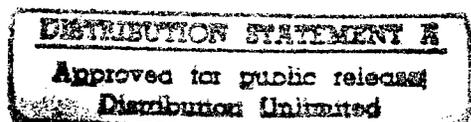Technical Paper 1033   TECHNICAL
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X-Ray Photoelectron Spectroscopy Study of Radiofrequency-Sputtered Titanium Carbide, Molybdenum Carbide, and Titanium Boride Coatings and Their Friction Properties

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OCTOBER 1977

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X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF RADIOFREQUENCY-SPUTTERED TITANIUM CARBIDE, MOLYBDENUM CARBIDE, AND TITANIUM BORIDE COATINGS AND THEIR FRICTION PROPERTIES

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SUMMARY

Radiofrequency (rf) sputtered coatings of titanium carbide (TiC), molybdenum carbide (Mo_2C), and titanium boride (TiB_2) were prepared for friction and wear testing and analysis by X-ray photoelectron spectroscopy (XPS). Wear testing was conducted with a pin of 304 stainless steel on disk apparatus, the disks being type 440-C steel that were rf sputter coated. Emphasis was placed on correlating friction and wear data with bulk film properties, that is, stoichiometry and impurity content and, secondly, with interfacial adherence.

Titanium carbide coatings achieved maximum stoichiometry and minimum bulk film oxygen contamination when bias deposited at -500 volts. Adding 10 percent hydrogen to the plasma in an attempt to further reduce the level of oxygen contamination in poorly adherent films that failed during friction testing very quickly. Oxidizing the 440-C substrates prior to deposition produced marked improvements in friction and wear properties. The bulk composition of molybdenum carbide coatings was also improved by biasing (-300 V); however, biasing was detrimental to coating adherence. Bias deposited coatings would not adhere to sputter cleaned 440-C substrates flaking off due to internal film stresses even though a thick, graded interface (>2500 Å) was obtained. Films deposited in such a manner as to form an oxide at the interface adhered strongly even if bias was subsequently employed to improve bulk film properties. Depth profile studies of two poorly adherent films showed little oxygen at the interface. Friction behavior of Mo_2C films was either good or bad depending on whether or not oxide was formed at the interface during deposition.

Titanium boride coatings also exhibited a dependence on interfacial oxides to achieve maximum adherence. Friction and wear data are markedly improved by deliberately pre-oxidizing the substrate material.

These results suggest strongly that some of the commonly used practices in the deposition of these films, particularly rigorously precleaning substrates or sputtering without bias can be detrimental to the production of adherent, stoichiometric films for certain compounds and substrates.

INTRODUCTION

In the field of friction and wear, there is considerable interest in the use of refractory compound materials in bulk forms and as coatings such as in wire drawing dies or foil bearings. Refractory compounds such as the molybdenum and titanium carbides, silicides and borides, are currently being investigated. The use of radiofrequency (rf) sputtering as a means of applying coatings of those materials is desirable for many reasons. Thin, dense coatings of a wide variety of materials including elemental metals, alloys, inorganic and organic compounds can be obtained on a wide variety of shapes and substrates without requiring high temperatures (ref. 1).

Previous work, however (ref. 2), has shown that the friction and wear behavior of rf sputtered films may not be satisfactory due to variations of stoichiometry, impurities, or poor adherence. X-ray photoelectron spectroscopy (XPS) was used to examine several compound coatings applied by rf sputtering (ref. 3).

Those results indicated that significant bulk coating effects due to target history, sputtering time, power levels, and bias voltages could be observed. The friction and wear performance of sputtered films, however, depends not only on bulk film properties but is very much dependent on the interface, that is, the transition region between film and substrates. The bonding at the interface is crucial to the adherence behavior of the sputtered coatings and, thusly, the friction and wear performance.

The objective of this report is to present data on additional investigations on the nature of rf sputtered coatings with emphasis on the interface and the coating adherence. XPS analyses of sputtered coatings and interfaces were conducted in conjunction with deposition studies and pin on disk friction and wear tests. The materials examined were titanium carbide (TiC), titanium boride (TiB_2), and molybdenum carbide (Mo_2C). They were deposited on 440-C steel substrates.

APPARATUS AND PROCEDURE

Radiofrequency Sputtering Apparatus

The sputtering of the materials used in this investigation was conducted in a commercial rf diode apparatus (fig. 1) operating at 13.56 megahertz. The material to be sputter deposited is in the form of a hot pressed compact which was commercially purchased. The specimen to be coated is placed 2.5 centimeters directly below the target on an electrically insulated block. 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 specimen may be moved out from under the target for cleaning. The target also can be cleaned in this manner without contaminating the specimen. 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 actually starting deposition, the target was cleaned by rf sputtering until little pressure rise due to outgassing occurred. Following target cleaning, the rf was turned off. If desired, the specimen could then be also cleaned by dc sputter etching at -1200 volts for 15 minutes. Following specimen cleaning, the selected power and bias voltage parameters were set and the specimen rotated back under the target and deposition initiated. Coatings thicknesses were 2000 to 3000 Å except for the interface studies which were 400 to 500 Å.

X-ray Photoelectron Spectroscopy

After deposition the films were analyzed by X-ray photoelectron spectroscopy (XPS). The principles of XPS are detailed in reference 4. X-ray photons striking an atom in the surface cause it to emit an electron. The electron will leave the atom with a kinetic energy K, which is the difference between the incident photon energy $h\nu$ and the binding energy E_B of the electron in the atom. The binding energy is characteristic of the atom excited and, in addition, depends slightly on the oxidation state of the atom. Thus, if the electron energies K emitted from a sample are measured and $h\nu$ is known, the atoms in the sample may be identified and some chemical information extracted by comparing the measured binding energies with binding energies measured previously on standard samples. Because of the low kinetic energies (<2 keV) of the electrons, the atoms more than 20 Å below the surface of a solid do not contribute to the spectrum.

