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THE FRICTION AND WEAR PROPERTIES OF SPUTTERED HARD REFRACTORY COMPOUNDS

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Abstract

The friction and wear properties of several refractory silicides, borides, and carbide coatings were examined. The coatings were applied to type 440C steel surfaces by radiofrequency sputtering. The friction and wear properties of the coatings were found to be related to stoichiometry and impurity content of the bulk coating as well as the degree of interfacial adherence between coating and substrate. Bulk coating stoichiometry could to large extent be controlled by the application of a negative bias voltage during deposition. Adherence was promoted by the formation of an oxidized layer at the interface. Deliberate preoxidizing of the 440C produced enhanced adherence for many compounds which is related to the formation of a mixed oxide transition region.

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INTRODUCTION

The use of hard coatings for improving wear resistance is commonly practiced. Coating of seals, cams, and valve heads are typical examples. Hardened surfaces are routinely prepared by conventional techniques such as carbonizing or nitriding. Hardfaced coatings can be applied by electroplating, welding, or plasma spraying (1). These methods of application are quite suitable for some substrates and some coating materials, but not for all. Limitations imposed by the high temperatures required for furnace or plasma spraying methods preclude their use on some component or alloy systems. In addition, mechanical stresses can be induced in components due to thermal gradients introduced during the coating operation. Further, design considerations may require expensive grinding to finished dimensions depending on the precision of the part.

Coatings applied by vacuum deposition methods are generally thin enough (<10 μm) so that for all practical purposes the finished dimensions are unchanged by the coating process. In addition, the surface being coated is not subjected to the high temperatures required by other methods. Adherent, dense coatings of both metals and nonmetals can be applied by the vacuum deposition methods. In particular, the refractory metal carbides, silicides, and borides can be deposited by radiofrequency (rf) sputtering.

These compounds are of interest because of their extreme hardness (up to 5000 kg/mm^2) and potential for use at elevated temperatures. Little work has been done on evaluating these materials as antiwear coatings when applied by rf sputtering. Some preliminary work did indicate that pronounced improvement in ball-bearing life was obtained when bearing races and cages were precoated with a refractory silicide before being lubricated with molybdenum disulfide (2).

The objective of this investigation was to examine the adherence, friction, and wear properties of some refractory compounds applied by radiofrequency sputtering to a steel substrate and to determine how the friction, adherence, and wear properties of these compounds are effected by bias and substrate preparation.

APPARATUS AND PROCEDURE

rf Sputtering

The sputtering of the materials used in this investigation was conducted in a commercial rf diode apparatus operating at 13.56 mHz. The apparatus is shown schematically in Fig. 1. The material to be sputter deposited is in the form of a hot pressed disk shaped compact, 15.2 centimeters in diameter which was commercially purchased. The compact or target as it is called when mounted, is cemented with a silver conductive epoxy onto a copper backing plate (0.60 cm thick). The copper backing plate is mounted onto a water cooled rf electrode also 15.2 centimeters in diameter. The specimen to be coated is placed 2.5 centimeters directly below the target on an electrically insulated block. The insulated block sets on the grounded substrate table. (The target and the grounded table comprise the rf diode.) An additional voltage from 0 to -1500 volts dc may be applied directly to the specimen either for specimen cleaning by dc sputter etching or for biasing the specimen during film deposition and growth.

Provision is made for rotation of the entire substrate table so the disk specimen may be moved out from under the target. The target thusly can be cleaned without contaminating the specimen. If desired the disk could be cleaned by sputter etching during this time.

The entire system comprising the diode is contained in a glass bell jar, 45 centimeters in diameter. The system is mechanically forepumped and oil diffusion pumped through a liquid nitrogen cooled baffle. During deposition, high purity argon (99.9995 percent) was bled continuously into the system through a leak valve and a dynamic pressure balance between the pumping system and argon leak of approximately 20 microns was maintained in the bell jar.

Prior to starting deposition, the target was cleaned by rf sputtering until little pressure rise due to outgassing occurred. Following target cleaning the selected bias voltage was set and the specimen rotated back under the target and deposition initiated. The power density was constant for all coatings at 1.64 watts/cm^2. Higher power levels were found to increase contamination by heating of the target (3). Deposition times were from 20 to 60 minutes, depending on material

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which produced coatings between 2000 Å and 3000 Å for all materials as determined by surface profilometer measurements of a step.

Friction Experiments

The testing of the rf sputtered films was done on a pin on disk apparatus. The pin on disk configuration is widely used for solid film lubrication testing. The apparatus shown in Fig. 2 consists of a flat 6.4 centimeter diameter disk which is mounted on the end of a rotating shaft. The disk specimen is a type 440C steel disk which has been rf sputter coated with one of the test materials.

Loaded against the surface of the disk is a 0.476 centimeter radiused pin of 304 stainless steel. The pin is mounted in a holder on the end of and perpendicular to a gimbal supported arm. The pin is loaded against the surface of the disk by hanging weights on the arm halfway between the pin and gimbal. Normal loads from 0.1 to 5 newtons were used. The end of the arm opposite the pin holder is attached to a strain gage bridge which measures the frictional force.

The entire apparatus is enclosed in a clear plastic box. A constant flow of dry nitrogen is maintained in the box prior to and during friction tests to minimize environmental effects.

The experiments reported in this paper were conducted at a constant speed of 25 centimeters per second. The duration of each friction experiment was 30 minutes. Following the friction experiments, the disks were examined by optical microscopy and surface profilometry to determine the extent, if any, of film wear or spalling from the 440C substrate. Film spalling was readily observed on the surface profile tracing by the appearance of sharp, vertical sided, flat bottomed cross sections which are characteristic of a brittle film spall. Rider wear volume was calculated from the measured pin wear scar diameter.

It is recognized that the pin on disk configuration provides extremely high contact stresses in contrast to the conforming type of contract. Because of the uncertainties with regard to modulus values for coated substrates, no attempts to calculate Hertzian stresses were made for the coated samples. However, the Hertzian stress for the uncoated disk contacted by a 304 stainless steel pin at a 0.5 newton load was 24.6 kg/mm^2. Any coating that performs well under extremes such as exist in these experimental conditions would be expected to perform well or better under less severe conditions. Thus in this regard, the pins on disk test can be regarded as an upper limit screening test for these coatings.

Specimen Preparation

The 440C disk specimens were all prepared in the same manner prior to coating. The disks were abraded on silicon carbide paper down to 600 grit. Then they were polished with 3 μm size diamond paste followed by lapping with 1 μm alumina. Following lapping, the disks were rinsed with alcohol, dried and when desired, inserted into a muffle furnace for deliberate oxidizing. The furnace was held at 340° C at times from 18 to 60 hours. This treatment was sufficient to produce a thin transparent oxide film with a slight reddish cast, without softening the disk. Follwing cooling to room temperature, the disks were inserted into the sputtering apparatus for coating. An Auger emission spectroscopy analysis of the oxidized 440C showed the surface to be primarily iron oxide. Very little chromium was observed in the Auger spectrum.

