

Conf - 9110.50 -- 10

ANL/CP--75737

DE92 010501

Review of Surface-Modification Programs in the
DOE-OTM Tribology Program*

by

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February 1991

Received by OSTI
APR 01 1992

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Presented at the 1991 Annual Automotive Technology Development Contractors Coordination Meeting (ATD/CCM), October 28-31, 1991, Dearborn, MI.

*Work was supported by the Tribology Program, Office of Transportation Materials, U.S. Department of Energy, under Contract W-31-109-Eng-38.

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Abstract

The use of surface-modification treatments is a widely accepted practice to reduce the wear and modify the friction behavior of surface regions while maintaining desirable bulk properties (e.g. strength, hardness, thermal conductivity, etc.) of the underlying substrate. These treatments range from conventional diffusion processes such as carburizing steels for case-hardening gears, to advanced non-equilibrium processes such as ion implantation or ion plating. The objective of this task area is to develop and investigate new or emerging surface-modification processes that show a potential for improving and controlling the tribological behavior of surfaces and thus permit engineers to design components for advanced heat engines based on desired bulk properties and near-surface tribological properties.

The research is oriented toward processes that are applicable in advanced transportation technologies and focuses on components. Especially germane in this respect is the case of advanced reciprocating engines where upper-cylinder areas may operate at temperatures that exceed the range of normal liquid lubricants. This is considered by most experts to be the most critical issue facing the development of advanced heat engines.

Analogous needs exist for low-friction surfaces in seals for the regenerator cores for automotive gas turbine (AGT) engines.

For many applications the use of conventional surface-modification treatments is adequate to meet or exceed the requirements imposed by industry. For example, conventional case-hardening of surfaces is sufficient to produce transmission components that outlive other components in an automobile or truck. However, in many situations current technology cannot meet the demands. This is particularly true for high-temperature applications in corrosive environments such as those found in advanced engines. A number of coating treatments currently under development show promise in overcoming some of these limitations. These include vapor deposition (both chemical [CVD] and physical [PVD]) and ion-implantation processes and combinations of both, via ion-beam-assisted deposition (IBAD). These processes have in general been developed for applications other than tribology (e.g. electronics and optics industries) and need to be adapted and thoroughly evaluated for friction- and wear-control applications. Examples of successful tribological applications include chemical vapor deposition of hard coatings on carbide cutting tools and ion implantation of critical bearing assemblies in jet aircraft engines. While

these treatments show promise, the basic phenomena involved in modifying the surface properties and how they influence tribological properties need to be better understood to take full advantage of their potential.

This paper reviews a number of programs funded through the Engineered Tribological Interface (ETI) Task area of the Tribology Program that utilize energetic beams of atoms to enhance the mechanical and microstructural properties of near-surface regions to improve the tribological performance of critical components. The processes used in these programs include techniques based on chemical vapor deposition (CVD), physical vapor deposition (PVD), and ion implantation (II). A common feature of these techniques is their ability to produce dense and adherent modified surfaces without need for subsequent grinding/polishing treatments. Another feature of these techniques is their ability to introduce a wide range of elements into near-surface regions.

Argonne National Laboratory:

Research at Argonne National Laboratory focuses on the use of ion-beam-assisted deposition (IBAD) technologies to deposit coatings as high-temperature solid lubricants and hard wear-resistant surfaces. The research involves: evaluating the tribological performance of ceramic and metallic surfaces (coated with lubricious oxides, soft metals, or diamond-like carbon - DLC) under dry and lubricated conditions from room temperature to 600°C, investigating the effects of processing conditions on the adhesion of the lubricious films (and hence their tribological performance), and characterization of processing conditions on the mechanical and microstructural properties of lubricious, hard coatings.

Research at ANL on the tribological performance of silver coatings deposited on ceramics under dry sliding conditions continued this past year. Specifically, an investigation was made of the effect of 2- μm -thick silver films on the tribological behavior of Si_3N_4 ceramics in humid and dry air. Friction and wear tests were carried out on a ball-on-disk tribometer under a load of 5 N, at velocities ranging from 0.1 to 6 m/s. The steady-state friction coefficients of Si_3N_4 on itself ranged from 0.6 to 0.8. For the Si_3N_4 balls sliding against IBAD-silver-coated Si_3N_4 disks, the friction coefficients ranged from 0.3 to 0.45 in dry air and from 0.35 to 0.7 in humid air. The wear of most IBAD silver-coated disks was practically unmeasurable, and the wear of the Si_3N_4 balls sliding against these Ag-coated disks was influenced by both humidity and sliding velocity. In dry air, ball wear was reduced by factors of up to 1100 below that of balls slid against uncoated disks.