The particular apparatus used here consisted of a commercial electron energy analyzer and X-ray source in a vacuum system designed to accommodate a variety of samples. The system is a stainless steel bakeable ultrahigh vacuum system. It is ion pumped and incorporates a titanium sublimation pump. An ion gun in the system was used to gradually sputter away the sample surface and determine the composition as a function of depth. Details have been given previously (ref. 2). In addition, the system was provided with a gold coated tungsten filament that was used to evaporate a thin layer of gold onto the sample surface for calibration purposes.

Resolution of the spectral peaks is no less than 1.5 eV full width at half maximum. The peak maxima can be located to ±0.1 eV at best. The energies are referenced to the

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carbon (1s) line at 284.0 eV or the gold $(4f_{7/2})$ peak at 84.0 eV and location of these lines adds ±0.2 eV to the absolute energy uncertainty. Therefore, ±0.3 eV is a reasonable estimate of the probable error of the binding energies quoted here. The reproducibility of peak height values was previously determined (ref. 3). The probable error in the peak heights ranged from ±2 percent to ±10 percent the larger value being for peaks near the limits of detectability. Peak ratios were generally good to ±10 percent or less.

The binding energy characteristic of an element in a particular compound must be determined by measurement on that compound. Samples of the pure material or powder scraped from the actual sputtering targets were used here. These energies appear in table I. These are the binding energies indicated in the figures. Reference will also be made to the ratios of peak heights. These peak heights were determined by XPS measurement of a standard for TiC. In the case of Mo_2C, the material used to mount the powder interferred with the carbon peak height measurement. Therefore, the ratio of C(1s) to $Mo(3d_{5/2})$ peak heights in Mo_2C was calculated from the theoretical photoelectric cross sections (ref. 5). The work of Brillson and Ceasar (ref. 6) indicates that this calculated value should be within ±10 percent of the true value.

The ion gun is a commercial unit operated at an ion energy of 2 keV. During sputter etching, the vacuum system is backfilled to 7×10^{-3} N/m^2 with argon gas. The titanium sublimation pump in the system is operated periodically to maintain the gas purity.

The procedure used was the same for all samples. The surface was rinsed with alcohol before the specimen was installed in the vacuum system. The pressure was allowed to reach 10^{-5} N/m^2 before any analysis was undertaken. Each type of material was sputter etched with argon ions at 2 keV energy for a time which previous trials had shown was sufficient to remove the surface layers and expose the bulk material.

Friction and Wear Apparatus

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 and details of this particular apparatus are available in the literature (ref. 2).

Briefly stated, the apparatus 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 440-C stainless stainless steel disk which has been rf sputter coated with one of the test materials and previously analyzed in the XPS system.

Loaded against the surface of the disk is a 0.476-centimeter-radius 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. 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 frictional tests to minimize environmental effects.

The tests reported herein were conducted at a constant speed of 25 centimeters per second at room temperature (20° C). The loads used were 0.10 to 5 newtons. After running, all wear tracks were examined by optical microscopy and surface profiliometry.

Specimen Preparation

The 440-C disk specimens used as the substrate were polished with silicon carbide paper down to 600 grit, then polished with 3-micrometer diamond paste compound. A final polish with 1-micrometer alumina was followed by an alcohol rinse. The disk sample could then either be coated by rf sputtering or preoxidized before sputtering. If an oxide film was desired, the 440-C disk was placed in a muffle furnace at 340° C for periods varying from 18 to 60 hours. Following a slow furnace cooling, the disk was placed into the sputtering apparatus. No sputter etching of preoxidized disk was used before coating.

The riders or pin specimens were AISI 304 stainless steel. The combination of 304 on 440-C is a poor bare metal couple and thus when failure occurs by film spalling, a rapid, sharp rise in friction is observed in contrast to much lower smoother friction associated with a good coating. The 304 rider specimens were prepared in a similar manner to the 440-C but were not oxidized or coated.

RESULTS

Titanium Carbide

Of the several refractory compounds that had been previously rf sputtered for friction and wear testing, titanium carbide coatings were superior, providing low friction $(0.25 < \bar{\mu} < 0.30)$ and good wear resistance at loads up to 1.0 newton. Beyond that load, film failure occurred resulting in higher friction and excessive substrate wear (ref. 1). In view of the subsequent findings (ref. 3) by XPS analysis of possible variations in composition and impurity content with bias voltage, it was determined that TiC sputtered coatings should be analyzed to determine if optimum sputtering conditions had been realized.

Figure 2 shows XPS data for sputtered TiC as a function of bias voltage. The composition closest to the standard (target material) and lowest oxygen concentration occurred at -500 volts, the same voltage as in the previous investigation (ref. 2). Figure 3 shows XPS peaks for the carbon (1s) and titanium ($2p_{3/2}$) peaks at the two extremes of bias. As was observed in reference 3 for CrB_2 and $MoSi_2$ coatings, oxidation of one or both constituent elements has occurred with no external bias (grounded). The titanium oxide peak at 458.6 eV is large in the unbiased sample in contrast to the much smaller peak at -500-volt bias. This is evidenced in the figure by the filling in of the "valley" between the titanium doublet peak. In addition, the carbon peak at 285 eV for the 0-volt sample shows that, because of the formation of TiO_2, the carbon normally combined as carbide is in the free state. This accounts for the much lower carbide to titanium ratio without bias in figure 2, and partially explains the reported poorer friction performance of sputtered TiC coatings done without bias (ref. 2).