RESULTS AND DISCUSSION

In order for any coating to provide wear resistance, it must adhere to the surface to be protected from wear. There are several sputtering parameters as well as substrate conditions that will affect coating adhesion. The first priority in studying thin, wear resistant coatings was to determine the sputtering conditions that would yield the best adherence. It is known from the literature (3) that sputter etching (cleaning) of the substrate can enhance adherence. Also, biasing the substrate with a negative potential during deposition is known to exert an influence on film properties. For example, biasing has been shown to affect the structure, electrical resistivity, impurity content, and stoichiometry of sputtered films (4, 5). Both of these methods were used in order to determine their effectiveness. Adherence is difficult to evaluate quantitatively, but several qualitative tests are used. The scratch test consists of drawing a stylus (diamond) across the coating at increasing loads until significant separation of the coating from the substrate occurs. This method has appeal for studying wear-resistant coatings because the test parallels a sliding friction experiment. The stresses are similar to those generated on an actual sliding surface. The scratch test was used as a compliment to full scale pin-on-disk tests in order to examine the adherence microscopically in the scanning electron microscope.

A diamond stylus scratch tester was incorporated into the specimen stage of a scanning electron microscope (SEM). The test specimens consisted of a rf sputter coated 2.0-centimeter-diameter 440C steel disk and a 25-micrometer-radius diamond stylus. The disk was mounted on an adapter to the rotary specimen feedthrough. The diamond stylus, which contacted the disk normally, was mounted in the end of an arm which projected into the chamber via a bellows from a gimbal system outside the chamber. The gimbal was controlled by a micrometer, which allowed for precise positioning and loading of the stylus on the disk. This device has been reported in the literature previously (6).

Effect of Bias

The general effect of biasing the substrate during film deposition is to produce a coating less prone to fracture and spalling in contrast to coatings that were deposited with the substrate held at ground potential. A typical series of scratches on a Cr_3C_2 coated 440C surface are shown in Fig. 3. Both tracks were made with the same applied load at the same speed. The cracking and fracture of the film was also evidenced in the friction coefficient tracings of the grounded deposited coating (fig. 4). Contrast the rough tracings with the lower smooth tracing for the biased sample. Similar results were observed during full scale pin on disk test. For example, Fig. 5 shows wear tracks for titanium carbide coated 440C with and without a bias voltage. Bias clearly has the effect of reducing wear on the coated surface.

These results prompted a further investigation into the effect of bias on the composition of the films and the interface between the coatings and substrate. Detailed results of that investigation are reported in the literature (7, 8) and another paper presented at this meeting (9). In general, it was found that samples deposited without bias were not stoichiometric and contained large amounts of oxide impurities. Bias deposited samples, on the other hand, were closer to target stoichiometry and considerably freed of oxides. For example, coatings sputtered from a chromium boride target without bias were almost 75 percent oxides while when a bias voltage of -300 volts was applied during deposition, the oxide content dropped to approximately one-third that level (5). This drop is due the backsputtering of the growing coating causing the oxides to be reduced.

Applications where a substrate bias was employed, either dc or rf, have been reported in the literature (10, 11). These observers have noted significant differences in coating properties depending upon bias conditions. Properties such as electrical resistivity and crystallinity are reported to be altered by biasing. Most of these studies, however, have been conducted with analyses of metallic films rather than inorganic compounds. Moreover, most results reported on composition variations are the result of indirect measurements such as relating oxygen impurities to electrical conductivity rather than the direct measurements done for these inorganic compounds.

It appears that improvements in adherence and wear of coatings applied with bias are related to improvements in the bulk quality of the films. This results specifically from maximizing the stoichiometry by a reduction of oxide impurities.

Specimen Preparation

Precleaning the substrate to be coated by argon ion bombardment (etching) prior to actually starting the deposition process is a common practice and it is widely accepted as a means of improving bonding between coating and substrate. Sputter etching is thought to promote bonding by removing contaminant layers and oxides so that the "clean" substrate can interact with the film constituents.

To determine if sputter etching would yield better bonding between the refractory borides, silicides, and carbides and the 440C substrate, all compounds were sputter deposited onto 440C substrates that had been sputtered etched for 15 minutes at -1200 volts prior to coating. While the results of these experiments were specific to each material, the general observation is that sputter etching did not, in any case, promote bonding and in some cases actually was detrimental to adherence. An example is given in Fig. 6. Shown in Fig. 6 are sputter etched 440C disks that had been coated with Mo_2C. One coating was applied with a bias chosen from Ref. 7 to produce maximum stoichiometry and minimum oxide impurities. The second coating, applied with the substrate grounded, was oxide contaminated. Both disks were cleaned by sputter etching before coating.

The bias deposited Mo_2C coating peeled off spontaneously (fig. 7) due to the intrinsic film stresses. The second coating remained intact. These results suggested that oxidized films adhere better than the high quality biased coatings or that oxide layers at the interface promote bonding. Figure 8 shows friction data for Mo_2C coatings applied to 440C under three different conditions. Also shown at the top of the figures are surface profile tracings of the wear tracks after running. The high friction of the grounded sample on an etched disk is due to poor bulk film properties. The second sample was done on an etched disk but the sample was kept grounded the first 2 minutes of deposition in order to form an oxidized layer. Following that the bias of -300 volts was applied in order to produce a high quality bulk carbide film on top of the oxidized layer. Low friction with no detectable wear was obtained for this specimen. A third specimen that was preoxidized in a muffle furnace before being placed in the sputtering apparatus was coated with -300 volts bias the entire time. Low-friction and wear were also obtained with this sample, clearly verifying the importance of the oxidized interface. The improvement in bonding was also observed for several other of the compounds, while for still others no apparent benefits were gained.

Titanium boride was another material which was better bonded to an oxidized disk (fig. 9). Also shown for comparison are friction and rider wear data for uncoated specimens, both as polished and as oxidized. Clearly oxidation of the disk surface, by itself, is detrimental due to the formation of abrasive hard iron oxide. While coating did reduce the overall rider wear, the average friction was high due to film spalling for the specimen applied to a sputter etched surface. In contrast, the friction and wear are both reduced when the disk is oxidized prior to coating.

With molybdenum silicide, the improvement in bonding was such that in contrast to spalling which occurred on an etched surface, the film after running was still intact and even exhibited a metallic transfer from the 304 rider onto the coated disk (10).

