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X-Ray Photoelectron Spectroscopy Study of Radiofrequency-Sputtered Refractory-Compound - Steel Interfaces

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Donald R. Wheeler and William A. Brainard
Lewis Research Center
Cleveland, Ohio
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SPUTTERED REFRACTORY-COMPOUND - STEEL INTERFACES
by Donald R. Wheeler and William A. Brainard
Lewis Research Center

SUMMARY

Radiofrequency-sputtered coatings of Mo$_2$C, Mo$_2$B$_5$, and MoSi$_2$ were deposited on 440C substrates. Deposition was performed with -300-volt bias on both preoxidized and clean sputter-etched substrates and with no bias on clean sputter-etched substrates. After deposition the coatings were analyzed by X-ray photoelectron spectroscopy while being slowly argon ion etched. The composition of the coating as a function of etching depth was determined, and the compositions of the interfacial regions in each case were compared.

There was evidence that biasing during deposition produced a graded interface in the case of Mo$_2$B$_5$ but not for Mo$_2$C. In all cases there were oxides of each film constituent (except carbon) in the interfacial region. There was also iron oxide, but in the preoxidized cases the iron oxide coating was thicker and the oxide concentration was at least twice that observed in the other cases. There was a deficiency of chromium oxide. In the MoSi$_2$ and Mo$_2$C samples there was a mixture of film and iron oxides in the interfacial region, but in the Mo$_2$B$_5$ sample the film oxides were mainly in a layer separate from the iron oxide.

Previous friction studies of these three coatings have shown that oxidation of the substrate improves the adhesion of MoSi$_2$ and Mo$_2$C but not Mo$_2$B$_5$. It is concluded that a graded interface is not sufficient to ensure adhesion of these coatings. Nor is the good adhesion on preoxidized substrates due to strong oxide-to-oxide adhesion. Rather a mixing of the oxides is probably the key to good adhesion.

INTRODUCTION

In the field of lubrication, there is broad interest in the use of refractory compound materials, both in bulk form and in particular as coatings. Refractory oxides, carbides, silicides, and borides are currently being studied.
The use of radiofrequency (rf) sputtering as a means of applying coating material is well recognized (ref. 1) and has been used to deposit refractory compounds on steel surfaces to increase wear resistance (ref. 2).

It has been observed in the course of earlier work on the wear behavior of sputtered refractory borides, silicides, and carbides that bulk film composition was markedly influenced by deposition conditions (refs. 3 and 4). In particular, bias sputtering improved stoichiometry by reducing oxide impurities for most refractory compounds. However, although coating composition was improved by biasing, adherence of the coating to the substrate was degraded by biasing (ref. 4). From this work it was suggested that the coating adherence is enhanced by the presence of an oxidized region at the coating-steel interface and that biasing acts to reduce or minimize this region. Because of the importance of good coating adherence to wear protection, a systematic study of the composition of the refractory compound - steel interface was needed to clarify the role of the oxidized region.

The objective of this investigation, then, was to characterize the composition of the interface formed by rf sputtering refractory compounds onto steel surfaces and to determine what interfacial properties are associated with good adhesion. The compounds examined were molybdenum carbide (Mo$_2$C), molybdenum boride (Mo$_2$B$_6$), and molybdenum silicide (MoSi$_2$). These compounds were deposited on type 440C bearing steel. The interfacial regions (the transition between bulk film properties and bulk steel properties) were investigated by X-ray photoelectron spectroscopy (XPS) in conjunction with controlled-depth profile sputter etching with argon ions.

**APPARATUS AND PROCEDURE**

**Radiofrequency Sputtering Apparatus**

The sputtering of the materials used in this investigation was conducted in a commercial rf diode apparatus operating at 13.56 megahertz. The sputter materials were commercially purchased hot-pressed compacts. The 440C steel substrate is placed 2.5 centimeters directly below the target on an electrically insulated block. An additional voltage from 0 to -1500 volt dc may be applied directly to the specimen either for cleaning by direct-current sputter etching or for biasing the specimen during film deposition and growth. The substrate may be moved out from under the target for cleaning. With the substrate in this position the target also can be cleaned without contaminating the 440C 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. A dynamic pressure balance between the pumping system and argon leak of approximately
20 micrometers was maintained in the bell jar.

