Thin-Film Coatings

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Thin-film coatings are used in a variety of industrial and commercial applications, including lubrication, corrosion, catalysis, and decoration. The thin, adherent, high-density films discussed in this paper are applied by the use of two plasma physics techniques: ion plating and sputtering. For those who are unfamiliar with these techniques, I will discuss how each operates, what surfaces can be coated, and what kinds of materials can be applied. The effects these films have on the mechanical and physical properties of solid surfaces will then be discussed.

Ion Plating

Ion plating is a relatively simple, unsophisticated process (fig. 1). One needs a relatively crude vacuum system (of the order of 10^{-5} of 10^{-6} torr) to house the ion-plating process. The essential ingredients or components of the process are the substrate, or component to be coated, and, of course, the coating. The substrate may be a bearing, gear, or seal, a catalytic surface, a surface that requires corrosion protection, or a surface such as the people in the automobile industry are using for decorative purposes, or any other part that needs to be coated. In addition, one must have a high-voltage power supply, so that a negative potential can be placed on the substrate surface, and a filament or heating source to evaporate the coating material. A number of sources can be used for heating the substrate. A filament heat source with a filament power supply can be used or induction

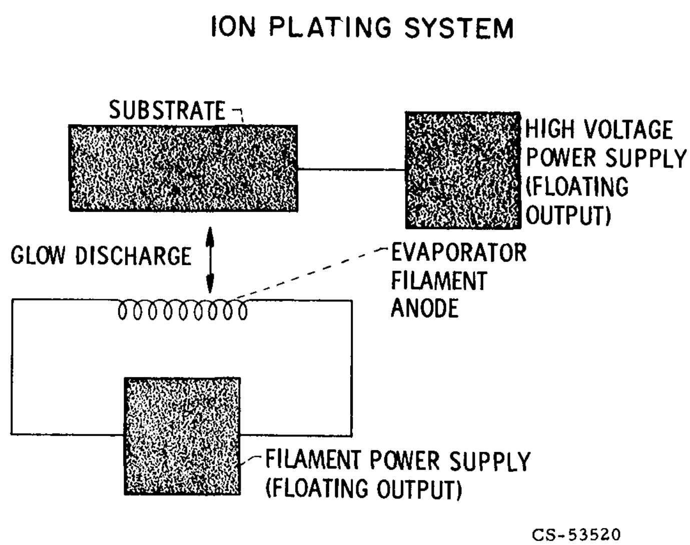

Figure 1

heating or electron beam heating can be used. Generally, the material to be coated is placed on the filament.

The method for operating the ion-plating system involves evacuating the chamber to a pressure of 10^{-5} of 10^{-6} torr and then backfilling the chamber with argon to a pressure of 10×10^{-5} to 20×10^{-3} torr, generating a negatively charged substrate surface. The positively charged argon ions strike or bombard the substrate surface with considerable energy, knocking off adsorbates and oxides and thereby generating a clean, nascent surface. This cleanliness ensures good adhesion of the coating.

In ion-plating we are restricted to using materials that can be evaporated; this means metals and simple alloys. We evaporate the coating into the glow discharge, that is, the argon plasma. All metals have lower ionization potentials than argon, and as a consequence the metal (or coating) becomes ionized, that is, positively charged. The ions are then carrried with the argon ions to the substrate surface where they deposit as a film on the substrate. Because this is a gaseous process, the material is carried to all points on the solid substrate. Because of the negative charge on the substrate, the positively charged metallic ions come in with a potential and bury themselves in the substrate.

The actual ion-plating process of operation is shown in figure 2 which is a photograph of ion-plating taking place. The glow about the substrate surface is due to the argon ions bombarding and cleaning the specimen surface. After the surface has been sufficiently cleaned, we see in the second photograph the filament being heated to incandescence. Metallic ions are evaporated into the plasma and then they are carried with the argon to the substrate surface, coating all points on the solid surface uniformly.