Even at -500 volts, however, the oxygen impurity concentration is rather high. Since increasing the bias voltage from -300 to -500 volts did not significantly reduce that level, it was felt that further increasing the bias voltage would not further reduce the oxygen impurity in view of the fact that the composition at -500 volts was already very close to the standard. Rather than change bias, a small amount (10 percent) of dry hydrogen (dew point: -100° C) was added to the argon supply to determine if the hydrogen would reduce the oxides and thus improve the coatings further. Figure 4 shows wear tracks generated on two coatings, one applied with pure argon (fig. 4(b)) the other with the hydrogen containing mixture (fig. 4(a)). Subsequent analysis showed the films deposited with hydrogen containing gas to be thinner than films deposited in pure argon with other conditions identical. The addition of hydrogen during the deposition process yielded films with extremely poor friction properties. Analysis of the disk wear tracks showed that the poor friction behavior was a result of spalling of the films; that is, poor adherence. The addition of hydrogen caused the adherence to decrease. The wider wear track for the poorer coating is a result of accelerated wear due to metal-metal contact after the film spalled off. These results suggested that the interface resulting from deposition with pure argon was broad while that done with 10 percent hydrogen added was sharp and more prone to fail. The better adherence of films deposited with pure argon was speculated to be due to a solubility of the oxides of the substrate and those formed in the growing deposited film. The hydrogen might have resulted in those oxides being reduced, thusly, eliminating a graded region which was providing the basis for the good adherence.

These results suggested that for improved adherence and, thusly good friction and wear performance, TiC films should be deposited on oxidized substrates rather than sputter etched surfaces as has been the practice. To determine if this was the case 440-C disks were placed in a furnace and heated in air to 340° C to promote the forma-

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tion of an oxidized layer. No attempt was made to measure the oxide thickness or determine its composition. Figure 5 presents friction and wear data for TiC rf sputtered onto 440-C disks, one disk having been sputter etched at -1200 volts for 15 minutes to remove the normal oxidized layer, another deliberately preoxidized for 18 hours and the third preoxidized for 60 hours. The coatings were all applied under the same sputtering conditions. The results are clear. Lower friction and wear were obtained with TiC on the preoxidized substrates. There results are directly related to improve film adherence. Figure 6 shows surface profile tracings on the wear track on TiC coated 440-C at a 5-newton load for a sputter etched disk and preoxidized disk. The results are dramatic and represent a significant exception to the usual concept of a need for a rigorously precleaned surface prior to coating.

Molybdenum Carbide

Previous work with rf sputtered Mo_2C coatings, in this laboratory, had yielded poor results with regard to friction and wear. It was felt that improvements in coating performance could be obtained by analyzing the films and interfaces so as to optimize the deposition conditions. Figure 7 presents XPS data for composition and oxygen impurity level for the Mo_2C coatings as a function of bias voltage. A -300-volt bias significantly improves stoichiometry while reducing the oxygen level. The standard value for comparison with the sputtered coating ratios at the top of the figure was calculated because of the unavailability of a reliable standard for measurement.

Figure 8 shows the C(1s) and $Mo(3d_{3/2}, 3d_{5/2})$ peaks taken from coating samples done at -300 volts and without bias. The size difference between the two molybdenum peaks for the two bias conditions are significant. The shift of the Mo peak without bias toward higher binding energy is very small (0.5 eV) but large enough to be greater than the instrumental error (±0.3 eV). The presence of a peak shifted to higher binding energy is confirmed by the filling in of the valley between the two Mo(3d) peaks in the unbiased case. A 0.5-eV shift has been observed previously on Mo foils exposed to air. We conclude that the shift is due to oxidation of the molybdenum yielding films that are really mixtures of oxides and carbides. Biasing at -300 volts significantly reduces the oxide yielding films with only about one-fifth the oxygen of films prepared without bias.

Sputter etched (-1200 V for 15 min) 440-C disks were coated with Mo_2C with no bias and -300 volts bias in order to determine the changes in the friction properties due to biasing. Figure 9 is a photograph of those two specimens after coating. The sample done at -300 volts was flaky. The film blistered (fig. 10) and subsequently peeled off due to the internal stresses in the film. Several other samples were prepared with similar results. XPS analysis of the 440-C surface after the coating peeled off showed

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no molybdenum remaining indicating that coating failure occurred at the interface itself. Depositing a coating with minimum oxygen impurity level (-300-V bias) onto a sputter etched disk produced extremely poor adherence. No friction data was taken on the samples done at -300 volts because of the obviously poor adherence and friction for the unbiased sample was high because of the poor bulk film quality. It was felt, based on the results with TiC, that oxides at the interface were important in achieving good adherence, and biasing and sputter etching worked to reduce that oxide formation. Figure 11 shows the effect on friction and film wear if a growing film is allowed to form an oxidized surface before any bias voltage is applied. The first 2 minutes of deposition were done without bias after which -300 volts was applied. This yielded an oxidized interface but still a high quality bulk film. The contrast in friction and film wear are conclusive. Also shown in figure 10 is friction and surface profile wear tracings for Mo_2C sputtered onto oxidized 440-C (20 hr at 340° C). The reduction in friction is the same as for the varied bias sample. In both cases, no wear track could be observed in the profile tracings done at high vertical magnification.

In order to further verify the importance of interfacial oxide formations in adherance of Mo_2C, samples were prepared for depth profile studies. The two samples were both sputtered at -300 volts bias, however, one sample was prepared with 10 percent hydrogen added to the argon supply in an attempt to reduce interfacial oxides. Each sample was analyzed by XPS while the film was slowly etched away by argon ion bombardment. The results, summarized in figure 12, are very definitive. The interface, when hydrogen is present, is very sharp while the interface of the sample done in pure argon is broad and graded. The sputtering rate was estimated to be approximately 20 Å/min. Based on sputter etching time, this means that the graded interface is perhaps greater than 2500 Å, much larger than would be anticipated for a sputtered film interface based on arrival energies. The oxygen content of both films is low. This is undoubtedly due to the substrate bias. Each sample shows an oxygen peak increasing to a maximum during etching and then decreasing as the molybdenum peak decreases. Both films exhibited very poor adhesion in spite of the great difference in interface thickness. Apparently, the presence of metal oxide is crucial to good film adhesion, no matter what the interface thickness is.

