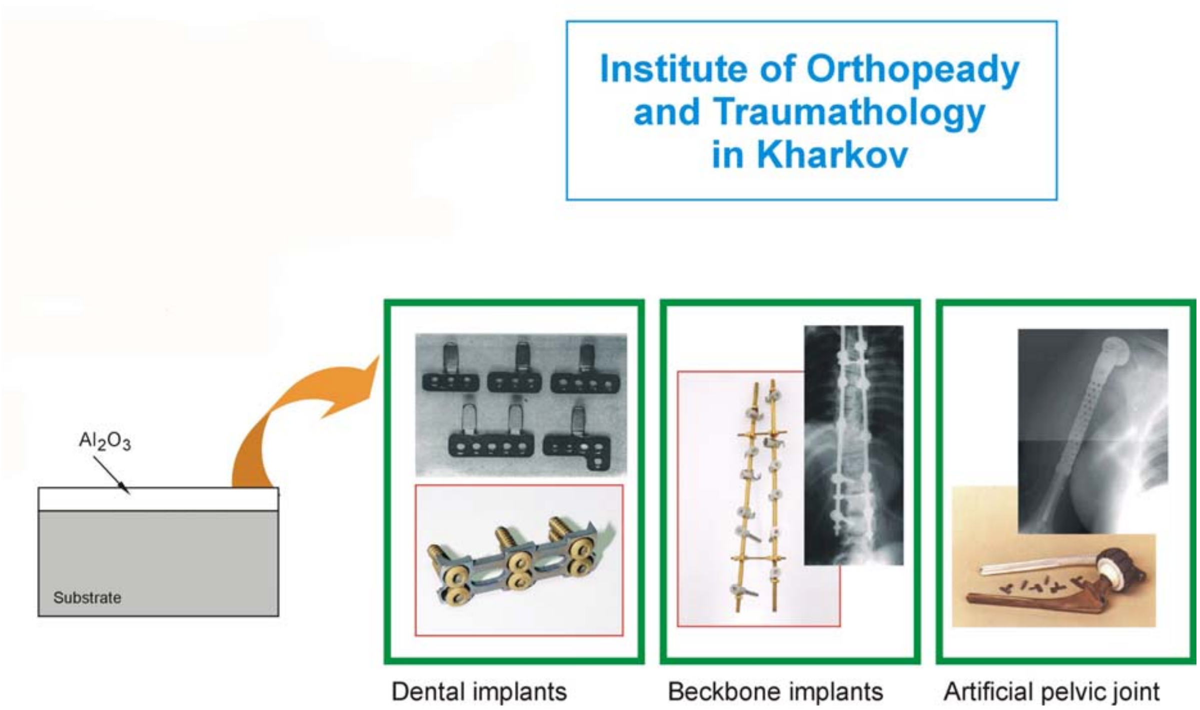
Very good anti-corrosion properties of alumina coatings deposited by the developed method of ICP enhanced reactive magnetron synthesis were practically exploited for improvement of corrosion resistance of locks accessories. Al_2O_3 coating is deposited in the Institute for Sustainable Technologies – NRI as the top layer in multilayer protective system: "carburized case/TiN coating/Al_2O_3 coating".



ES3e - The surface treatment technology for increase of biocompatibility of medical implants.

1. Name of improvement: The surface treatment technology for increase of biocompatibility of medical implants.
2. Name of company: Institute for Sustainable Technologies – National Research Institute 26-600 Radom, Pułaskiego 6/10, Poland
3. COST 532 project code: M12
4. Name of project manager and organisation: Jan Walkowicz, Institute for Sustainable Technologies – National Research Institute, 26-600 Radom, Pułaskiego 6/10, Poland
5. Description of the improvement in commercial use by the company mentioned above:

Aluminum oxide coatings deposited according to the developed technology were applied for improvement of wear and corrosion resistance of artificial hip joints as well as for improvement of corrosion resistance of special dental plates. Coatings were deposited by reactive magnetron synthesis method in Scientific Centre of Physical Technologies in Kharkov National University and were clinically tested in the Institute of Orthopaedy and Traumatology in Kharkov, Ukraine.



ES7 – HVOF coatings

1. Name of company: Faculty of Mechanical Engineering,Technical University in Košice
Welding Research Institute, Department of Powder Materials and Metallurgy,Bratislava, Slovakia

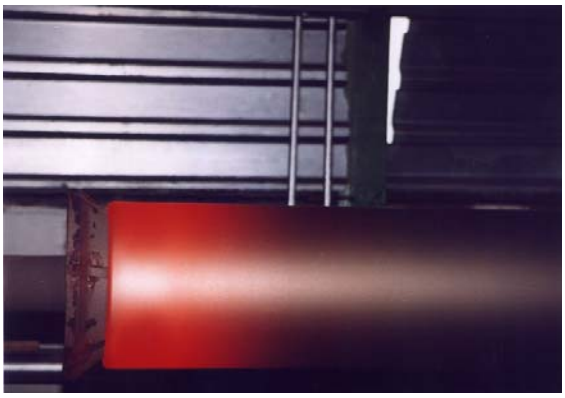
2. Description of the improvement in commercial use by the company mentioned above:
It is encouraged to include illustrative material such as figures, photographs etc., but do not include confidential information.

1) **Industrial improvements**

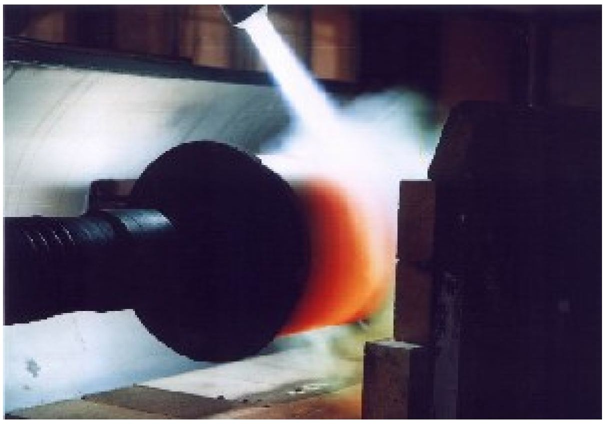
1) The powders from productions of Research Welding Institute (Department of Powder Materials and Metallurgy), Bratislava were applied in U.S. Steels Košice, s r.o. , Slovakia for heat-rolling of steel strips.