The oxidation time of the disk prior to sputter coating was 18 to 20 hours. A few samples were allowed to remain in the furnace for a longer period to determine if more oxidation would further benefit friction properties. Figures 11 and 12 show friction and wear data for titanium carbide coated onto disk with three different preparations. Clearly longer oxidation times were beneficial in this case. A separate investigation to determine the optimum oxidation conditions for each compound is probably required. However such a study was beyond the scope of this work.

The importance of oxides in the bonding of ceramic to metals is not new to this study. Early work done on cermets (12) clearly established that large gains in bonding could be obtained if deliberate oxidizing was included in the processing sequence. In addition, coatings of metallic electrical contacts on ceramic insulating surface (e.g., Al_2O_3) were found to adhere better by the mixing of oxides and/or spinel formation (13, 14). Also, work done, on the shear strength of metal-ceramic contacts in vacuum showed large increases in the strength of some of these junctions if the clean metal component was exposed to oxygen prior to contact (15). Interestingly enough even the adherence of vapor deposited noble metal films on glass was found to increase if the deposition was done with a high partial pressure of oxygen present (16).

The question that arose during this investigation was why some compounds were better bonded to oxidized surfaces, while others showed little if any improvement. The answer likely is related to the degree of interaction between the oxidized surface (Fe_3O_4) and the oxidized components of the film constituent elements. Analysis of some of the interfacial regions formed during deposition of three molybdenum compounds are shown in Fig. 13. These data were taken by X-ray photoelectron spectroscopy of the depth profiled interfaces (8). The schematic representations show the approximate half maximum widths of the interfacial oxides. The silicide coating has both oxides of silicon and molybdenum at the interface. There is a fair amount of mixing between the iron oxide and the two film constituent oxides. The boride coating, although also exhibiting oxides of both constituents, shows very little mixing with the iron oxide. This likely accounts for the fact that the friction and wear of Mo_2B_5 coatings were not enhanced when the surfaces were oxidized (fig. 14). The molybdenum carbide interface shows only molybdenum oxide, the oxide(s) of the other constituent element (carbon mon-/di-/oxide), presumably being pumped off due to its gaseous state. The molybdenum oxide is very mixed into the iron oxide and this explains the major improvement in adherence and thusly friction when the disk was oxidized (fig. 14).

The variation in oxide mixing that occurs is likely to be influenced by a number of factors not yet investigated such as oxygen partial pressure, deposition rate, bias level, and so forth. Attempting to predict on the basis of thermodynamic considerations such as free energies or oxidation potentials (17), is difficult because the state of the reactants is not defined. In addition, ceramic phase diagrams assume equilibrium conditions - also not necessarily the case in sputtering.

It of course must also be recognized that these results are specific to the material used as the disk (440C). The fact that bonding is promoted by the formation of iron-oxide does, however, suggests that these results may in general be applied to the coating of most steel surfaces where iron oxides would be expected to form at the surface. For nickel base alloys or for austenitic stainless steels, different coating-substrate interactions must be considered.

CONCLUSIONS

CONCLUSIONS

Extensive testing and analysis of radiofrequency sputtered refractory silicide, borides and carbides coatings clearly show that the performance of any friction and wear coating is controlled by two factors. First, the bulk properties of the film, itself, and second, its ability to adhere to the substrate.

The bulk properties can be significantly improved by property biasing the substrate during deposition. Stoichiometry is generally improved by the reduction of oxide impurities.

Substrate bias, while producing good bulk film properties can adversely affect adhesion by removing interfacial oxide layers. Sputter cleaning of substrates prior to deposition produced poor adhesion for the same reason. Deliberately preoxidizing the substrate prior to coating produced significant gains in coating adherence for many compounds. The improved adherence could be related to the formation of a mixed oxide interface.

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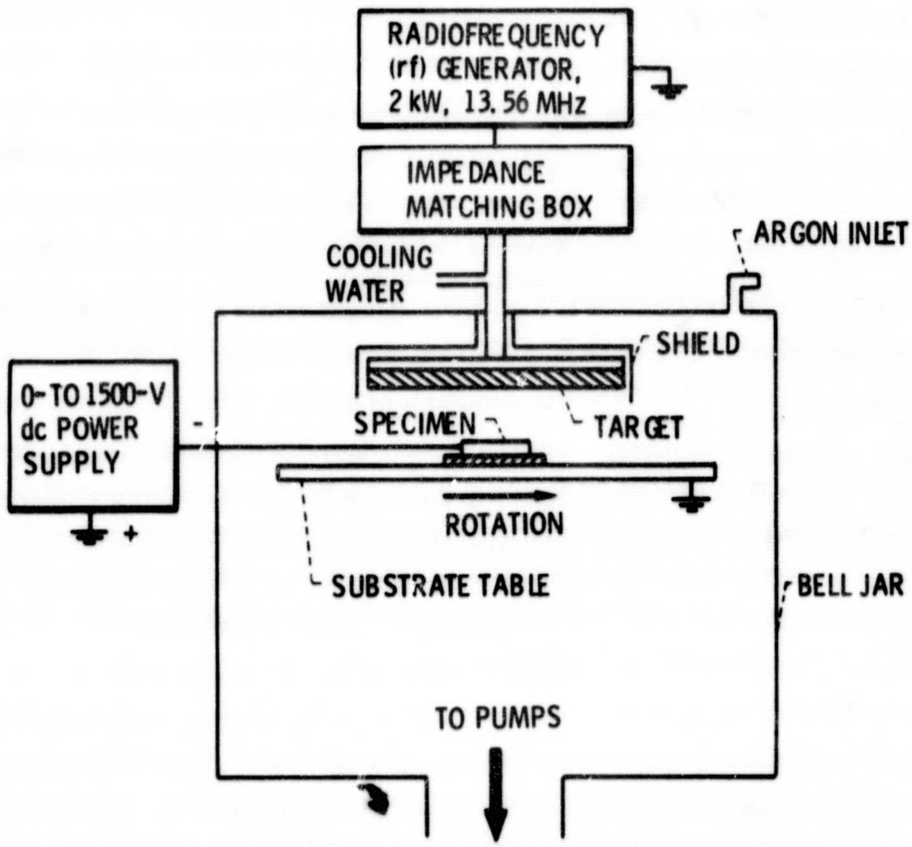


Figure 1. - Schematic of radiofrequency sputtering apparatus.