Dry sliding tests were also initiated at Argonne National Laboratory to investigate the tribological properties of diamond-like carbon (DLC) films ion-beam-

deposited on SiC , Si_3N_4 , and ZrO_2 . The friction coefficients of carbon films sliding against Si_3N_4 and sapphire balls were in the range of 0.02-0.04 in N_2 and Ar, but significantly higher (≈ 0.15) in humid air. The wear rates of ceramic disks coated with carbon films were below detectable limits, and, depending on the test environment, the wear rates of counterface ceramic balls were reduced by two to four orders of magnitude below those of balls slid against uncoated ceramic disks. Micro-laser-Raman spectroscopy and scanning electron microscopy were used to analyze the structure and chemistry of worn surfaces and to elucidate the graphitic and/or diamond-like behavior of DLC films.

In another effort at ANL, tribological characterization of self-lubricating boric acid films continued. Specifically, an investigation was made of the effect of contact pressure on the friction coefficients of boric acid films forming on boric oxide coatings. Using the Hertzian contact model, the shear strength of boric acid was estimated. It was found that the friction coefficient of self-lubricating boric acid films decreases substantially with increasing contact pressures. Regression analyses of a large number of friction data suggested that the shear strength of boric acid films was about 22.9 MPa. This value is comparable to the shear strength of MoS_2 (e.g. 24.8 MPa).

ANL research on the lubricated performance of IBAD Ag-coated ceramics also continued this past year. Initial results at temperatures up to 150°C indicate that low friction and wear can be achieved through the combined action of solid and liquid lubricants. The friction coefficients (at room temperature and 150°C) of silicon nitride pins rubbed against IBAD Ag-coated silicon nitride flats in the presence of a synthetic lubricant (SDL-1) were approximately an order-of-magnitude lower than those for silicon nitride pins rubbed against uncoated flats under dry conditions. For similar comparisons, the wear rates (of the mating silicon nitride pins) were reduced by approximately three orders of magnitude in spite of the observations of coating detachment during long-time room-temperature wear tests with the liquid lubricant. At 250°C and up to 50N normal load the friction and wear were substantially reduced in all cases, showing again the effectiveness of combined solid and liquid lubrication of ceramics. Formation of a deposit from the oil was observed at 150°C and prolonged exposure of the Ag coating to oil lubrication reduced the durability of the coating. Subsequent tests discussed below indicated the effect of the deposit could be reduced by using an indium bond coat between the substrate and the silver coating.

Additional tests on the effects of liquid lubricants (SDL-1) on zirconia substrates were also performed at ANL. Thin silver films 1 to 2 μm thick were produced on ZrO_2 flats by ion-beam-assisted deposition (IBAD) and used as the solid lubricant. Wear tests were performed on an oscillating-slider wear test machine at

temperatures up to 250°C. For the specific test conditions explored, we found that (a) without any type of lubrication, the friction coefficients of ZrO₂/ZrO₂ test pairs were on the order of 0.6, and the average wear rates of pins were in the range of 5 x 10⁻⁵ to 10⁻⁴ mm³/N/m, depending on the test temperature, (b) the use of IBAD silver coatings alone reduced the friction coefficients of sliding pairs by factors of 2 to 4 and the wear rates of pins by 3 orders of magnitude, (c) the use of liquid lubricant reduced the friction coefficients of ZrO₂/ZrO₂ test pairs by a factor of about 5 and the wear rates of pins by 1 to 2 orders of magnitude, and (d) the concurrent use of silver films and lubricant oil resulted in virtual elimination of the wear of both the pins and the flats and in reduction of the friction coefficients to approximately 0.05 at room temperature and approximately 0.15 at 250°C.

In another area, ANL provided IBAD Ag-coated piston rings for evaluation in an instrumented single-cylinder diesel test engine at Wayne State University. The engine was instrumented to continuously measure both the instantaneous friction torque (IFT) of the engine, and, the friction force associated with the piston-ring assembly as a function of the crank angle. Comparison of IFT measurements on a single-cylinder engine test stand (without the cylinder head) outfitted with conventional piston ring-packs and IBAD-treated ring packs indicated the IBAD-treated ring packs produced 14 to 28% lower frictional torque than the conventional rings. Comparison of the IFT and piston-ring frictional force of IBAD-coated vs. uncoated rings with the engine fired (but under no load) indicated the IBAD-coated rings reduced both the IFT and frictional forces associated with the piston rings.