The powders marked VUZ- NP 62 R were used for two step technology of thermally spraying (remelting).

Two steps technology of metal powders spraying (powder NP 62)

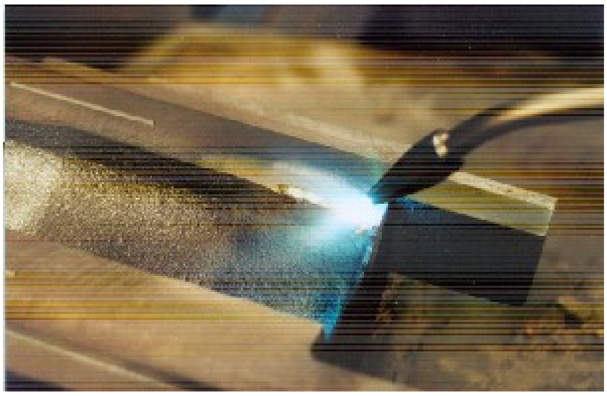


Cooling of roll after thermally spraying



Remelting

2) Application of powder NP 22 for treatment of moulds for glass production



Application of powder NP 22 for treatment of moulds for glass production

TS1 – Oil-free powertrain

1. Name of company: Fraunhofer Institute for Material and Beam Technology, Dresden (Germany) (Developing institute of coating)

2. Description of the improvement in commercial use:

The coating Diamor was developed by the Fraunhofer Institute for Material and Beam Technology in Dresden, Germany. The coating was partly developed in the project "Oil-free Powertrain" and investigated within WP 3 "Ceramic coatings". The coating is available for commercial use and is currently tested and used in different applications. The applications can be found in mechanical engineering industry, food industry or automotive industry. Main aim of the coating is the avoidance of fretting and wear and the decrease of friction. More information on the possible applications can be found on the institute's web-page: www.iws.fraunhofer.de

Table 1. Properties of the coating Diamor.

Parameter	Unit	Diamor
Microhardness	HV	5500 - 6000
Coating thickness	µm	≈ 5
Young's modulus	10^5 N/mm^2	4,0 - 4,5

In the following the main properties and experimental results, which were found within the project "Oil-free Powertrain" are shown. The coating is a hydrogen-free tetrahedral amorphous carbon-coating, Table 1 shows the main properties.

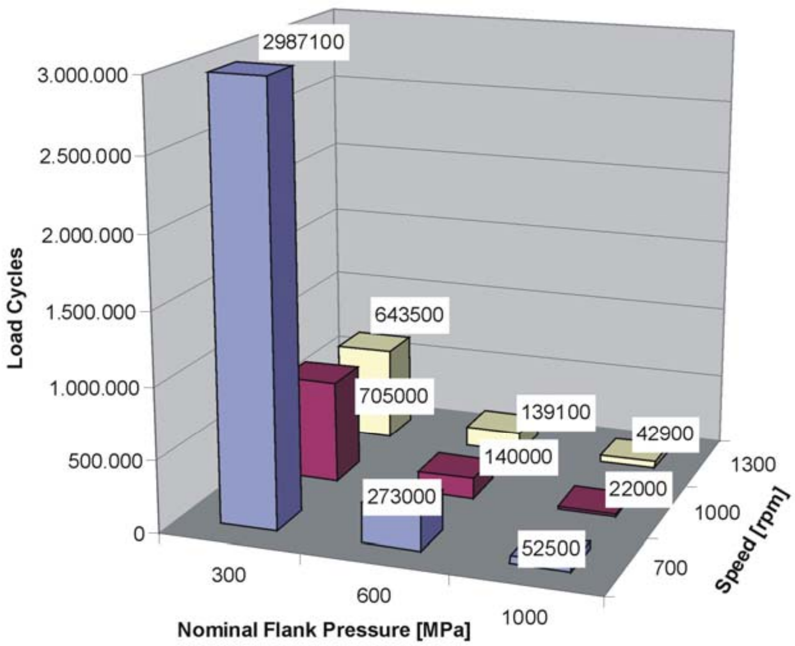


Fig. 1. Tests with the coating Diamor at dry lubrication.

Within the project "Oil-free Powertrain" Diamor coated gears were tested. Figure 1 shows the results of the tests with the coating at different loads and speeds at dry lubrication. As a result a clear dependence of lifetime on the load was found. A clear dependence of lifetime on speed could not be observed. In all tests the coating failed first, followed by fretting damage (high speeds and high loads) or wear (low speeds and low loads).

Figure 2 shows the results of comparative tests. Nominal flank pressure was at 600 N/mm^2 and pinion speed was at 1000 rev/min. A higher lifetime could be achieved when a higher coating thickness or a better surface quality, that means a lower surface roughness, was used. Coating of just one gear was not successful. The results show, that the coating Diamor achieved the same or even higher lifetime compared to other coatings in combination with standard spur gears. However the highest lifetime by far was achieved with coated low-loss gears. Lifetime of these combination was about 18 times higher compared to lifetime of standard spur gears. These low-loss gears were developed within WP 1.1 and show very low power losses compared to standard spur gears. The idea of those gears is, that tooth contact is concentrated around the pitch point, where pure rolling occurs. Thus sliding is reduced.