Titanium Boride

Boride coatings rf sputtered without careful attention to optimizing deposition conditions will be poor. Early samples, prepared without XPS data as a quality control check, of chromium, molybdenum, and titanium borides all yielded very poor friction performance. Even when XPS data indicated that good bulk film quality was obtained; that is,

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maximum stoichiometry and minimum impurity level, friction performance was still poor. In these cases, the films were failing by spalling at the interface.

In view of the suggested importance of oxidized interfaces on adherence and of the fact that all previous boride coatings had been deposited on substrates which had the normal oxide layer sputter etched away, it was felt that by depositing the coatings on oxidized surfaces, adherence could be improved. Figure 13 summarized some friction and wear results for sputter coated and uncoated samples. All TiB_2 coatings were deposited at -300-volt bias which produced maximum stoichiometry for CrB_2 in reference 3. It was felt that the effect of bias on a class of compounds like the refractory borides is probably quite similar and that a whole range of compositions as a function of bias voltage need not be investigated separately for TiB_2 coatings.

Note in figure 13 that deliberately oxidizing the 440-C for 20 hours at 340° C produced an increase in friction over the unoxidized sample and a fivefold increase in rider wear. The increase in wear and, to some extent friction, no doubt is related to the formation of hard metallic oxides (e.g., Cr_2O_3 and Fc_2O_3).

The TiB_2 coated 440-C sample which had been cleaned by sputter etching prior to deposition showed some decrease in wear but no decrease in friction. Analysis of those films showed extensive spalling. Coatings deposited on oxidized surfaces (20 hr at 340° C) showed very low friction (~0.20) and a further 25 percent reduction in wear. It also must be noted that, as with TiC, oxidizing the 440-C disks for a longer period might be expected to further improve the friction properties. In any event, the results clearly show that the reduction in friction and wear is due to the combination of disk oxide and the TiB_2 coating. Either alone does not reduce friction.

DISCUSSION

The friction data obtained during this investigation when viewed along with previous results (refs. 2 and 3) demonstrate the two important aspects in coating quality. Specifically, for a sputtered coating to yield maximum performance in friction and wear application, it must first adhere to the surface being coated and, secondly, the deposition conditions must be carefully controlled so the bulk film composition is representative of the intended (target) composition. However, great care must be taken to ensure that, while promoting one aspect of coating quality, the other does not suffer. For example, with Mo_2C, biasing was found to significantly improve stoichiometry and reduce the oxygen level producing a higher purity bulk film. The biasing, however, was detrimental to adherence. The high purity film that was deposited would not adhere to the substrate. The data reported also clearly demonstrates that some of the commonly accepted practices in the vacuum deposition of coatings, such as rigorously polishing

and cleaning surfaces prior to coating, may actually be detrimental to coating adherance, at least with regard to the refractory compounds. The role of oxygen or oxides in the adherence of these refractory compound coatings appears to be significant. The data reported for all three materials shows major improvements when oxides were deliberately introduced into the interface by oxidation prior to coating even though no attempt was made to optimize either oxide thickness or composition. Such efforts might reasonably be expected to produce even further improvements. The value of an oxide layer in promoting adherence was recognized by researchers depositing gold on SiO_2 surfaces. Significant gains in adherence were made by performing the deposition in the presence of oxygen (ref. 7).

Similar observations are found for other systems in the literature (ref. 8); however, there is little qualitative information on the chemistry of the sputtered interface. A recent paper, although not specifically dealing with sputtered coatings, does report significant increases in metal-oxide shear strengths when the metal is deliberately oxidized prior to joining to the oxide surface (ref. 9). These measurements may be applicable to thin film adherence.

The reduced adhesion of Mo_2C when hydrogen is added to the sputtering gas correlates with a reduced interface thickness as revealed in XPS depth profiles. Since a lack of oxide at the interface also reduced adhesion, it might be inferred that an oxide film has a greater interface thickness and, hence, greater adhesion due, perhaps, to solubility of the coating and substrate oxides. On the other hand, it may be that the oxides are inherently more tenacious when bonded to each other and to the respective, unoxidized materials. Further XPS depth profiles will be required to resolve the question.

CONCLUSIONS

The performance of any friction and wear coating is limited by two factors. First, the bulk properties of the film, itself, and second, its ability to adhere to the substrate. The following conclusions from this study bear on both these factors:

1. For TiC, TiB_2 and Mo_2C coatings, adhesion to the substrate was improved by oxidizing the substrate prior to sputtering and/or by sputtering initially without a substrate bias. Heavily oxidized substrates exhibited better adhesion than mildly oxidized substrates.

2. Even when the interface thickness was up to 2500 Å, poor adhesion of Mo_2C coatings to 440-C resulted when no oxide was present.

3. TiC and Mo_2C contain high concentrations of metal oxide and uncombined carbon when deposited on an unbiased substrate. Their friction properties are correspondingly

poor although they adhere well. A substrate bias of -300 volts is sufficient to produce stoichiometric (low oxide) Mo_2C films while a bias of -500 volts is required for TiC.

4. Substrate bias, while producing good bulk film properties in films, can adversely affect adhesion by removing interfacial oxide layers. Sputter cleaning of substrates prior to deposition produced poor adhesion for the same reason. Although biasing and rigorous cleaning are commonly used in an attempt to increase adhesion of other coatings, care must be taken when used with these refractory compounds.