The 440C steel specimens were 6.3-centimeter-diameter disks that are normally used as friction and wear test specimens. The disks were mechanically polished to a mirror finish by abrading them with silicon carbide papers to 600 grit and polishing them with diamond (3 μm) paste and then with aluminum oxide (1 μm) paste. After polishing, the disks were rinsed with ethyl alcohol and dried. The disks then were either placed directly into the rf sputtering apparatus or placed in a muffle furnace to preoxidize the steel surface. The furnace was held at 340°C for 18 to 20 hours. This treatment was sufficient to produce a thin transparent oxide film with a slight reddish cast. After cooling to room temperature, the disks were inserted into the sputtering apparatus for coating.

Before starting deposition, an additional cleaning procedure was used. The target was cleaned first by rf sputtering it until little pressure rise due to outgassing occurred. Following target cleaning, the rf was turned off. The unoxidized disk specimens were cleaned by direct-current sputter etching at -1200 volts for 15 minutes. After specimen cleaning, the power and bias voltage parameters were set, and the specimen was moved back under the target and deposition begun. Five minutes deposition time at 300 watts power was used for all samples.

X-ray Photoelectron Spectroscopy

After a film had been sputter deposited the disk was rinsed with ethyl alcohol and mounted in the spectrometer vacuum chamber. The base pressure in the chamber was allowed to reach about 5x10⁻⁷ pascal. The first X-ray photoelectron (XP) spectra were then obtained. Then with the ion pump off the pressure was raised to 6.7x10⁻³ pascal with argon, and the ion gun operated for an interval. The chamber was then pumped back to about 5x10⁻⁷ pascal and the XP spectra again recorded. This procedure was continuously repeated with sputtering times varying from 5 to 30 minutes, depending on how rapidly the spectrum was changing, until the interface was completely sputtered through.

The principles of XPS have been detailed in our previous publications (refs. 3 and 4) and in the literature (ref. 5). 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 it 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. The gun used argon ions of 5-keV energy. The ion gun was equipped with deflection plates, which permitted the beam to be scanned in a raster pattern while sputtering. Thus a uniform sputtering rate was obtained over
an area larger than the area analyzed by XPS. The sputtering rate was measured on an anodized tantalum oxide film, 1000 Å thick, and on a 550-Å gold film evaporated onto a silicon substrate. In both cases the sputtering rate was 5 Å per minute. The width of the gold-silicon interface, measured by extrapolating the steepest part of the gold peak-height versus depth curve (fig. 1), was found to be 125 Å, which is taken to be the depth resolution characteristic of this study.

The positions of peaks in the XP spectrum identify the elements present in the surface of the sample and give some information about the oxidation states of those elements. The sizes of the peaks are related to the amounts of the corresponding elements. The appendix gives a detailed description of how the various peaks were identified and how molar concentrations of each compound were determined.

RESULTS AND DISCUSSION

When the molar concentrations are plotted as functions of depth in the film, the result is a depth profile of the film such as that for Mo₂C in figure 2. Film depth is calculated from the ion etching time. The etching rate is taken to be 5 Å per minute. In such a profile the substrate region is on the right and the film surface on the left.

It should be noted that no interface sharper than the 125 Å found for gold evaporated on silicon should be expected here. This limit is probably determined by surface roughness and the angle the ion beam makes with the surface and by the thickness of the damaged or "homogenized" layer produced by the 5-keV ions (ref. 6).

Each film was deposited on a preoxidized 440C substrate with -300 V bias and on sputter-etched substrate both with and without bias. In figures 2 to 10 depth profiles of the nine specimens are presented.

Interfacial Oxides

It has been observed previously that the main contaminants in sputtered refractory compounds are oxides (refs. 3 and 4). These oxides result from target degassing and are reduced by substrate bias. It can be seen here that even with substrate bias and without preoxidation of the surface, there was normally an increase in the concentration of all oxides, including iron oxide (Fe₃O₄), in the interface (figs. 3, 6, and 9). This may have resulted from an initial burst of oxygen that had diffused to the target surface while the substrate was being sputter etched, or it could have resulted from leaks at the feedthroughs for the manipulators that move the substrate under the target just before film deposition. The Fe₃O₄ concentration reached 15 to 25 percent in these cases. This should be compared with the 55 to 65 percent observed on the oxidized
substrates (figs. 2, 5, and 8). Figure 10 shows an abnormally high-iron-oxide concentration and a second oxide layer deposited soon after film deposition began. This was not observed again and is probably due to unusually heavy target outgassing, in this one case. Normally, on unoxidized substrates the interface is about 200 Å thick, from the 50 percent iron to the 50 percent bulk film depths.