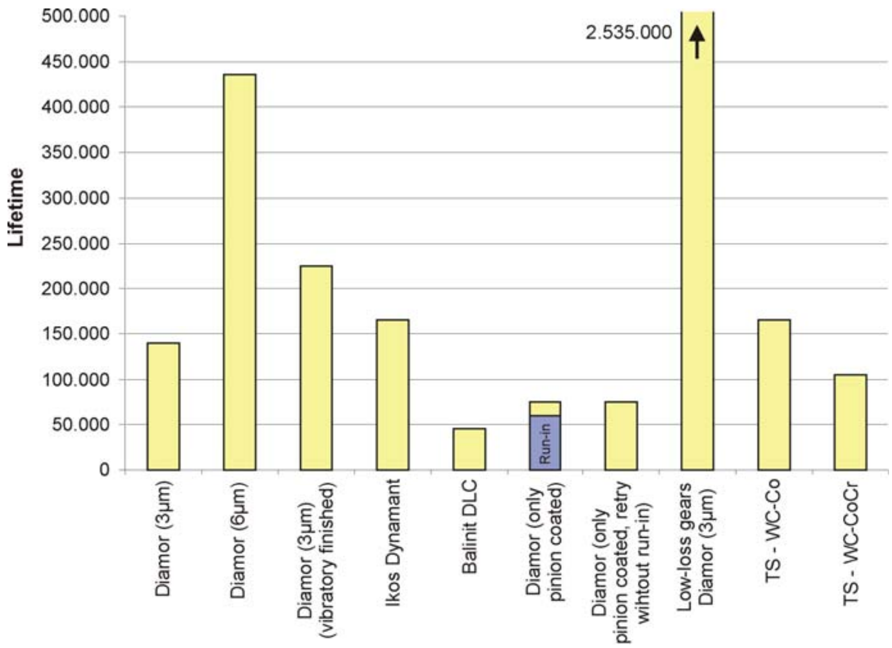


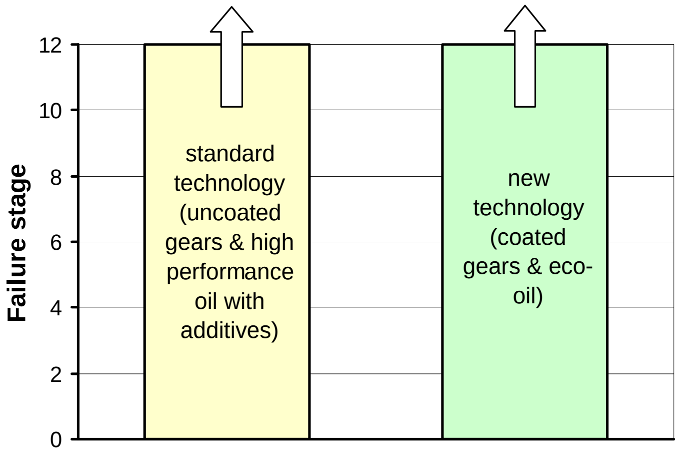
Fig. 2. Results of comparison tests.

TS2 – Low friction coated machine parts

1. Name of improvement: The new technology for steel heavy-loaded machine components.
2. Name of company: The results of the projects are applied to the industry in cooperation with:
   - CMG KOMAG Mining Mechanization Centre Gliwice (Poland),
   - Invenio Ltd. Bielsko-Biała (Poland).
3. COST 532 project code: TS2 (L6)
4. Name of project manager and organisation:
5. Description of the improvement in commercial use by the company mentioned above:

A new technology for manufacturing steel heavy-loaded machine components covered with low friction coatings enables increase service life of components and allows lubricating with environmentally friendly oils. This will increase the reliability of machines and reduce pollution of the environment by oil.

The new technology allows for the extension of the life-cycle of heavy loaded machine components through optimisation of the common action of coatings and lubricants in a variety of contacts, such as gears or rolling bearings.



The implementation of new technology and their further development is subject to an agreement between the Institute for Sustainable Technologies – National Research Institute, CMG KOMAG Mining Mechanization Centre, Gliwice (Poland) and Invenio Ltd., Bielsko-Biała (Poland). The agreement concerns the improvement of durability of heavy-loaded transmissions systems used in mining industry.

TS3 – Coating modelling

1. Name of improvement: Tape Test Development by Instrumented Test and Modelling Approach
2. Name of company: Savcor Corporation, Finland (Savcor Coatings)
3. COST 532 project code: TS3 (E4)
4. Name of project manager and organisation: Dr Helena Ronkainen, VTT Technical Research Centre of Finland
5. Description of the improvement in commercial use by the company mentioned above:

In order to evaluate the adhesion of metallic thin films on plastics tape test is typically used. In order to improve the reliability of results, there was a need for a tape test technique that would give reliable force-time curves, possibility to study the fracture patterns and to further evaluate and refine the results. VTT developed a VTT Instrumented Automated Tape Test Device (TTD) for the repeatable and reliable tape tests. The equipment is described in Figure 1. The tape testing with the equipment will be carried out automatically by pulling a tape with peeling time of 0.5 seconds in 60° angle. The force-time curve (Figure 2) is automatically recorded for further calculations.

An energy release rate evaluation will be carried out on the basis of tape test results. The analysis is using fracture mechanics for evaluating debonding of the bimaterials. The current analysis used enables only qualitative reasoning. Use of fracture mechanic analysis enables linking of defect to fracture toughness and to applied loading. Implementing a software tool enables the post-processing of the tape test results in order to get quantitative results for adhesion evaluation.