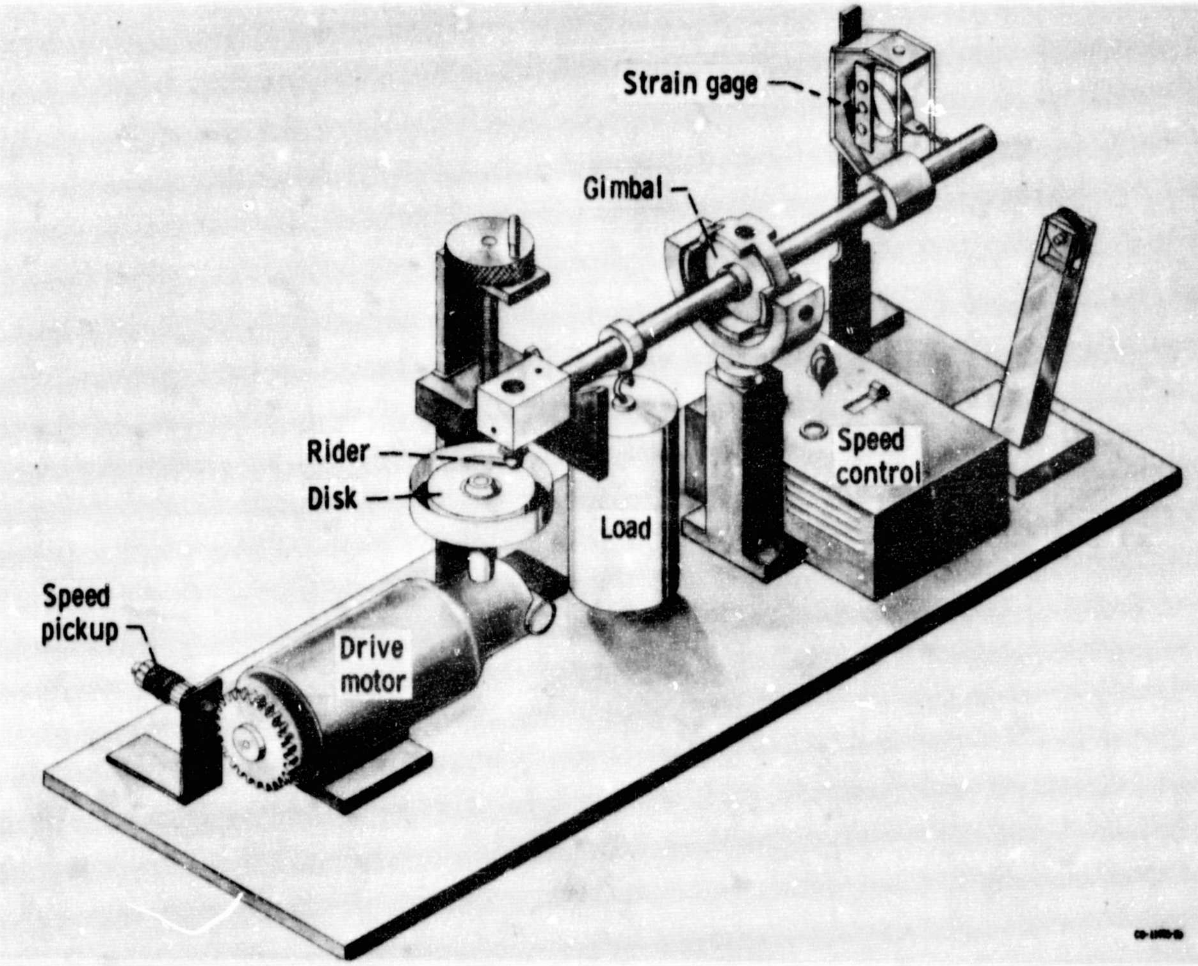
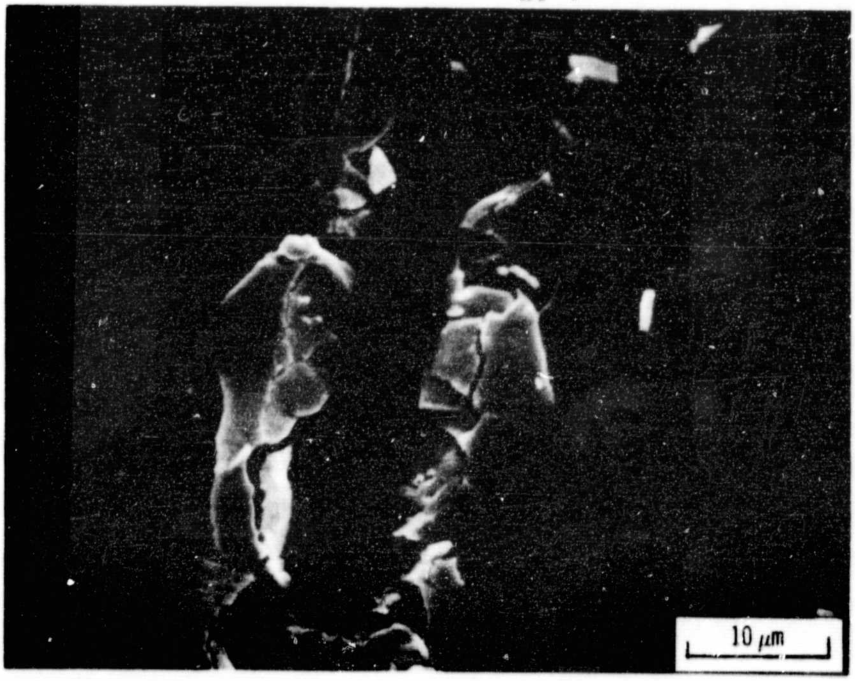
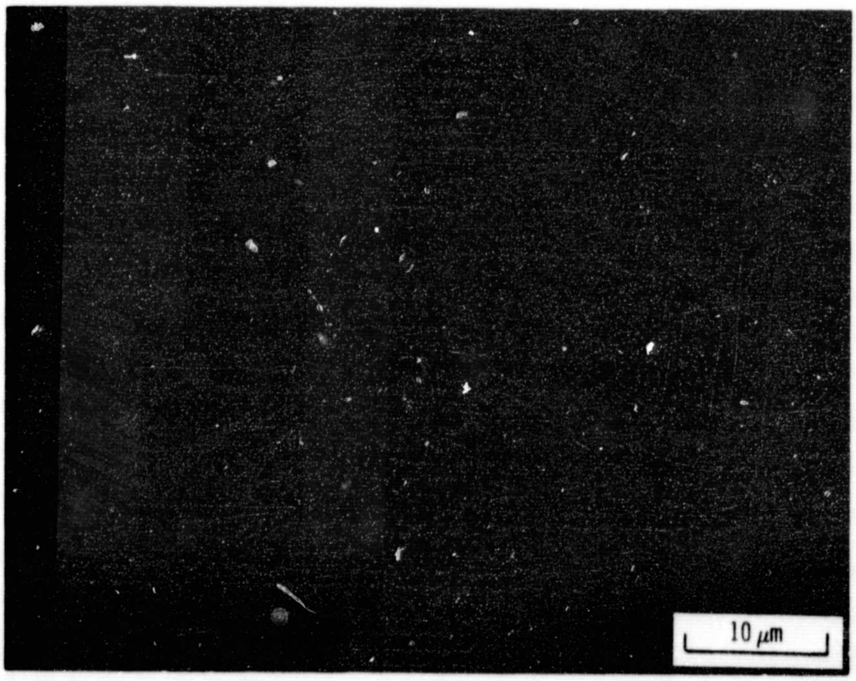


Figure 2. - Pin on disk friction and wear tester.