When the 440C is deliberately oxidized before film deposition, a thick Fe$_3$O$_4$ layer reaching 55 to 65 percent concentration is found in the interfacial region (figs. 2, 5, and 8), but very little chromium oxide is found. Figure 11 shows iron and chromium XPS peaks at several depths in a Mo$_2$C film deposited on an oxidized 440C substrate. The components of the peaks due to the metals and oxides have been resolved and identified as described in the appendix. The outer layer of the oxide (etching depth of 375 Å) is iron rich. The area under the iron peak is more than 10 times the area under the chromium peak. In clean 440C the iron peak area is 4.7 times the chromium peak area. Midway through the oxide region (etching depth, 575 Å) the iron present is almost entirely oxidized, while the chromium peak shows a substantial proportion of elemental chromium. Since the ion etching process will tend to mix the film and reduce variation with depth, the outer oxide region is probably even more predominantly iron oxide than this analysis indicates. The preoxidized region is 350 to 550 Å wide, and there is penetration into the 440C substrate. This results in a less abrupt transition from 0 to 100 percent iron than occurs in the unoxidized substrates. For instance, compare figures 5 and 6.

A comparison of figures 3, 5, and 8 shows a difference in the distribution of oxides in the interfacial regions of the three films. To facilitate the comparison a schematic representation of these three interfacial regions is shown in figure 12. Here the half maximum points of each concentration curve in the depth profiles have been found. The concentration of a component is taken to begin or end abruptly at these points. The heights of the schematic concentration curves in figure 12 are one-half the true maximum concentrations. Such a representation helps visualize the extent that one component is mixed with another. In Mo$_2$C and MoSi$_2$ films the oxides of the film constituents are substantially mixed into the iron oxide. The interface in the Mo$_2$B$_5$ film shows a pronounced layered structure with much less mixing.

Substrate Bias

Biasing the substrate during deposition of refractory compounds has previously been shown to improve the bulk film purity and stoichiometry (ref. 3). Here, attention is focused on the effect of bias on the interfacial region. It has often been supposed (ref. 7) that biasing causes a more gradual transition from film to substrate: a graded interface that would improve film adhesion. One indication of this would be a more
gradual increase in iron concentration in a biased sample than in an unbiased one. A comparison of the iron curves in figures 3 and 4 and in figures 6 and 7 indicates that there is indeed a more graded iron interface in Mo$_2$B$_5$ but not in Mo$_2$C. Because oxidation produces effects similar to biasing on the iron curve and because the unbiased MoSi$_2$ film (fig. 10) shows such heavy oxidation of the substrate, a comparison of figures 9 and 10 is inconclusive. Biasing would also be expected to produce a more gradual decrease in the refractory material concentration as depth increased. However, the bulk properties of the compounds were so degraded by lack of bias (i.e., high bulk film oxide levels) that no comparison of the biased and unbiased films can accurately be made.

Correlation with Film Adhesion.

Earlier friction and wear measurements (ref. 8) on the adhesion of Mo$_2$C, Mo$_2$B$_5$, and MoSi$_2$ to clean and oxidized 440C substrates found that adhesion to clean substrates was poor. Oxidizing the substrate improved the adhesion of Mo$_2$C and MoSi$_2$, but had no effect on Mo$_2$B$_5$. In all cases substrate bias was used during film deposition.

From the depth profiles presented, it is clear that oxidation of the substrate causes a graded interface. If this were the case of the improved adhesion, there should be an improvement in Mo$_2$B$_5$ film as well as the other two films. Furthermore, biasing alone produces a graded interface in the case of Mo$_2$B$_5$, but its adhesion is very poor. Thus, a graded interface alone does not cause improved adhesion of these coatings to 440C.