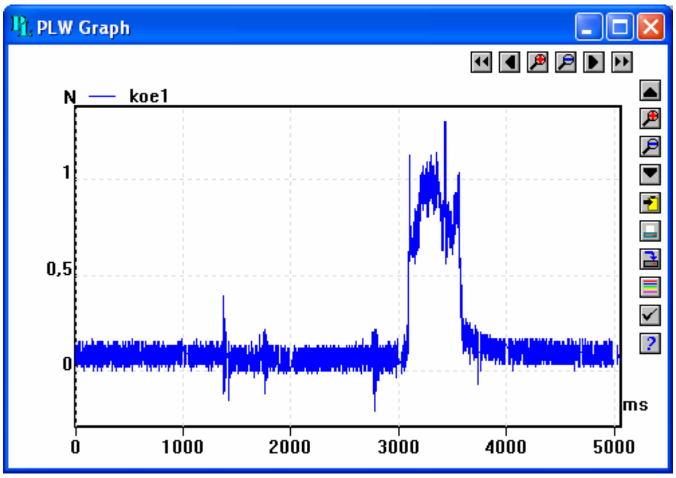


Figure 1. The VTT Instrumented Automated Tape Test Device (TTD)

Figure 2. The force-time curve received by the VTT Instrumented Automated Tape Test Device

TS4 – DLC for transmission systems

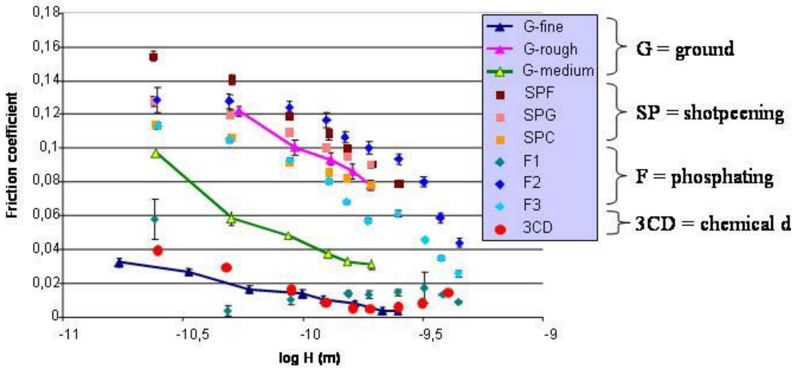
1. Name of company: Volvo Cars, Volvo Technology
2. Description of the improvement in commercial use by the company mentioned above:

It is encouraged to include illustrative material such as figures, photographs etc., but do not include confidential information.

Industrial improvement was achieved with a clear indication of the effect of different surface and interface preparation, used for the gear transmission systems. The project results enable more inexpensive and more tailored interface properties with using the different surface roughness, oils and coatings.

The results of the effect of DLC coatings, but also other surface modifications (3CD, phosphating) and effect of substrates (through- and case-hardened steels) were gained and implemented to improve the performance of transmission systems at Volvo Cars. New results are directly related to industrial use and enable implementation to production.

The result will be used in Volvo Cars, but also by Volvo Technology for transfer of knowledge to other Volvo companies.



Friction as a function of different surface treatments on case hardened real-scale wheel-on-wheel tests [gear-shaver tester, Base oil, 225 MPa contact pressure]

TS5 - Nanogrease

1. Name of improvement: Nanogrease
2. Name of company: JSC "AZMOL Berdyansk, Ukraine
3. COST 532 project code: TS5 (L5)
4. Name of project manager and organisation:

Leonid M. Kulikov
Affiliation: Institute for Problems of Materials Science, NASU (IPMS NASU)
3, Krzhyzhanovsky Str., 03680 Kiev-142, Ukraine
Tel: +380(44) 424 22 01, Fax: +380(44) 424-21-31
sem_kob@ipms.kiev.ua

5. Description of the improvement in commercial use by the company mentioned above:
It is encouraged to include illustrative material such as figures, photographs etc., but do not include confidential information.

Experimental - industrial pilot lot of nanogrease was produced. Exploitation ability are discussed

TS13 – Wet clutch design

1. Name of companies: Haldex Traction AB and Statoil Lubricants AB
2. Description of the improvement in commercial use by the company mentioned above:

The aim of this project is to gain knowledge about the frictional performance and lubrication regimes in these types of applications, and thereby be able to optimise the lubricant and the clutch control software to minimize variations in transferred torque.

A test apparatus, which is able to monitor friction and temperature as a function of applied force, sliding velocity and oil flow have been developed and is operational.

The friction-temperature behaviour of the clutch has been investigated under high clutch disc pressure conditions. The results obtained show that increase in the surface temperature lowers the friction by as much as 40% under typical operation conditions, Figure 1.

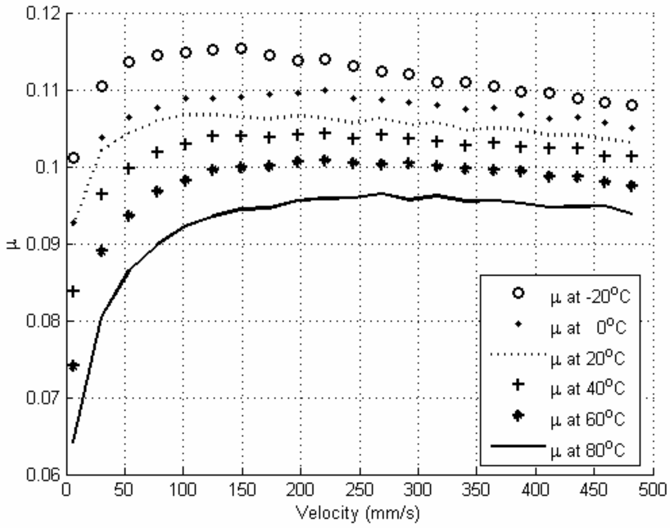


Fig. 1. Friction-velocity characteristics measured at different initial temperatures.

A method for measuring and presenting anti-shudder properties has been developed. The friction is presented as a discrete function of velocity at a constant temperature. By using this method it is possible to compare anti-shudder properties obtained under different conditions, since the data are not influenced by the chosen test conditions, Figure 2.