(a) GROUNDED



(b) BIASED-100V

Figure 3. - Friction tracts generated on chromium carbide sputter-coated 440C stainless steel. Diamond stylus radius, 25 micrometers; load, 0.49 newton (50 g).

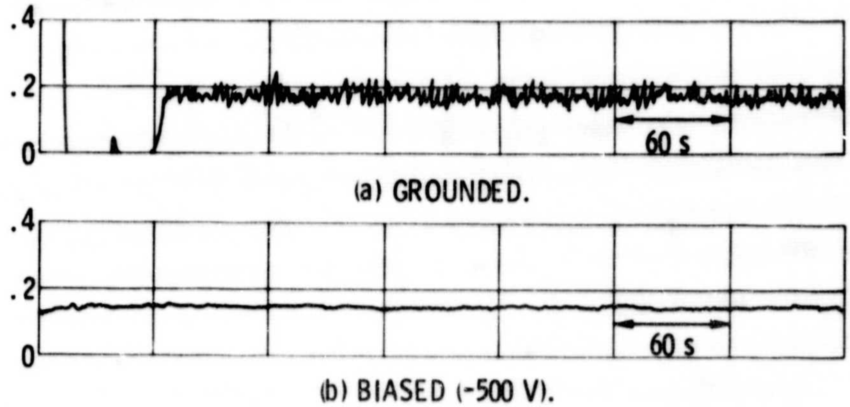
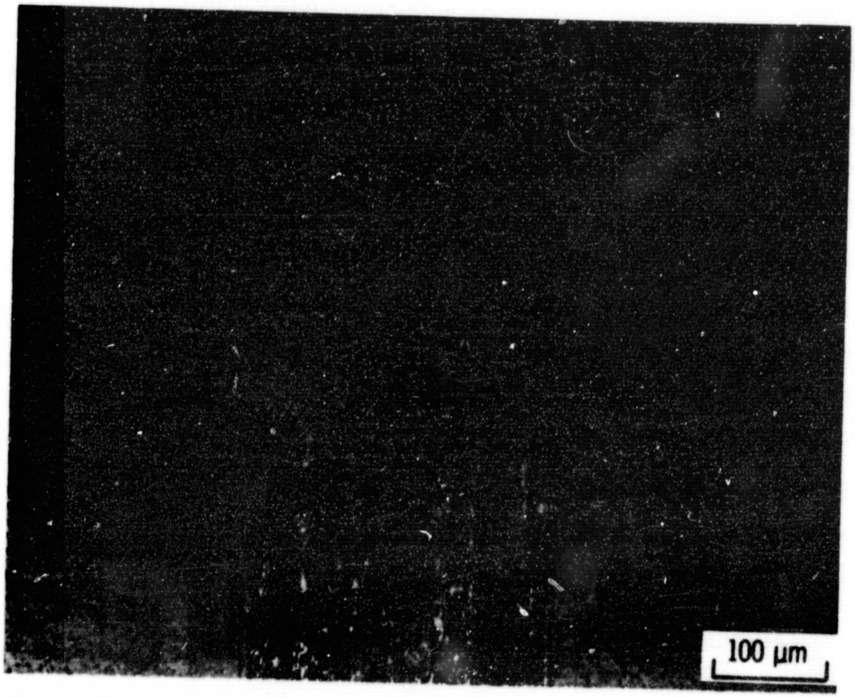
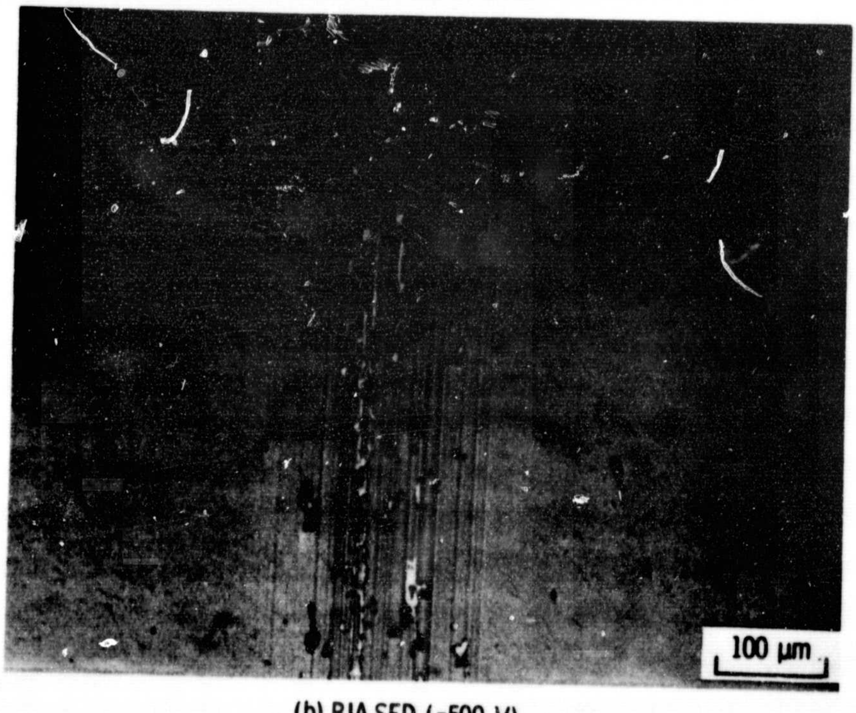


Figure 4. - Friction coefficient for molybdenum silicide sputter-coated 440C stainless-steel disk. Diamond stylus radius, 25 micrometers; stylus load, 0.20 newton (20 g); atmosphere, nitrogen.



(a) GROUNDED



(b) BIASED (-500 V)

Figure 5. - Wear tracks for titanium carbide sputter-coated 440C stainless steel disk. Rider material, AISI 304 stainless steel; load, 0.49 newton (50 g); atmosphere, nitrogen.