Lewis Research Center,
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TABLE I. - BINDING ENERGIES

Element	Level	Compound	Binding energy, eV	Source
Mo	$3d_{5/2}$	Mo	227.6	Measured on Mo foil
		Mo_2C	227.8	Measured from target material
		MoO_2	230.9	Ref. 10
		MoO_3	232.5	Ref. 10
C	1s	TiC	282.1	Measured from target material
		C	284.1	Ref. 10
Ti	$2p_{3/2}$	TiC	455.0	Measured from target material
		TiO_2	458.6	Ref. 10
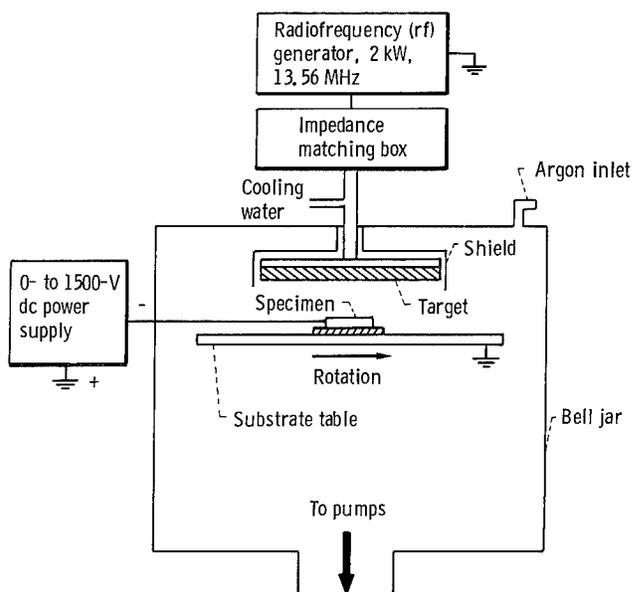
Figure 1. - Schematic of rf sputtering apparatus.
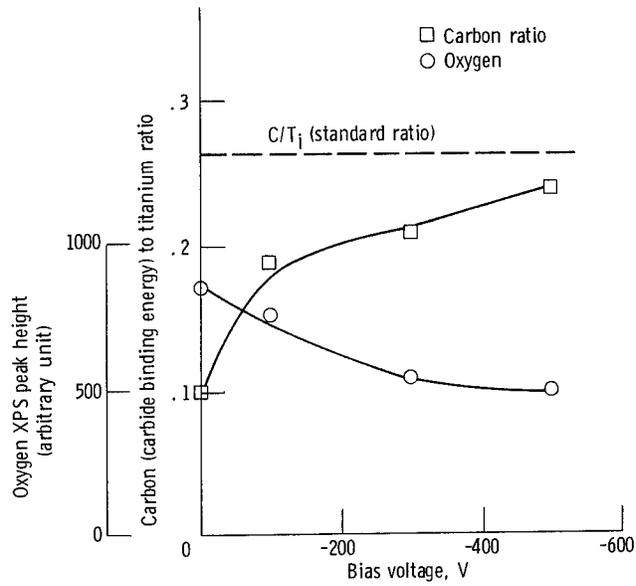
Figure 2. - Variation of oxygen (1s) XPS peak height and ratio of C(1s) to Ti($2p_{3/2}$) peak heights in sputtered TiC films as a function of substrate bias.
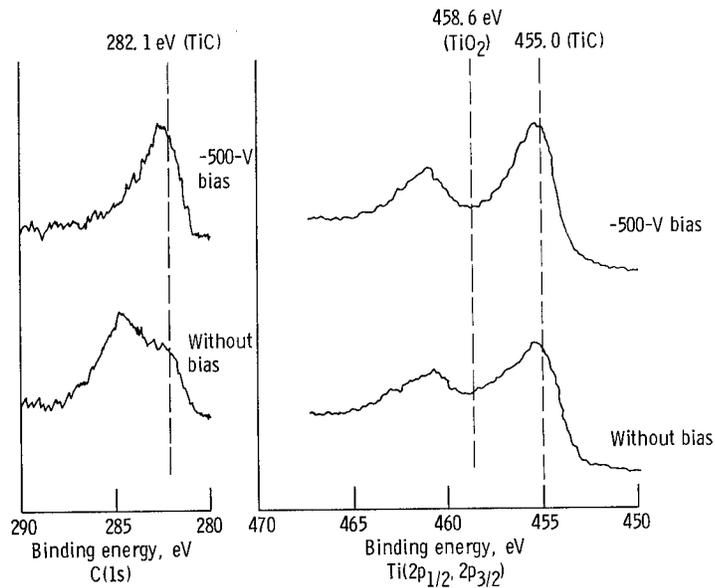
Figure 3. - Representative C(1s) and Ti(2p) XPS peaks from biased and unbiased TiC sputtered coatings.
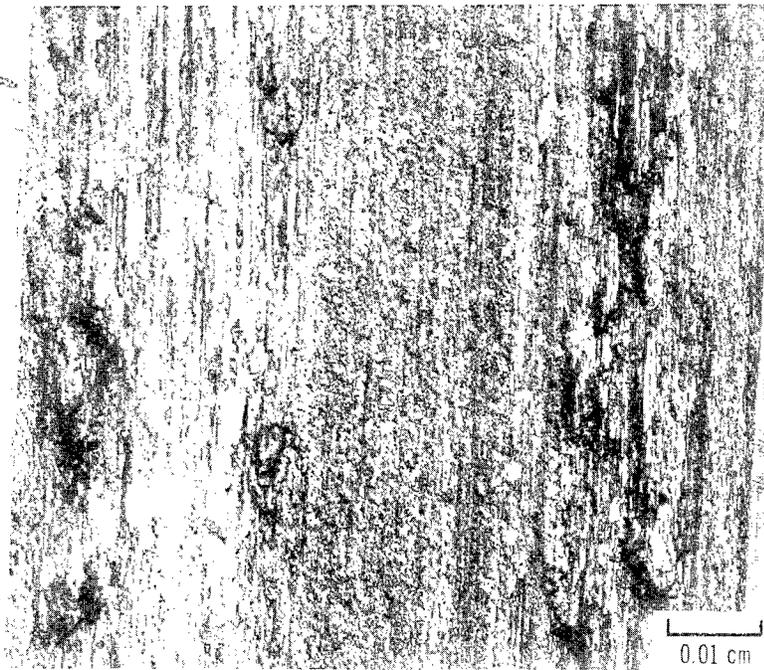
(a) 10% H_2-90% Ar.
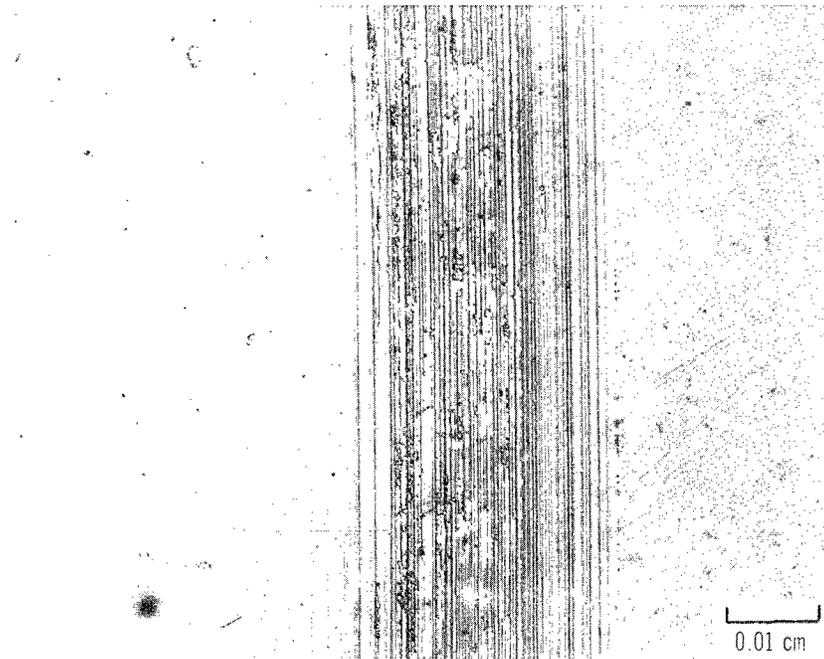
(b) 100% Ar.