GLOW DISCHARGE DURING ION PLATING

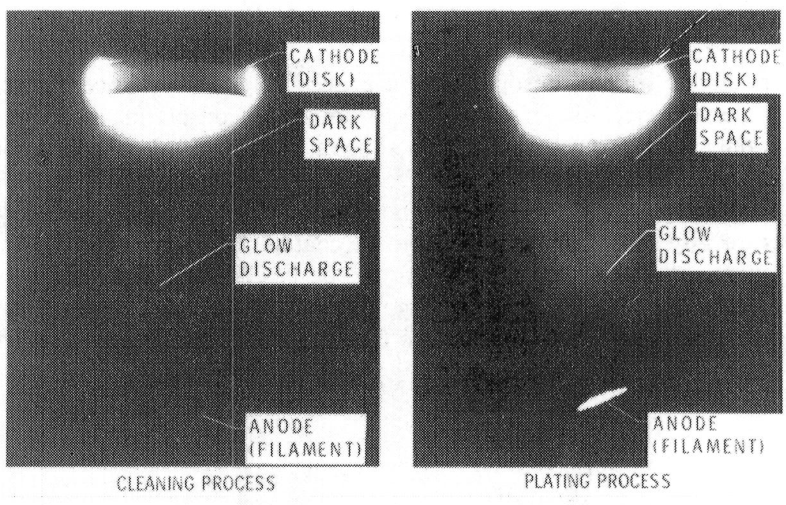

Figure 2

What are the advantages of ion-plating over other processes for depositing thin films?

(1) High kinetic energy of ionized material producing
  (a) Sputter etched surface
  (b) Graded interface
(2) High nondirectional throwing power, that is, complex surfaces coated

Because of the high energy involved and because of the sputter cleaning, we can actually clean and etch the substrate surface to promote strong adhesion. Because of the potential on the substrate the coating ions are driven into the substrate surface, and we obtain what is referred to as a graded interface. Instead of having a sharp line of demarcation between coating and substrate, we obtain a diffuse or graded interface (fig. 3). As a result of the nondirectional nature of the gaseous plasma, very complex geometric surfaces can be coated very uniformly with thin films. Film thickness can be controlled to 50 angstroms.

ABRUPT AND GRADED INTERFACES

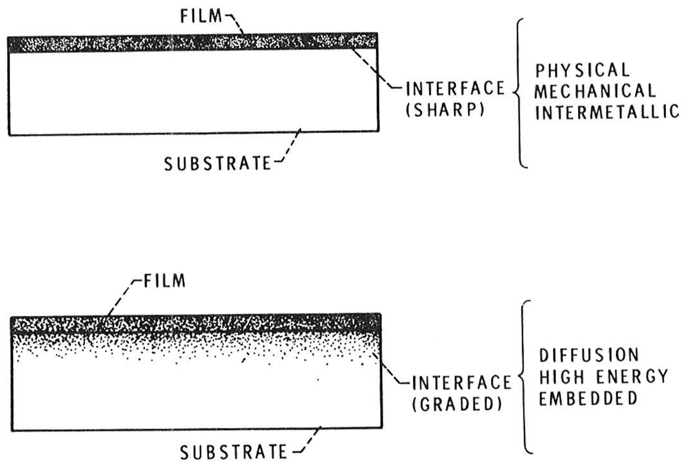

Figure 3

Figure 4 is a photomicrograph of a tungsten surface that has been ion-plated with a nickel film. It is impossible to find the interface, which lies over a broad area. We do not know its boundaries. The photomicrograph shows, essentially, a coating of nickel, a tungsten substrate, and, someplace in betweeen, an interfacial region. There is, however, no sharp line of demarcation between the coating and the substrate.

For many applications this type of interface is ideal because there is no way of mechanically removing the coating from the substrate except by grinding or machining it, and part of the substrate, away. It cannot be removed by conventional techniques or by the mechanical forces involved in practical tribological systems. This is a very desirable interface.

Some of the types of materials that can be coated by ion-plating are shown in figure 5. These are polymer bearing cages, ceramic tubes, and Teflon tubing (coated inside and out with metallic films) and many conventional metal and alloy parts, some with very complex geometries.