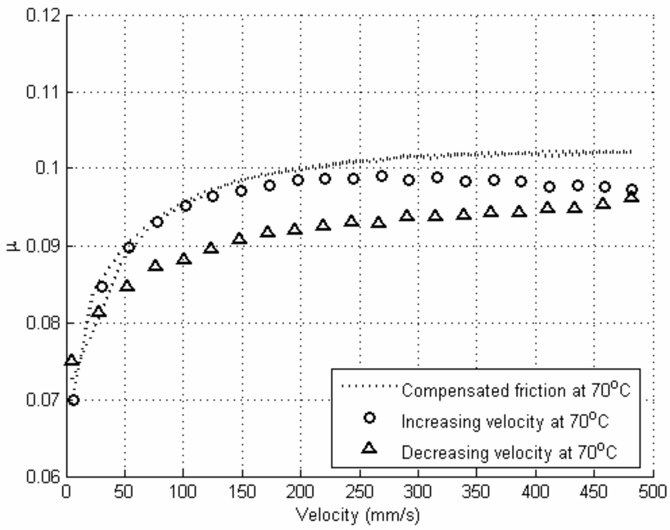


Fig. 2. Friction characteristics measured during speed increase and speed decrease, and the same two curves compensated for the different conditions during measurements.

A successful method to develop transmission fluids has been developed. Formulated fluids allow good anti-shudder properties to be combined with good lubrication performance for other machine elements present in the transmission. Interactions between different additives must be considered which can, in many cases, completely alter the friction characteristics since additives compete for the same adsorption surface. Extreme pressure additives have been found to be particularly troublesome when used in combination with other additives as far as their ability to maintain good anti-shudder properties is concerned.

Based on the knowledge of clutch performance obtained from the research presented in this thesis, a model to predict transmitted clutch torque has been developed. This accurately determines the transferred torque from the current operating conditions and the thermal history of the clutch, Figure 3.

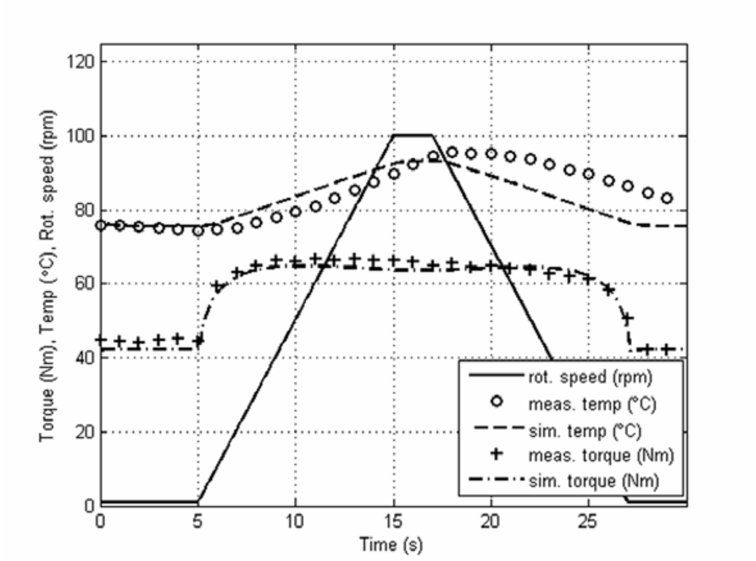


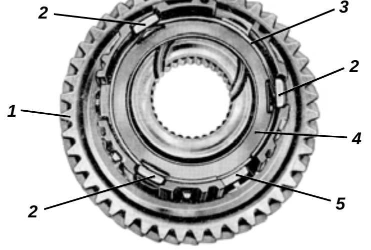
Fig. 3. Comparison between measurements and simulation with an axial force of 25.3kN.

It can be concluded that thermal effects have a significant influence on the torque transferred by the clutch, and it is therefore necessary to have a thermal model of the clutch combined with a temperature dependant boundary friction model based on empirical friction data for the friction material/transmission fluid combination of interest. Thus, the project has led to both new design of wet clutches for use in four-wheel drive cars and to new fill-for-life lubricants formulated to give improved traction.

TS16 – Lubricant for car gear box

1. Name of improvement:
2. Name of company: "Zastava automobili" - Kragujevac, Serbia
3. COST 532 project code: **TS16 (P12)**
4. Name of project manager and organisation:
   Prof Danica Josifovic, University of Kragujevac, Faculty of Mechanical Engineering
5. Description of the improvement in commercial use by the company mentioned above:

Determining the effect of lubricant type and service destination on element durability of synchronization systems (Fig.1) implemented in Zastava vehicles' gearboxes was conducted after the research, which had FIAT-Zastava's technical standard as its starting point. The tests have been done on complete gearbox. The loads on the test bench were as high as the exploitation loads.



1 - Gear
2 - Spacer
3 - Spring
4 - Synchromesh hub
5 - Synchromesh bulk ring

Fig. 1. Synchronization system assembly.

Measurements were conducted at the Laboratory for static and dynamic testing of the R&D Centre Automobile Institute "Zastava". Testing included 100.000 cycles of alternate engagement third and 4th gear. The complete test conditions and methodology of investigation are presented in [1-3].

For performing the experimental investigations, the following transmission (gearbox) and engine oils produced by NIS Oil Refinery Belgrade were used:

- Gearbox oil viscosity grading SAE 80W-90, of service destination API GL-3
- Gearbox oil of viscosity grading SAE 90 of service destination API GL-4
- Gearbox oil of viscosity grading SAE 90 of service destination API GL-5
- Monograde engine oil of viscosity grading SAE 40, of the API SF/CD level
- Monograde engine oil of viscosity grading SAE 40, of the API SF/CD level (with rerefined base oil)

When choosing the type and formula of oil submitted to testing, transmission oil SAE 80W-90 with the service destination of API GL-3 was taken as the reference type, as it is oil type which has already been implemented in "Zastava" vehicles.