Figure 4. - Disk wear tracks for 440-C disk rf sputter coated with TiC (-500-V bias); rider, 304 stainless steel; load, 0.25 newton; sliding time, 30 minutes.
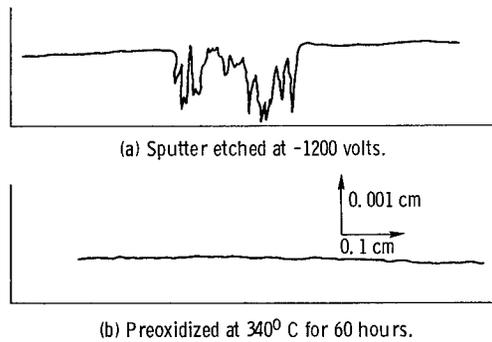
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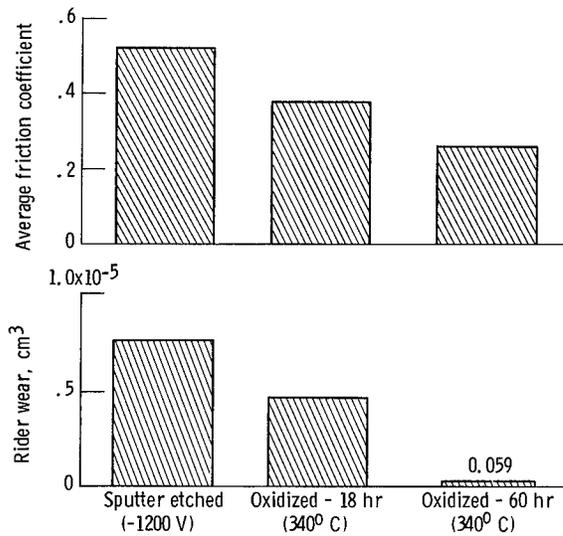
Figure 5. – Average friction coefficient and rider wear for
440-C disks rf sputter coated with TiC (-500-V bias); rider,
304 stainless steel; load, 2.0 newtons; sliding time, 60
minutes; N_2 atmosphere.

(a) Sputter etched at -1200 volts.

(b) Preoxidized at 340^0 C for 60 hours.