An important aspect in achieving the improvements in the tribological properties described above for the IBAD-coated substrates is the adhesion of the coatings to the underlying material, particularly for ceramic substrates. During the past year, research continued on investigating how deposition conditions (type of ion, ion current density, and ion energy) and use of intermediate bond-coats affect the adhesion of metallic films to ceramics. One effort at Argonne found that the use of a Ti bond layer coupled with ion-beam-assisted deposition (with Ar, N₂, or O₂ ion beams) resulted in the greatest adhesion of Ag films to silicon nitride. Without the use of a thin Ti bond layer, adhesion of Ag to silicon nitride was below 20 MPa. With the Ti bond layer, however, adhesion strengths in excess of 70 MPa were achieved. In other tests, indium was co-evaporated with silver to examine the effects of small alloying additions of In on the adhesion of Ag to silicon nitride substrates. Pull-test measurements indicated that a thin layer (approximately 30 nm thick) of silver alloyed with 5 to 25 at. % In increased the adhesive strength from about 5 MPa at 0 at. % In to 40 MPa at 25 at. % In. Subsequent tribological tests indicated that incorporation of the In interlayer into Ag coatings

significantly improved the durability of the coating as a boundary film during oil lubrication. The optimum amount of In was observed to be about 20 at%. At higher concentrations of In, the possible formation of intermetallic compounds appears to have a detrimental effect on the tribological performance of the film at room temperature. When the concentration of In is less than 20 at%, the adhesion of the Ag coating increased with increasing amount of In and no detrimental effect on the tribological performance was observed.

Research was also initiated at ANL to develop hard, lubricious coatings because of their potential applications in LHREs and gas turbines. Research designed to complement the effort at the NRL was started on reactive ion-beam-assisted deposition (RIBAD) of TiN. Hard TiN films deposited by IBAD were examined by X-ray diffractometry to determine the effect of processing conditions on the orientation of the deposited films. The results indicate the texture of the IBAD films was dependent on the ratio of the Ar ion to Ti atom arrival rates and the N₂ partial pressure. The results also indicated the textures of the IBAD films were different from TiN films produced by conventional ion plating and reactive sputtering processes. The occurrence of Ti₂N and TiN phases was correlated with the film composition as determined by AES. The results indicate that the IBAD titanium nitride films deposited at high Ar⁺/Ti ratio and low nitrogen partial pressure may have reduced nitrogen concentration which makes the formation of Ti₂N phase possible.

Investigations on RIBAD of hard BN films were also initiated at ANL. Initial microhardness data on BN films deposited by RIBAD indicate quite hard films can be deposited. Film hardnesses as high as 36.4 GPa were achieved, with the hardness being strongly dependent on the deposition conditions.

Naval Research Laboratory:

During FY 91, the third year of a three-year program at the Naval Research Laboratory, research focused on the adhesion and room-temperature tribological performance of TiN and Cr₂O₃ coatings deposited by IBAD. The friction and wear behavior of chromium oxide coatings deposited using the IBAD technique at two different deposition rates and two different thicknesses onto single-crystal silicon substrates was evaluated using a silicon nitride ball as the mating component. The wear rates of 0.5 micrometer-thick Cr₂O₃ coatings were high and the coatings were removed after approximately 50 revolutions under 1 or 2 N loads (6-mm-diameter balls). In contrast, 2 micrometer-thick Cr₂O₃ coating remained intact after 500 passes with virtually no wear being detected.

The adhesion strength and failure modes of IBAD TiN coatings were examined at NRL using a

Revetest acoustic-emission scratch tester. It was found that the adhesion strength which is represented as a critical normal load and the failure modes of the coated system are influenced by the coating thickness, the coating and substrate material properties and the ratio of incident argon ions to titanium atoms (R). The critical load increased with increasing substrate hardness. For coatings of thicknesses 0.5, 2.0, and 5.0 micrometers and with $R = 0.4$, the highest critical load was obtained for the intermediate-thickness coating. For coatings of thickness 2 micrometers and with R values of 0.1, 0.4, and 0.7, the highest critical loads were obtained for the $R = 0.4$ coatings. The rapid increase in acoustic emission could be correlated with the spallation of the coating. Further, the change in slope of the coefficient of friction of the diamond stylus sliding on the coated system could be correlated with the removal of the coating from the scratch track.