Oxidation of the 440C substrate causes a large increase in iron oxide concentration and thickness of this film in the interface. However, the mere presence of iron oxide does not assure better adhesion. If it did, Mo$_2$B$_5$ would adhere better to an oxidized substrate. Consideration of figure 12 showed that with the Mo$_2$B$_5$ coating, the film oxides are segregated from the iron oxide. Apparently the improved adhesion of Mo$_2$C and MoSi$_2$ is related to the mixing of the oxides that occurs on the preoxidized substrates, rather than to adhesion of the film oxides to the iron oxide.

This interpretation is consistent with early work on cermets (ref. 9), which showed enhanced adhesion of metals to ceramics in oxidizing atmospheres when the ceramic and metal oxide could form a spinel structure. It is also consistent with experience in the electronics industry indicating that metal oxides improve the adhesion of metals to oxide substrates (ref. 10), when mixing of the oxides is thermodynamically favorable.
CONCLUSIONS

Study of the depth profiles for Mo$_2$C, MoSi$_2$, and Mo$_2$B$_5$ films radiofrequency-sputtered onto oxidized and etched 440C substrates both with and without -300-volt bias leads to the following conclusions regarding the interfacial region between film and substrate.

1. On unoxidized substrates the interfacial region was up to 200 Å thick.
2. Biasing at -300 volts during deposition caused the iron concentration curve to change less abruptly in the Mo$_2$B$_5$ film. This is evidence of a graded interface.
3. Oxides of iron and all the film constituents except carbon were present in the interfacial region in all the films. Preoxidation of the substrate, however, produced a thicker, higher-concentration iron oxide region.
4. The preoxidized substrate has a coating that was predominantly iron oxide (Fe$_3$O$_4$) and, especially in its outer layer, was deficient in chromium and chromium oxide.
5. Molybdenum carbide and molybdenum silicide films show extensive mixing of the film and iron oxides. The molybdenum boride film showed clear separation of the oxide layers.

Taken together with previous data on the friction and wear properties of Mo$_2$C, MoSi$_2$, and Mo$_2$B$_5$, these conclusions indicate that the adhesion of these coatings is enhanced by the presence of a graded oxide interface. The graded interface produced by biasing without oxidation is not effective. Nor is oxidation alone effective without substantial interpenetration of the film oxides into the Fe$_3$O$_4$ substrate oxide.

Lewis Research Center,
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506-16.
APPENDIX - ANALYSIS OF X-RAY PHOTOELECTRON SPECTROSCOPY DATA

Binding Energies

Each peak in the XP spectrum occurs at a position corresponding to the binding energy of the electron in the atom contributing to that peak. These binding energies identify the atom and the particular electron in that atom. They are labeled below in spectroscopic notation (e.g., the gold (4f<sub>7/2</sub>) level).

The spectral peaks are not less than 1.5-eV wide at half maximum height. The energy calibration of the spectrometer is determined by reference to the gold (4f<sub>7/2</sub>) line at 84.0 eV. A reasonable estimate of the probable error in calibration and measurement of the binding energy at the peak maximum is ±0.3 eV.

The oxidation state of an atom determines the exact value of the binding energy of each electron in the atom. The binding energy characteristic of an element in a particular compound must be determined by measurement of that compound. Some values are available in the literature and others were measured for this study. All the binding energy standards used here and their sources are listed in table I.

Since oxides were the main contaminant in all the films studied (refs. 3 and 4), it is important to be able to distinguish the peaks in the spectra due to oxides from those of the sputtered compound or elemental constituents. For example, figure 13 shows representative Si (2p) and B (1s) peaks. In both cases the peaks due to oxide (i.e., Si in SiO<sub>2</sub> and B in B<sub>2</sub>O<sub>3</sub>) are well separated from those due to the molybdenum compound (i.e., Si in MoSi<sub>2</sub> and B in Mo<sub>2</sub>B<sub>5</sub>).

The Fe (2p<sub>3/2</sub>) peak normally has a sharp component at 706.3 eV with a tail extending to high binding energy. When the iron is oxidized to Fe<sub>3</sub>O<sub>4</sub>, there is a broad peak at about 709 eV. In this case an analog curve resolver was used to resolve these two components as shown in the three Fe (2p<sub>3/2</sub>) peaks of figure 11. When a 440C specimen is ion-beam etched until no oxygen is detected on the surface there is still a broad 709-eV peak with about 0.31 times the height of the 706.3-eV peak. Therefore, only the presence of a 709 eV component in excess of 0.31 times the 706.3-eV component is considered evidence of Fe<sub>3</sub>O<sub>4</sub>. Little if any Fe<sub>2</sub>O<sub>3</sub> is present, and FeO would be highly unlikely under the conditions of oxidation used here. Chromium was a minor component of the substrate and was not analyzed in detail.