Although transmission oils of service destination of API GL-4 and API GL-5 are monograde compared to the reference type they have 3-4 units larger viscosity, they have been chosen because they implement the most frequently used quality levels of transmission oil in modern day automobiles. The attempt was to test and evaluate the influence of these oil types on materials and functioning of the existing construction of gearbox system synchronization of "Zastava" vehicles.

Following the newest trends in contemporary automobile industry that engine and transmission lubrication be performed with same type of lubricant, a monograde engine oils were included as well. It was taken into consideration that viscosity gradation of engine oil SAE 40 is equivalent to the viscosity gradation of the reference type oil.

Influence of lubricant on synchronization element wear implemented in Zastava vehicles' gearboxes was conducted after the research, which had Zastava's technical standard as its starting point. The tests have been done on complete gearbox.

Measurements were conducted at the Laboratory for static and dynamic testing of the R&D Centre Automobile Institute "Zastava". Testing included 100.000 cycles of alternate engagement 3rd and 4th gear, with the speed of input shaft in lower gear being 6000 min^{-1}, fork load of 400÷500N, frequency of gear engagement of 20 cycles/min and oil temperature in the gearbox of 80÷90^{o}C.

As criteria for evaluating the state of elements and the complete system for synchronization has taken the wearing of frictional surfaces through height and clearance of synchronizer assemble-gear (conical contact) (Fig.2) and the change of gear synchronization functional characteristics (Fig 3).

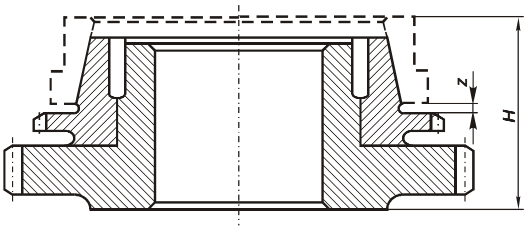
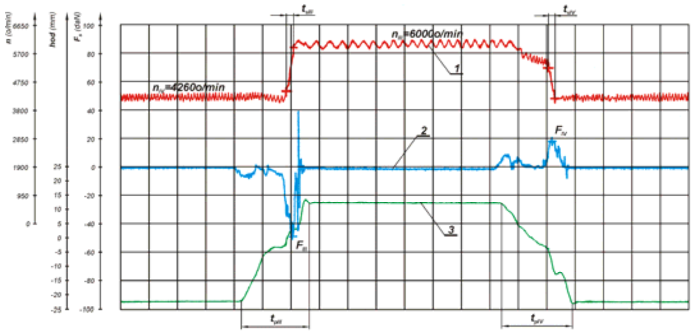


Fig. 2. Synchronizer assembly-gear.



F_s - Synchronization force,
t_s - Synchronization time,
t_p - Total time of engaging

Fig. 3. General form of records for gear synchronization functional characteristics.

While testing, it was noticed that failure of the assembly and thus wearing of surfaces were less with the elements for engagement of the III gear then with the IV gear elements. Due to effects of oil circle resistance at changing from the III gear into the IV gear the synchronization time and path of sliding are increased therefore the increased wearing of the synchronized IV gear elements is a direct result of the described process. Since the engagement of the III gear is reached by changing from lower to higher number of revolutions, wearing of the III gear elements is less and due to lower impact loads that then appears.

Fig.4 shows elements of the synchronization systems where the greatest wearing has been noticed.

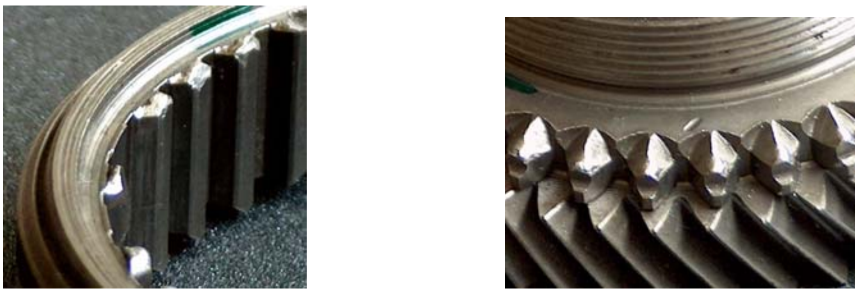
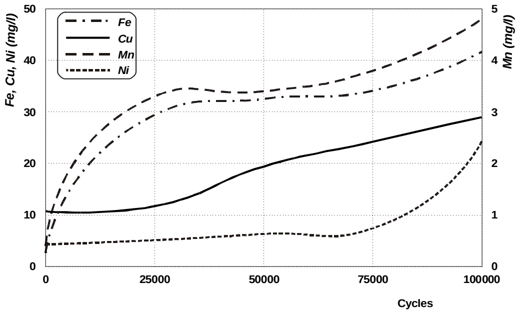


Fig. 4. Wearing of synchronization system elements.

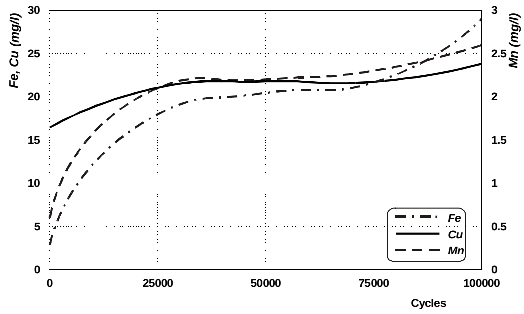
Estimation of the synchronization system wearing level and the degradation of additives and oils in the whole was preformed after the concentration of metal in oils had been defined by atomic absorption spectrophotometer (AAS).