Figure 6. – Surface profile tracings of disk wear track for
440-C disk rf sputter coated with TiC (-500-V bias); load,
5 newtons; sliding time, 60 minutes; N_2 atmosphere.
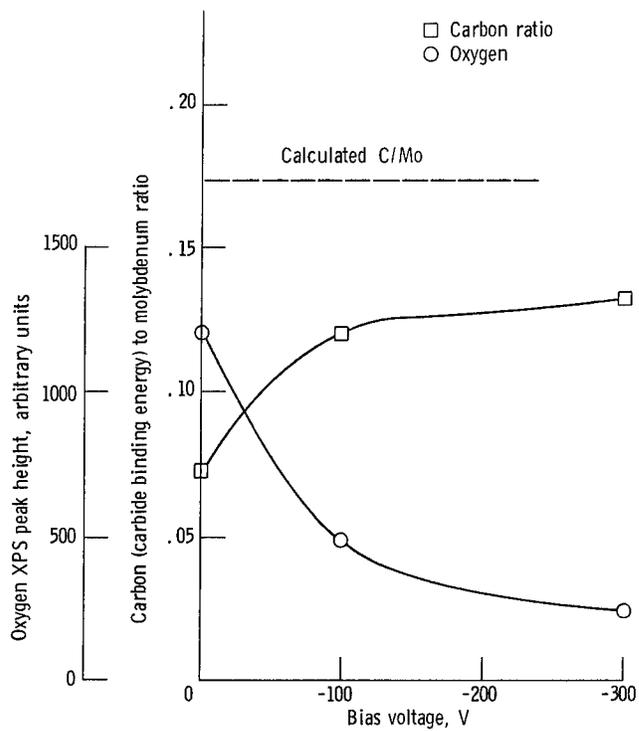
Figure 7. – Variation of oxygen (1s) XPS peak height and ratio of
C(1s) to Mo(3d$_{5/2}$) XPS peak heights in sputtered Mo$_2$C films
as a function of substrate bias voltage.
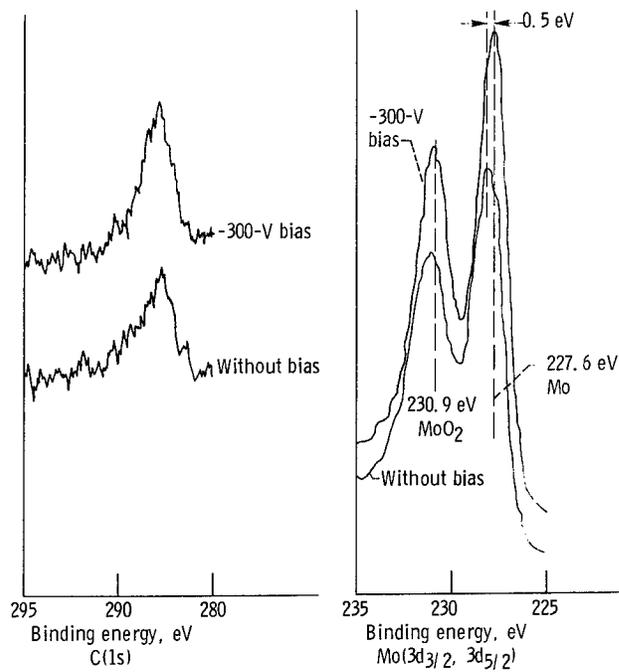
Figure 8. – Representative C(1s) and Mo(3d) XPS peaks from
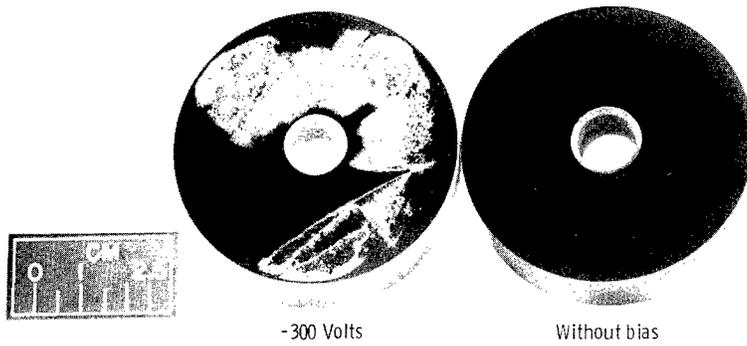biased and unbiased Mo$_2$C sputtered coatings.

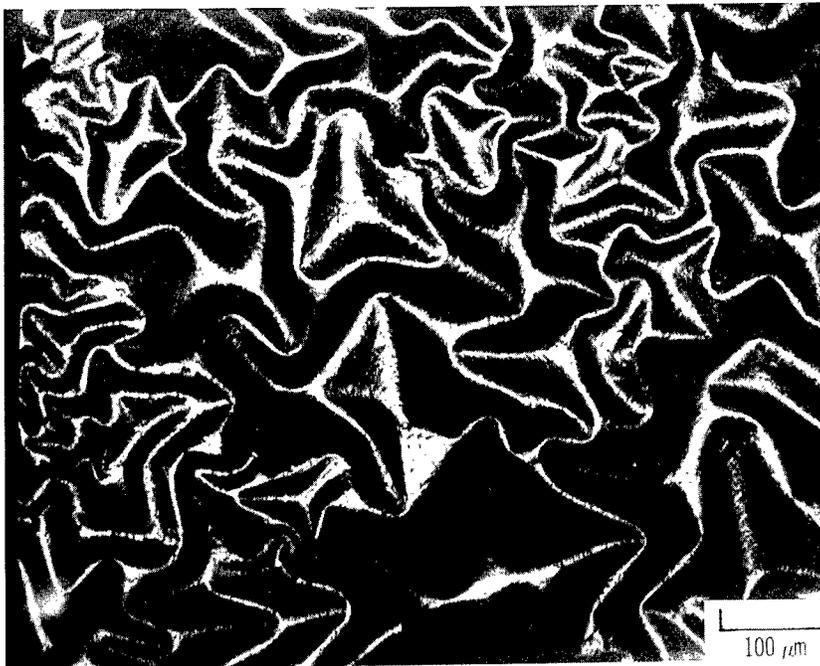Figure 9. - Two 440-C disks sputter coated with Mo_2C at two bias conditions (disks precleaned by sputter etching at −1200 V for 15 min).