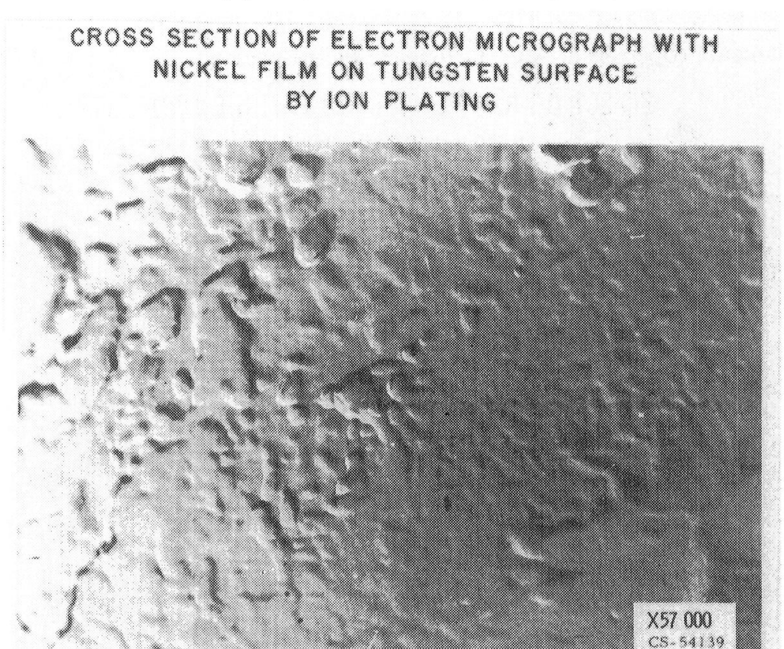

Figure 4

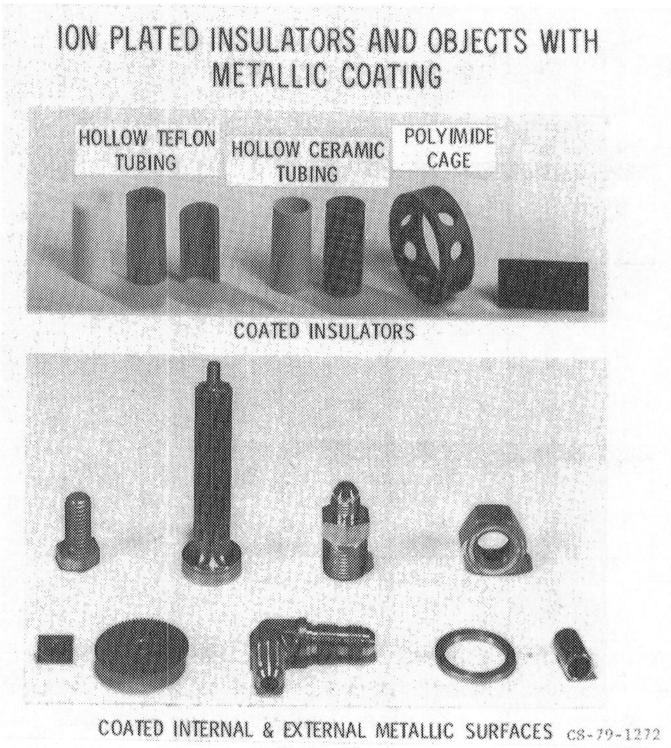

Figure 5

Because of the graded interface and the tenacous bond, the very dense and pore-free coating has a pronounced influence on the mechanical and physical properties of the substrate material. One particular property, for example, so influenced is fatigue life.

The influence of ion-plating on fatigue life is shown in the data of figure 6, a plot of stress as a function of cycles to failure for three sets of data: steels, steels coated with gold by conventional electroplating, and steel coated with gold by ion-plating. Essentially steel and the electroplated steel display no difference in fatigue life: The curve is essentially one for both sets of data. The curve for ion-plated steel, however, indicated a marked improvement in the fatigue life.

Other mechanical properties are also influenced by the presence of ion-plated films. In the area of