The samples of tested motor and transmission oils that were received following the conducted 25000, 50000, 75000 and 100000 cycles of activated gear speeds during tests of system durability to synchronization were analyzed. Oil samples ($2cm^3$) were treated with concentrated sulphuric acid and paired up until dry. Samples dried in such a manner were burned with flame (70-80 minutes) and then annealed at 550^oC. After cooling, the samples were processed with concentrated hydrochloric acid (6 cm^3) and filtrated. The filtrate was diluted with distilled water (up to $25cm^3$), after which the determination of contents of iron (Fe), copper (Cu), nickel (Ni), manganese (Mn), and zinc (Zn) was conducted.

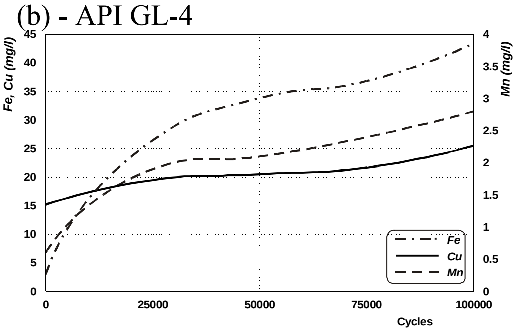
Figure 5 (a-d) show the results of metal concentration tests in the test samples of gearbox and engine oils SAE 40 depending on the number of performed gear shift cycles



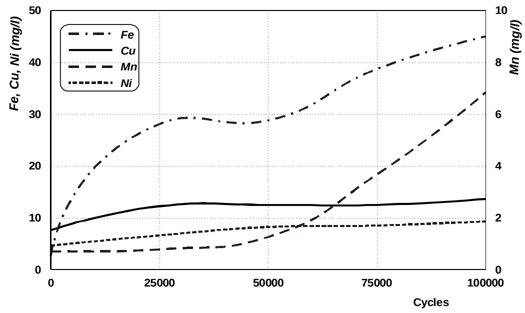
(a) - API GL-3



(b) - API GL-4



(c) - API GL-5



(d) - engine oil SAE 40

Fig. 5. Changes in concentration of metals during testing of oils.

The complete results and analysis of results presented in [1-7].

The results of testing the system for synchronization of Zastava gearboxes showed that the influence of transmission oils of service destination API GL-4 and API GL-5 and engine oil SAE 40 on the value of wearing of elements of synchronization of the gearbox of Zastava vehicles is minimal. It is obvious that transmission oil of service destination API GL-3 contributes to increase wearing of the assembly, but in spite of that the system for synchronization keeps functioning during the determined number of cycles. The analysis of results showed that the rerefined engine oil SAE 40-R considerably affects the functioning of the system of synchronization and gearbox as a whole, and leads to its failure, and is thus inadequate for use in this assembly.

Based on the complete results of tests on the synchronization system under the work conditions with various oil formulations it may be concluded that the API GL-4 gearbox oil was better than others and that there is justification for its further use for "Zastava" motor car gearboxes.

CONCLUSION**:**

As an output function of the performed researches, was be a introduction of new service destination gearbox oil for "Zastava" motor cars, namely the replacement of service destination API GL-3oil by oil of service destination API GL-4.

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Annex:

1. Participating countries
2. Organisation, list of Management Committee members
3. Implementation statistics (publications, projects, financing etc)
4. Participating institutes
5. Participating companies

Scientific Final Report, Appendix 1:

Participating Countries

Belgium
Bulgaria
Croatia
Czech Republic
Denmark
Estonia
Finland
France
Germany
Greece
Hungary
Ireland
Israel
Italy
Lithuania
Malta
Netherlands
Norway
Poland
Portugal
Romania
Serbia & Montenegro
Slovakia
Slovenia
Spain
Sweden
Switzerland
Ukraine
United Kingdom
USA

Scientific Final Report, Appendix 2:

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Scientific Final Report, Appendix 3:

Implementation Statistics

1. **TOTAL WORK EFFORT** in person years (py)

COST 532 Total	**260 py**
Engine Systems	34 py
Transmission System	143 py
Tribochemistry	83 py

2. **FUNDING** in thousand Euro (ke)

given as % public - % industrial - % own = total

COST 532 Total	**43 - 27 - 30 = 12.093 k€**
Engine Systems	56 - 18 - 26 = 2.491 k€
Transmission S.	40 - 30 - 30 = 7.369 k€
Tribochemistry	42 - 25 - 33 = 2.233 k€
Plan: COST 532 total	*55 - 15 - 30 = 9.000 k€*

3. **COMPANIES INVOLVED**

COST 532 Total	**103**
Engine Systems	19
Transmission System	47
Tribochemistry	37
Plan Total	*60*

4. **PROJECT WORK PRECENTAGE OF REALISATION BY END OF ACTION**

COST 532 Total	**92 %**
Engine Systems	92 %
Transmission System	92 %
Tribochemistry	93 %

- 28 projects out of 42 were finished (= 100 % realisation)

5. PUBLICATIONS AND REPORTS

given as int. journal + int. conference + nat. report = total

- **COST 532 Total 166 + 318 + 144 = 628**
- Engine Systems 25 + 79 + 37 = 141
- Transmission Syst. 50 + 173 + 58 = 281
- Tribochemistry 91 + 66 + 49 = 206
- *Plan: 100 + 100 + 100 = 300*

6. INDUSTRIAL IMPROVEMENTS IN COMMERCIAL USE

- **COST 532 Total 32**
- Engine Systems 10
- Transmission System 10
- Tribochemistry 12
- => 18 projects of 42 have resulted in industrial improvements
- *Plan: 40 new innovative products and process methods*

7. STATUS BY END OF ACTION

- Total of 42 projects including 58 research institutes and 103 companies from 27 countries
- Total volume: 260 person years and 12.093.000 €
- Three Working Groups
- WG1 Engine Systems: 11 projects
- WG2 Transmission Syst.: 17 projects
- WG3 Tribochemistry: 14 projects
- *Plan: 40-50 projects from 15 countries*
- **Web page: http://ltds.ec-lyon.fr/cost532/**