Universal Energy Systems:

At Universal Energy Systems (also in their third year of a three-year program), the thermal stability of MoS_2 synthesized by ion implantation of ceramics was studied. They demonstrated that an MoS_2 phase can be formed in an SiO_2 substrate by Mo^+ and S^+ implantation. The MoS_2 phase was found to be more stable in an oxygen-free atmosphere compared to that in air. Also, the ion implantation-induced MoS_2 phase in SiO_2 remained stable at room temperature after storage for a year compared to sputter-deposited MoS_2 coatings which oxidized in 6 to 8 months at room temperature. Since the oxidation temperature of the MoS_2 phase obtained by ion implantation is found to be higher compared to the reported oxidation temperature of the MoS_2 coating, it is expected that the ion-implanted MoS_2 synthesized surface may provide a higher-temperature lubricating ability as compared to that of an MoS_2 coated surface.

Basic Industry Research Laboratory:

The research effort at the Basic Industry Research Laboratory (BIRL), which entered its second year of a four-year effort, investigated the tribological properties of nitride and carbide coatings of Ti, Zr, and Hf deposited using the high-rate reactive-sputtering (HRRS) process. This program addressed some basic tribological questions on the friction and wear properties of these coatings that were raised in a previously funded ECUT program on hard coatings for cutting-tool applications. Another aspect of the BIRL program focuses on the doping of these coatings with small amounts of As, Sb, and Bi to increase their hardnesses. Reactively sputtered TiN coatings were tested under rolling-contact-fatigue (RCF) and scuffing environments. Results of the RCF tests demonstrated that the thickness of the deposited TiN film has a large effect on the RCF lifetime. Films with thicknesses greater than approximately 2 micrometers actually had lower RCF

lifetimes than uncoated samples (4118 steel) while substrates coated with 0.25 micrometers of TiN had RCF lifetimes approximately 6 times that of uncoated steel. Scuffing tests performed on uncoated and coated 4118 steel demonstrated the presence of a 0.25 (or 1.0) micrometer TiN coating increased the scuffing load by a factor of 2 to 3.

Further research at BIRL investigated the effects of substrate hardness and coating hardness on the tribological behavior of titanium nitride-coated steel rollers with a roller-on-cylinder tribo-tester. TiN coatings with varying coating parameters were coated on different-hardness substrates. The properties of both the substrate and the coating were found to be very important in determining the wear performance of the rollers. From experimental results it was found that the relatively hard TiN coatings (29.4 GPa) enhanced the scuffing failure load by ten times when deposited on relatively hard substrates (Rc 62), and did not improve the performance of soft substrates (Rc 45). For relatively soft substrates (Rc 45), the benefit of using a relatively soft TiN coating (21.6 GPa) rather than a hard TiN coating has been demonstrated.

Colorado State University:

At Colorado State University, in its second year of a three-year program, research on the use of ultrahigh current-density ion implantation for tribological applications continued. The goals of this program are 1) to investigate the behavior of metallic and ceramic substrates implanted with gaseous ions such as N^+ , and 2) to develop an ion source capable of implanting substrates at ultrahigh current densities of metallic ions such as Cu, Fe, etc. During the past year significant progress has been made in characterizing the wear behavior of 304 stainless steel implanted with N ions and in assembling components for the metallic ion source. The high-current-density, metallic-ion-implantation system was operated extensively on copper and operating procedures that facilitate process control were established. System design deficiencies identified during these tests were corrected and improvements were made which enabled copper-ion-beam extraction at current densities ranging from 100 to 500 $\mu\text{A}/\text{cm}^2$. Subsequently, the implanter was operated on titanium at current densities as high as 400 $\mu\text{A}/\text{cm}^2$. Beam energies were typically varied from 20 to 50 keV during the tests.

Summary

DOE-funded research is under way at several laboratories to assess the potential of advanced surface-modification techniques to improve the tribological performance of materials that will be used in advanced, fuel-efficient engines. Significant advances have been made in proving the technical capability of a number of ion-beam-based technologies for improving the

tribological performance of metallic and ceramic compounds. Work is currently underway to develop collaborative research efforts with transportation industries to assess the viability of these technologies.

Acknowledgments

This work was supported by the Tribology Program, Office of Transportation Materials, U.S. Department of Energy, under Contract W-31-109-Eng-38.

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