The peaks due to molybdenum (3d<sub>5/2</sub>) and (3d<sub>3/2</sub>) form a double peak (fig. 14) that makes detection of the molybdenum oxide difficult. Occasionally, before ion-beam etching, a doublet structure above 232 eV would be present, indicating a surface of MoO<sub>3</sub>. In the films, however, there was no evidence of this higher oxide. Instead, the shape of the Mo (3d<sub>5/2</sub>, 3/2) doublet changed in a way that can be attributed to the presence of MoO<sub>2</sub>, causing peaks at 1.5 to 2.0 eV higher binding energies than the peaks due to the sputtered compound. The effect is shown in figure 14. The presence of the
MoO\textsubscript{2} caused an increase in the Mo (3d\textsubscript{5/2,3/2}) doublet minimum, which can be seen by measuring the ratio of the minimum height A to the Mo (3d\textsubscript{5/2}) peak height B. This ratio \( A/B \) varied from 0.21 in a clean molybdenum sample with no detectable oxygen to 0.52 in some of the films deposited without bias. It was found that the ratio was directly proportional to the height of the O (1s) peak at 529.5 eV when there was no detectable iron oxide or chromium oxide. Thus this ratio was taken to be evidence of MoO\textsubscript{2}, and the 529.5-eV O (1s) peak was assigned to that oxide.

In the Mo\textsubscript{2}C film there was a single O (1s) peak at 529.5 eV, which from table I and this discussion can be attributed to the metal oxides. In MoSi\textsubscript{2} and Mo\textsubscript{2}B\textsubscript{5} films a second oxygen peak at about 531.5 eV could be resolved on the analog curve resolver. This is attributed to SiO\textsubscript{2} or B\textsubscript{2}O\textsubscript{3} since its height was directly proportional to the 99.1-eV Si (2p) or 187.7-eV B (1s) peak. This is confirmed by separate measurement for B\textsubscript{2}O\textsubscript{3}, as shown in table I.

Peak Heights

The area under a peak above the background level is proportional to the amount of the particular molecular species in the sampled volume that contributes to the peak. When the shape of the peak is constant, the same is true of the peak height. Thus XPS is semiquantitative. Because the number of molecular species present at any level in these films is limited and because in some films only one species is present at some levels it has been possible to interpret the peak heights as mole fractions of the species they represent. The calculated mole fractions give a better idea of the relative concentration of the film components than would raw data peak heights. The technique will be described briefly here and its limitations noted.

The simplest case was iron. Clean 440C was prepared and the Fe (2p\textsubscript{3/2}) peak height was measured. This was called 100 percent Fe although there are other minor elements (particularly Cr) present. After the films deposited on oxidized disks had been ion etched for some time, a level was reached where primarily Fe and Fe\textsubscript{3}O\textsubscript{4} were present. The amount of Fe\textsubscript{3}O\textsubscript{4} was assumed to be proportional to the height of the 709-eV peak in excess of 0.31 times the height of one 706.3-eV peak height as discussed previously. The actual mole percent Fe\textsubscript{3}O\textsubscript{4} was 100 minus the calculated mole percent Fe. Thus a calibration factor for the Fe\textsubscript{3}O\textsubscript{4} 709-eV peak height was obtained.

In MoSi\textsubscript{2} bias deposited films there was very little oxide contamination. Thus, the Si2p peak at 99.1 eV (Si in MoSi\textsubscript{2}) was taken to be proportional to the amount of MoSi\textsubscript{2}, which was 100 percent before reaching the interface. Since the 103 eV peak (Si in SiO\textsubscript{2}) was clearly separated from the 99.1 peak and since 100 percent SiO\textsubscript{2} would give 1/2 the peak height of 100 percent MoSi\textsubscript{2}, a calibration for SiO\textsubscript{2} was obtained. A calibration could also be obtained from the 531.5-eV O (1s) peak.
The amount of MoO$_2$ was deduced from the height of the 529.5-eV O (1s) peak, after allowing for any Fe$_3$O$_4$, or from the peak to valley ratio $A/B$ in figure 14.