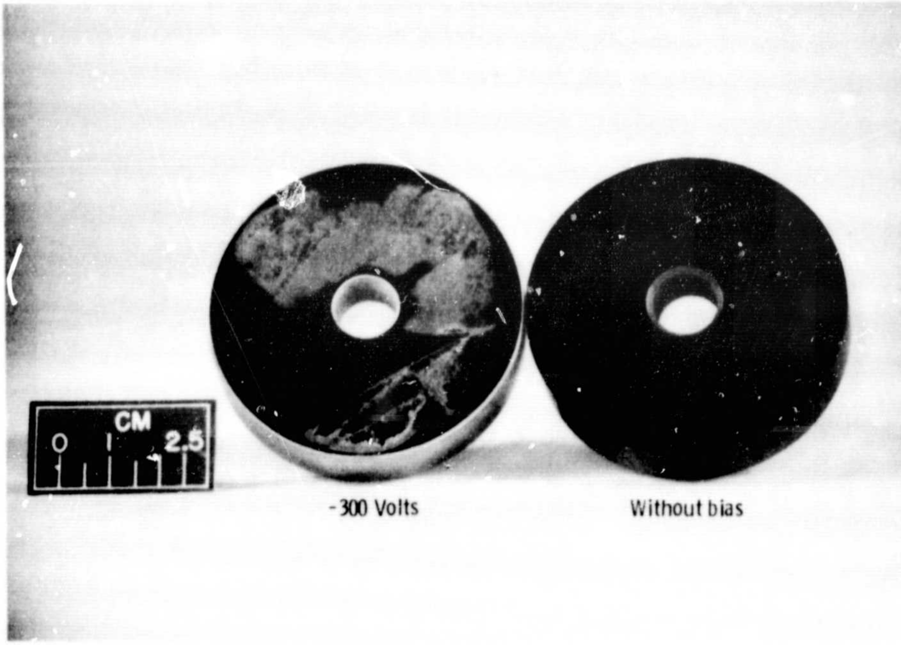


Figure 6. - Two 440-C disks R F sputter coated with Mo_2C at two bias conditions (disks precleaned by sputter etching at -1200 V for 15 min).

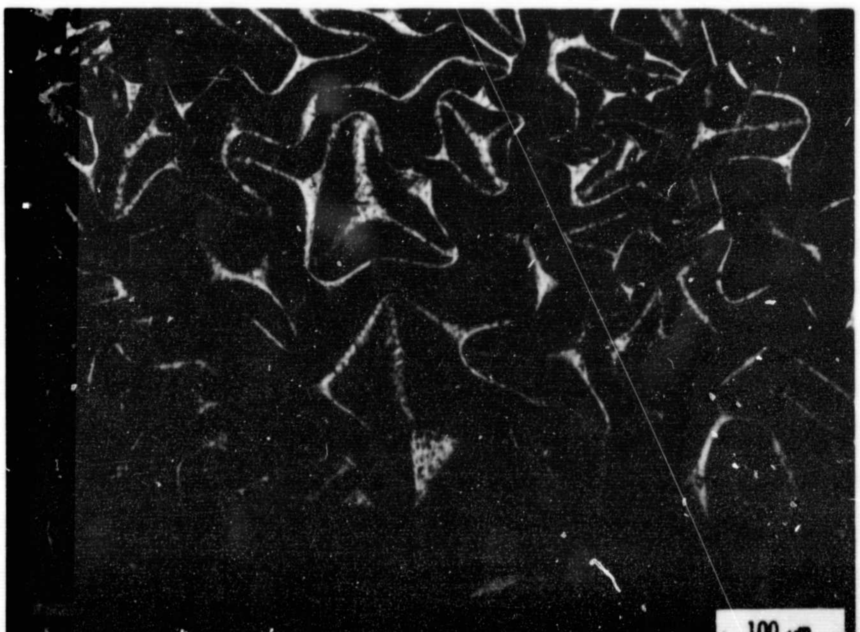


Figure 7. - Photomicrograph of surface of 440-C disk R F sputter coated with Mo_2C (-300 volts bias).

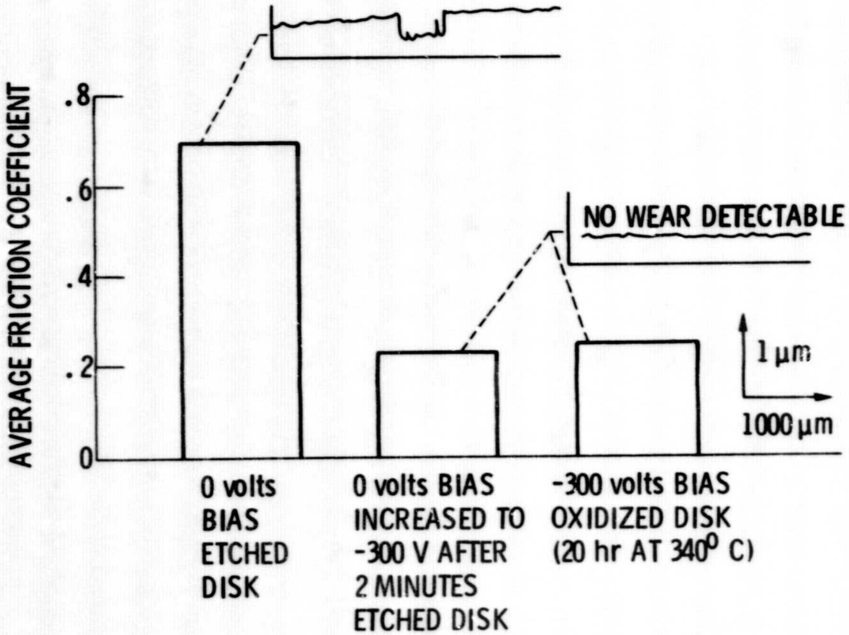


Figure 8. - Average friction coefficient and coating wear traces for RF sputtered Mo_2C on 440-C disk, 304 rider, 0.10 NT. Load, N_2 atmosphere.