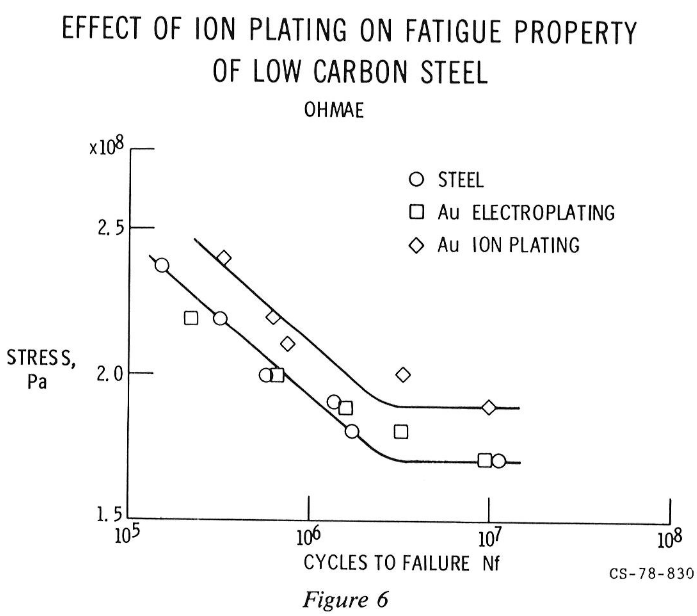

Figure 6

tribological coatings (coatings for lubrication), fantastic improvements are found in lubricating performance by use of the ion-plating technique.

Sputtering

The sputtering process has some similarities to and some differences from ion-plating. Among its features are these:

(1) Versatility
(2) Momentum transfer
(3) Stoichiometry
(4) Sputter etching
(5) Target geometries (coating complex surfaces)
(6) Precise controls
(7) Flexibility
(8) Adjustable sputtering rates
(9) Ecology

One of the best features of the sputtering process, however, is its versatility. We can deposit almost anything on anything; polymers on metals, ceramics on metals, metals on ceramics, metals on polymers—nearly any combination of coating material and substrate material.

Sputtering, like ion-plating, is a momentum transfer process; however, with sputtering the proper compound chemical or atomic ratios can be maintained: In other words, if you wish to deposit a complex compound on a substrate surface, you can do it with the sputtering process.

As in ion-plating, the substrate can be sputter-etched, or cleaned, before deposition to gain good adhesion. The adhesion, however, is not like that obtained with ion-plating, in that sputtering produces a sharp interface. It is a good interface, however, and it forms a very strongly bonded coating to the substrate.

One can have variations in target geometries with sputtering. There is precise control with the process. As in ion-plating, film thicknesses can be controlled to 50 angstroms. It is flexible, in that sputtering rates can be varied to obtain different depositions in various time elements. Ecologically, it is a very clean system; like the ion-plating process, because it is done inside a vacuum.

Just as in ion-plating, a relatively unsophisticated vacuum chamber houses the sputtering process. There are two types of sputtering, dc (direct current) and rf (radiofrequency). Figure 7 happens to depict the rf process. In the vacuum chamber is the target, that is, the coating material and the

SCHEMATIC OF SPUTTERING PROCESS

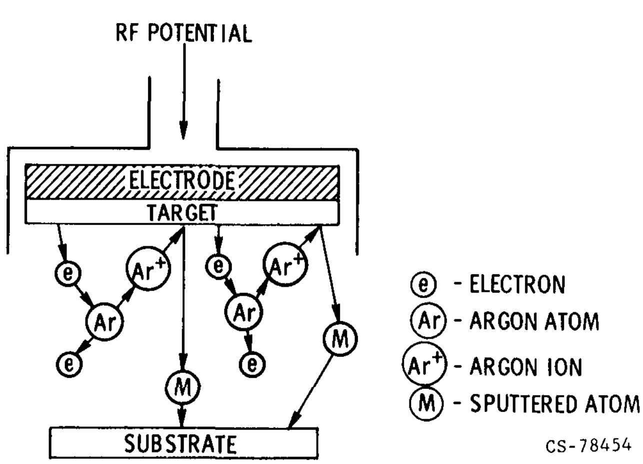

Figure 7

substrate. Into the chamber argon is emitted and positive charged argon ions are generated. A negative charge placed on the target causes the positively charged argon ions to bombard the target and knock material from the target to the substrate surface, thereby applying a coating to the substrate. A preliminary step can be introduced by simply directing the argon ions to the substrate and cleaning it just as is done in the ion-plating process. A very uniform coating on very complex geometric surfaces can be obtained with the rf sputtering process.

Figure 8 reveals the process in actual operation. In the figure the substrate happens to be a bearing cage. The holes are the pockets that hold the ball bearings. A ring has been provided in figure 8 for the sputter cleaning of the substrate surfaces.