Similar procedures were followed for each type of film. The mole percents were then calculated at every analyzed depth in the film. When the total mole percent varied systematically from 100 percent, it could be corrected by small adjustments of one or another of the calibration factors. For any one type of film the factors were the same in all cases, and for a particular atom they were in the correct ratio in different molecules. The Fe and Fe$_3$O$_4$ calibrations were always the same.

While the results of this procedure are internally consistent, giving total mole percents of 100±10, they must be regarded as approximations. X-ray photoelectron spectroscopy, like any spectroscopy, is subject to matrix effects. Peak heights may vary if the atoms contributing to the peak are in different surroundings. If the analyzed volume is homogeneous there is no problem, but in this case the film composition varies with depth. Thus calibration factors that are good at one level in the film may be wrong at another level. Furthermore, when the amount of a film constituent was below about 20 percent, its peak height measurement was uncertain. It is in just such cases where there were often several components of a film present simultaneously. The significance of concentration differences in such cases must be considered with care.
REFERENCES


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Figure 1. - Gold (4f₇/₂) peak height versus sputtering time for 500 Å gold film evaporated onto a silicon substrate.

Figure 2. - Depth profile of Mo-C radiofrequency sputtered onto oxidized 440C substrate. Bias, -300 volts.
Figure 3. Depth profile of Mo-C radiofrequency sputtered onto sputter-etched 440C substrate. Bias, -300 volts.

Figure 4. Depth profile of Mo-C radiofrequency sputtered onto sputter-etched 440C substrate. No bias.

Figure 5. Depth profile of Mo-Fe sputtered radiofrequency sputtered onto oxidized 440C substrate. Bias, -300 volts.
Figure 6. - Depth profile of Mo$_2$B$_5$ radiofrequency sputtered onto sputter-etched 440C substrate. Bias, -300 volts.

Figure 7. - Depth profile of Mo$_2$B$_5$ radiofrequency sputtered onto sputter-etched 440C substrate. No bias.

Figure 8. - Depth profile of MoSi$_2$ radiofrequency sputtered onto oxidized 440C substrate. Bias, -300 volts.

Figure 9. - Depth profile of MoSi$_2$ radiofrequency sputtered onto sputter-etched 440C substrate. Bias, -300 volts.
Figure 10. - Depth profile of MoSi$_2$ radiofrequency sputtered onto sputter-etched 440C substrate. No bias.

Figure 11. - Iron (Fe 2p) and chromium (Cr 2p) XPS peaks at different depths in Mo-C film radiofrequency sputtered onto an oxidized 440C steel substrate. Bias: -300 volts; vertical scale, arbitrary units.
Figure 12. - Schematic representation of interfacial region of Mo-Fe, MoSi₂, and Mo-B₃ radiofrequency-sputtered coatings on oxidized 440C substrates. Bias, -300 volts.

Figure 13. - X-ray photoelectron spectroscopy peaks showing separation of peak due to oxides from that due to molybdenum compound.
Figure 14. Mo\(3d_{5/2} - 3d_{3/2}\) doublet in Mo\(_2\)C radiofrequency sputtered film.

(a) Before ion etching (substantial oxide). Minimum height to Mo\(3d\) \(5/2\) peak height ratio, A/B, 0.41.

(b) After etching 85 minutes (less oxide). A/B, 0.31.
Radiofrequency sputtering was used to deposit Mo$_2$C, Mo$_2$B$_5$, and MoSi$_2$ coatings on 440C steel substrates. Both sputter etched and preoxidized substrates were used, and the films were deposited with and without a substrate bias of -300 V. The composition of the coatings was measured as a function of depth by X-ray photoelectron spectroscopy combined with argon ion etching. In the interfacial region there was evidence that bias produced a graded interface in Mo$_2$B$_5$ but not in Mo$_2$C. Oxides of iron and of all film constituents except carbon were present in all cases but the iron oxide concentration was higher and the layer thicker on the preoxidized substrates. The film and iron oxides were mixed in the MoSi$_2$ and Mo$_2$C films but layered in the Mo$_2$B$_5$ film. The presence of mixed oxides correlates with enhanced film adhesion.