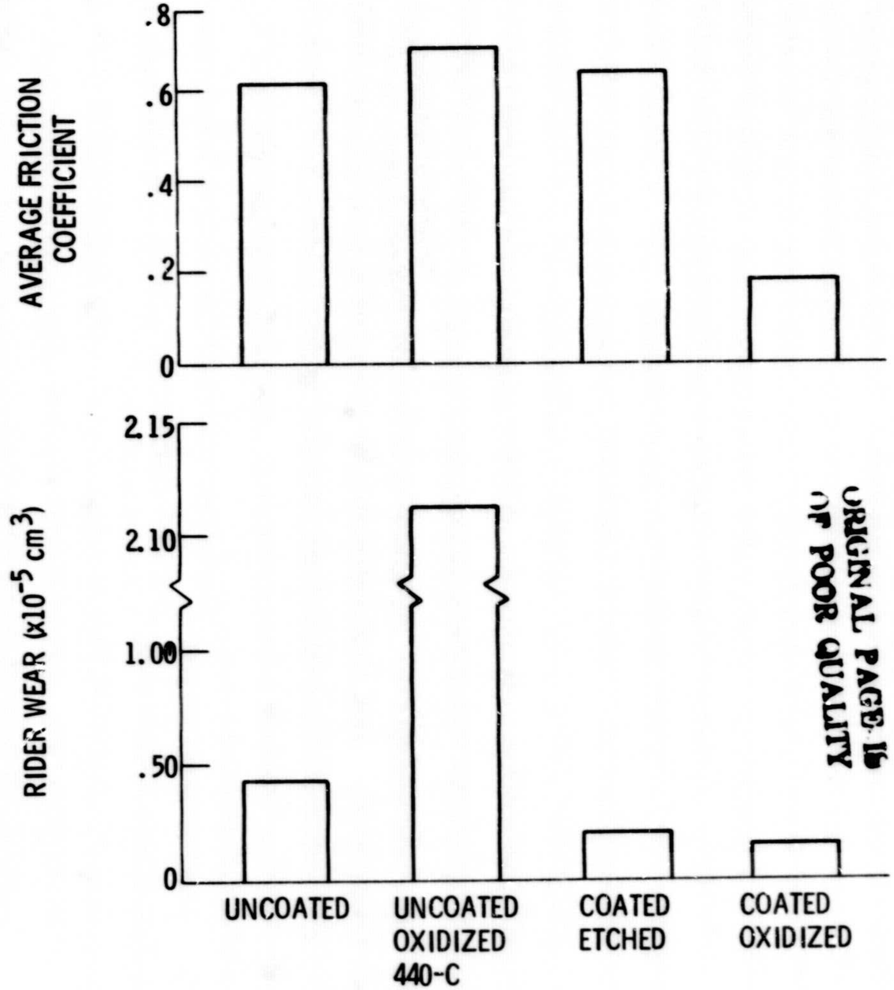


Figure 9. - Average friction coefficient and rider wear for 440-C disks either sputter etched (-1200 V for 15 min) or oxidized (20 hr at 340° C). Coated disks are RF sputtered with TiB_2 (-300 V bias); load, 0.5 NT; N_2 atmosphere.

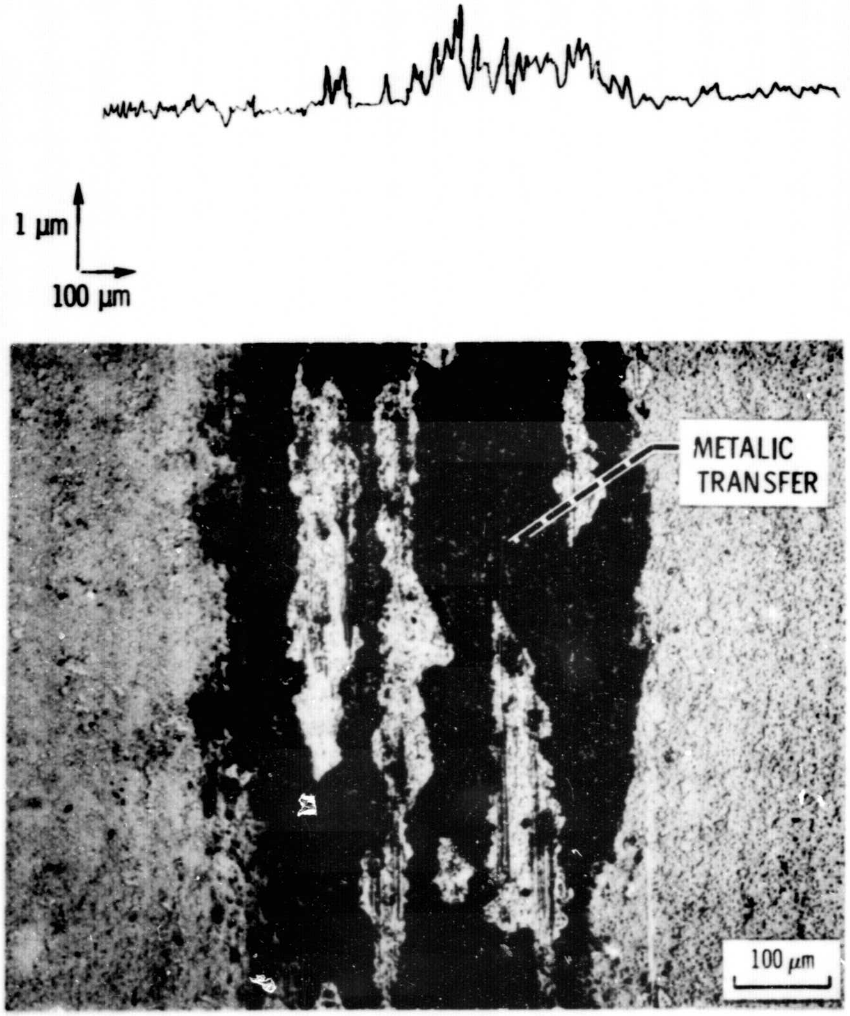


Figure 10. - Surface profile trace and photomicrograph of wear track on oxidized 440-C sputter coated with $MoSi_2$ (-100 volts bias) 0.10 NT load, 25 cm/sec.