Figure 10. - Photomicrograph of surface of 440-C disk rf sputter coated with Mo_2C (-300-V bias). Disk sputter etched (-1200 V for 15 min) prior to coating.
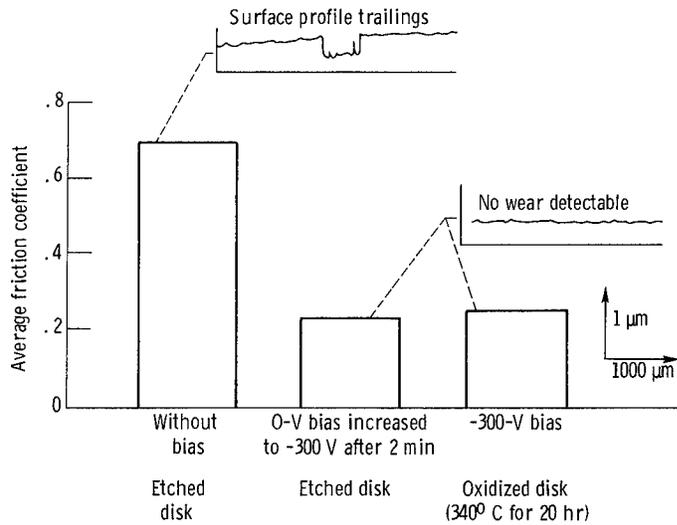
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Figure 11. – Average friction coefficient and coating wear traces for 440-C disk rf sputter coated with Mo_2C; rider, 304 stainless steel; load, 0.10 newton; sliding time, 30 minutes; N_2 atmosphere.
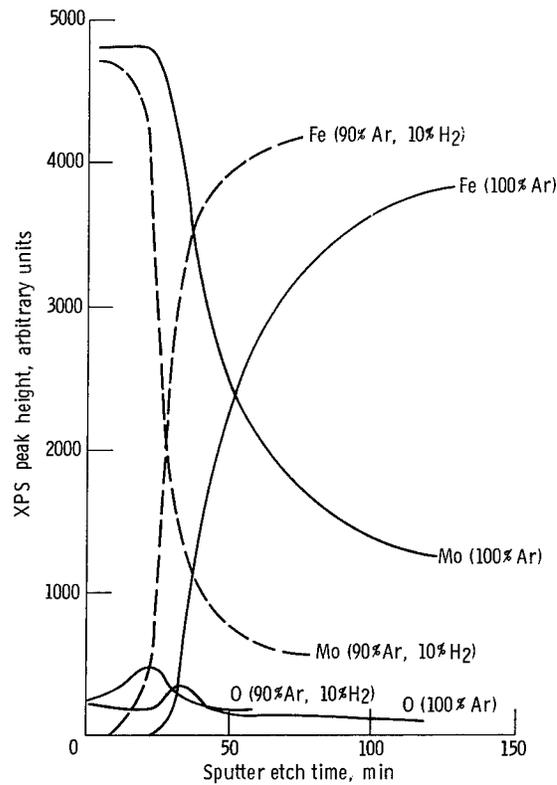

Figure 12. – Variation of Mo, Fe, and O_2 concentration with sputtering time for two Mo_2C sputtered coatings (-300-V bias).
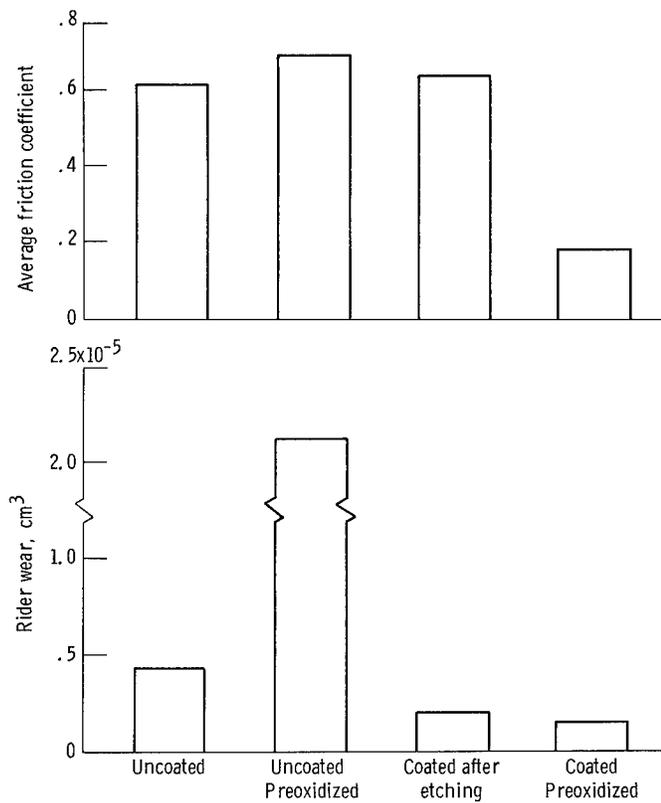
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Figure 13. – Average friction coefficient and rider wear for 440-C disks
either sputter etched (-1200 V for 15 min) or oxidized (20 hr at 340° C).
Coated disks are rf sputtered with TiB_2 (-300-V bias); load, 0.5 newton;
sliding time, 30 minutes; N_2 atmosphere.

1. Report No. NASA TP-1033	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF RADIOFREQUENCY-SPUTTERED TITANIUM CARBIDE, MOLYBDENUM CARBIDE, AND TITANIUM BORIDE COATINGS AND THEIR FRICTION PROPERTIES		5. Report Date October 1977
		6. Performing Organization Code
7. Author(s) William A. Brainard and Donald R. Wheeler		8. Performing Organization Report No. E-9102
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135		10. Work Unit No. 506-16
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Technical Paper
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Radiofrequency (rf) sputtered coatings of titanium carbide (TiC), molybdenum carbide (Mo_2C) and titanium boride (TiB_2) were tested as wear resistant coatings on 440-C stainless steel in a pin on disk apparatus. X-ray photoelectron spectroscopy (XPS) was used to analyze the sputtered films with regard to both bulk and interface composition in order to obtain maximum film performance. Significant improvements in friction behavior were obtained when properly biased films were deposited on deliberately preoxidized substrates. XPS depth profile data showed thick graded interfaces (>2500 Å) for bias deposited films even when adherence is poor. The addition of 10 percent hydrogen to the sputtering gas produced coatings with thin poorly adherent interfaces. The results suggest that some of the common practices in the field of sputtering may be detrimental to achieving maximum adherence and optimum composition for these refractory compounds.

17. Key Words (Suggested by Author(s)) Sputtering ESCA Refractory Friction	18. Distribution Statement Unclassified - unlimited STAR Category 27		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 20	22. Price* A02

* For sale by the National Technical Information Service, Springfield, Virginia 22161