Scientific Final Report, Appendix 4:

Participating Institutes

BE Ghent Univ., Dept. Mechanical Construction and Production
BE Katolieke Univ. Leuven, Dept. Metallurgy and Materials Engineering
CH CSEM Centre Suisse d'Electronique et de Microtechnique SA, Neuchatel
CH Laboratoire Dubois, La Chaux-de-Fonds
CH EMPA Swiss Federal Laboratories for Materials Testing and Research, Thun
CH Ecole d'ingenieures de l'Arc Jurassien, Le Locle
CZ Brno Univ. Technology
CZ Univ. West Bohemia, Inst. Interdisciplinary Studies
CZ Institute of Physics, Academy of Sciences of the Czech Republic, Prague
DE Fraunhofer Inst. for Material and Beam Technology, Dresden
DE BAM Federal Inst. for Materials Testing, Berlin
DE Technische Univ. München, FZG Forschungsstelle für Zahnräder und Getriebebau
DE Stiftung Inst. Werkstofftechnik
ES Fundacion Tekniker, Eibar
ES CENIM National Centre for Metallurgical Research, CSIC High Council for Scientific Res.
ES Inst. de Ciencia de Materiales de Madrid, CSIC
FI VTT Technical Research Centre of Finland, Industrial Systems
FI Helsinki Univ. of Technology
FR Ecole Centrale de Lyon
FR INSA Lyon
FR Ecole Centrale de Paris, Lab. CFH, Paris
GR Aristotle Univ. of Thessaloniki
HR Faculty of Mechnanical Engineering and Naval Architecture, Zagreb
HU Bay Zoltan Inst. for Material Science and Technology, Budapest
HU Research Inst. Technical Physics and Material Science, Academy of Science, Budapest
IL Technion, Haifa
IR Dublin Inst. Technology
IT Univ. Trento, Dept. Materials Engineering
JP Tohoku Univ., Sendai
LT Lithuania Energy Inst., Material Research and Testing Lab., Kaunas
LT Academy for Int. Science and Technology Development Programmes in Lithuania, Vilnius
MT Univ. Malta, Msida
NO Norwegian Univ. of Science and Technology, Trondheim
PL Institute for Terotechnology, Radom
PL Inst. of Nuclear Physics PAN, Krakow
PT Univ. Coimbra, Dept. Mechanical Engineering
RO Univ. Galati, Faculty of Metallurgy and Materials Science
RO Univ. Targu-Mures
SE Lund University, Machine Elements Division

SE Luleå Univ. Technology
SE Halmstad Univ., School of Business and Engineering
SE Uppsala Univ., Ångström Laboratory
SI Univ. Ljubljana, Centre for Tribology and Technical Diagnostics
SI Univ. Maribor, Lab. For Characterisation and Processing of Polymers
SK Technical Univ. Kosice, Dept. Technologies and Materials
SK Welding Research Inst., Dept. Powder Materials and Metallurgy
SK Technical University, Dept. Non-Ferrous Materials and Treatment of Wastes
SK Slovak Academy of Sciences, Inst. Materials Research
UA National Academy of Science of Ukraine, Inst. for Problems of Materials Science, Kiev
UA Kharkov National Univ., Scientific Centre of Physical Technologies
UA L'viv National Univ., Dept. Inorganic Chemistry
UA Inst. Orthopaedy and Traumatology, Kharkov
UK Univ. Central Lancashire
UK Univ. Leeds
UK Univ. Southhampton, Surface Engineering and Tribology Group
US Argonne National Laboratory, Chicago
YU Univ. Kragujevac
YU Univ. Novi Sad

COST Action 532: TRIBOSCIENCE AND TRIBOTECHNOLOGY - SUPERIOR FRICTION AND WEAR CONTROL IN ENGINES AND TRANSMISSIONS

Scientific Final Report, Appendix 5:

Participating Companies

AU FMS Fachverband der Maschinen- und Stahlbauindustrie Österreichs
AU Prinz Maschinenfabrik
BE Lubriquip
BE Dana, Spicer Off-Highway Products Division
BE Falex Tribology
BE LionOil
CH CSM Instruments
CH Sulzer
CZ Skoda Research
CZ Advanced Technology Group
CZ SST Association of manufacturers and Suppliers of Engineering Technique
CZ AIA Automotive Industry Association
CZ Ecosond
CZ SVUM
DE M.Jyrgensen & Co
DE KVT Kurlbraum GmbH
DE Klüber Lubrication
DE Balzers
DE Euroflamm
DE VDMA Verband Deutscher Maschinen- und Anlagenbau
DE KTV Kurlbaum
DE MCP HEK
DE Pallas GmbH & Co. KG
DE RVS Technology
DE RHV Technik Rybak+Höschele GmbH
DE H.C. Starck GmbH
ES Guascor
ES Tarabusi
ES Krafft
ES Abamotor
FI Wärtsilä
FI Suomen Petrooli
FI Sisu Diesel
FI Savcor Coatings
FR HEF
IL Surtech
IL FriCSo
NL SKF ERC
HR RS-Metali, Novaki-Zagreb
HU Magosz National Association of Hungarian Engineering Industry

LI Balzers Liechtenstein
MT Surface Engineering Limited
SE Elforsk
SE Indexator
SE GE Energy
SE Haldex Traction
SE Scania CV
SE Statoil Lubricants
SE SKF Engineering and Research Centre
SE SKF Sverige
SE Volvo Technology Corporation
SE Volvo Car Corporation, Transmission Development
SE Scania CV, Materials Technology
SK EKL-IN Slovakia
SI Petrol
SI Olma
UK Lubrizol
UK Optimol
UK TeerCoatings
US GM