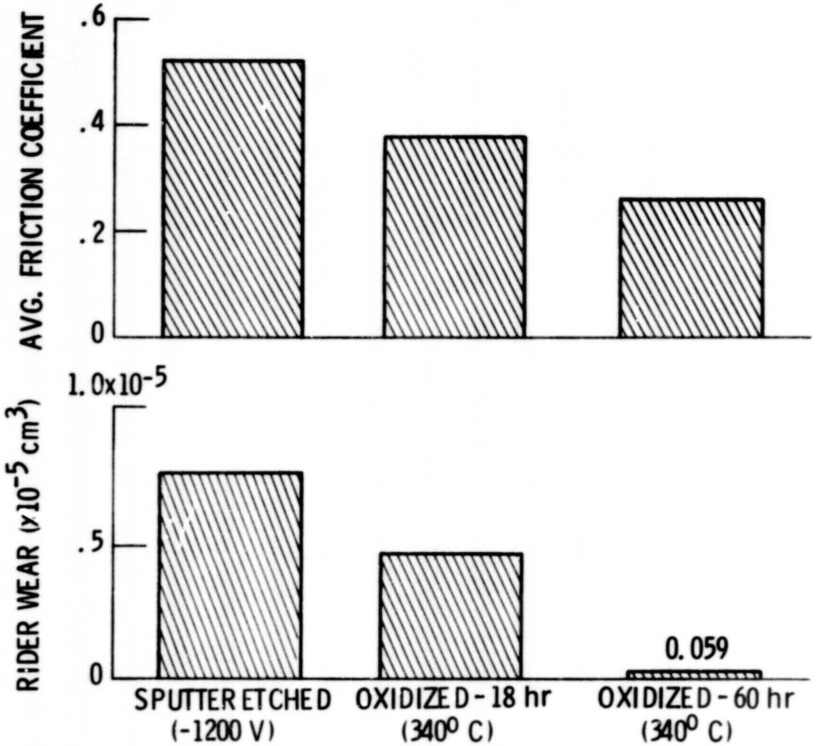
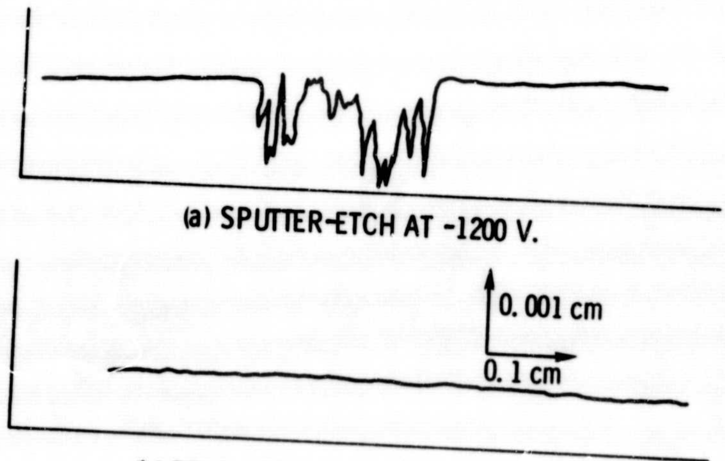


Figure 11. - Average friction coefficient and rider wear for RF sputtered TiC (-500 V bias) coated 440-C disks, 304 SS rider, load, 2.0 newtons, 60 minutes, N_2 atmosphere.



(a) SPUTTER-ETCH AT -1200 V.

(b) PREOXIDIZED AT 340° C FOR 60 HR.

Figure 12. - Surface profile tracings of disk wear track, 440-C disk RF sputter coated with TiC (-500 V bias), 5 NT, load, 60 minutes in N_2 atmosphere.

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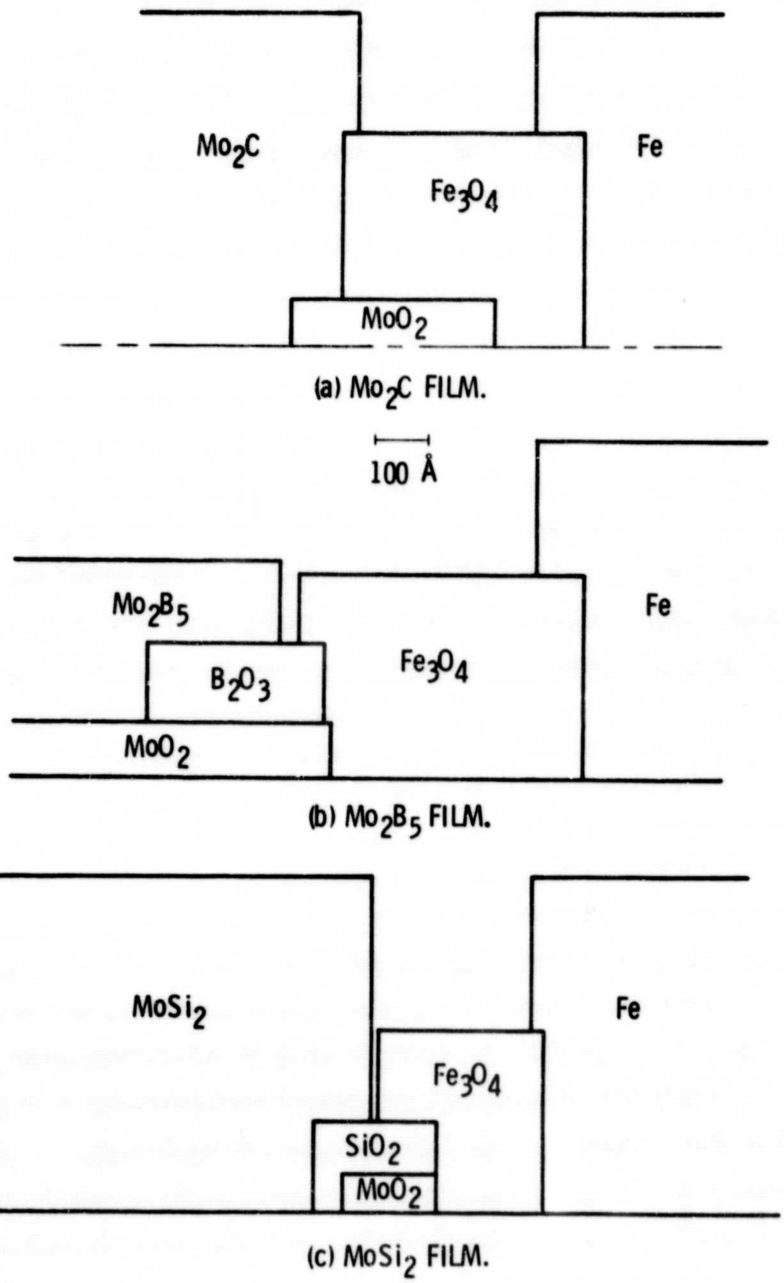

Figure 13. - Schematic representation of interfacial region of RF sputtered coatings on oxidized 440-C substrates, -300 V bias.

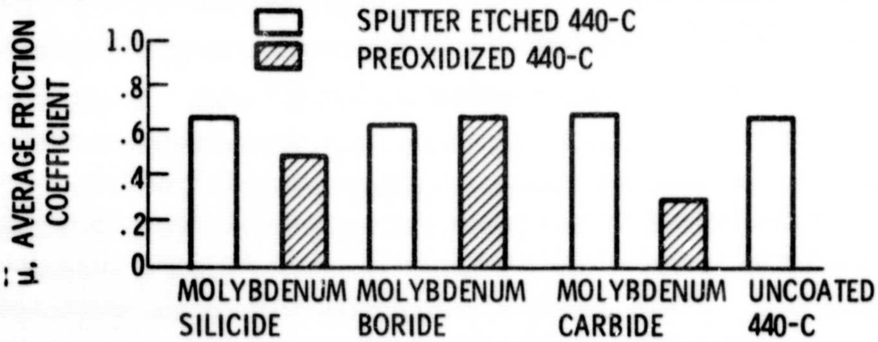

Figure 14. - Average friction coefficient for 440-C with several sputter coatings, load 0.25 NT, speed 25 cm/sec, N_2 atmosphere, 304 steel rider.

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