As mentioned earlier, sputtering is a very versatile process in that almost anything can be coated with anything. For example, figure 9 shows hypodermic needles that have been coated with a Teflon film. When a needle is injected into the skin it is friction resistance which causes the pain felt. The

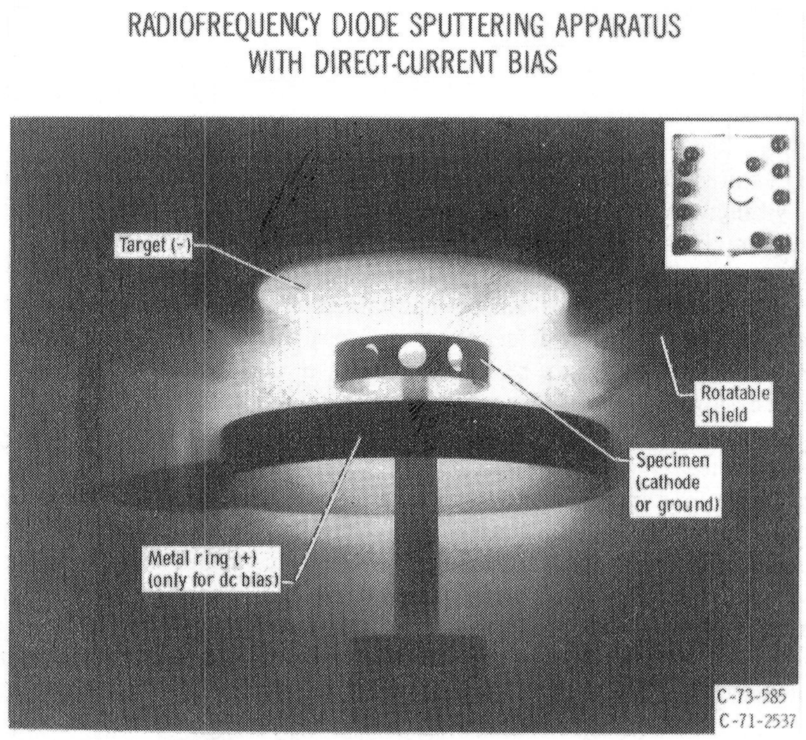

Figure 8

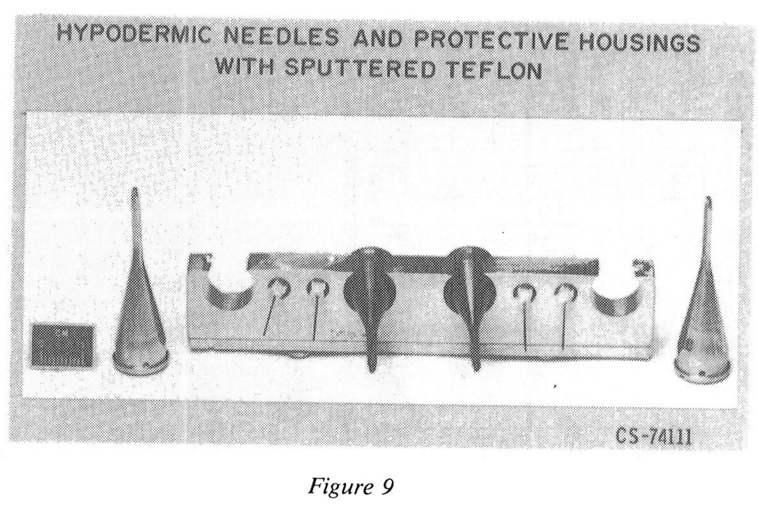

Figure 9

Teflon coating reduces the pain associated with injections by reducing friction. This process was perfected in our laboratory.

The sputtering process is used very heavily industrially. For example, figure 10 is a video record. I am sure most all of you have seen the television commercial for the video records that are currently being marketed. Before Magnavox got into the business, RCA was working on the process. RCA built a vacuum chamber—a very sophisticated system with conveyor belts and interlocks—where two coatings were applied by sputtering. The first coating was a 900-angstrom gold film over the surface of the polymeric record. The second was a 600-angstrom film of molybdenum disulfide for lubricating purposes. Figure 10 is an actual video record with very small fine grooves on its surface, much finer than a conventional audio record. The company intended to commercially produce these records and sell them for approximately $9.95 a piece. It is a very economically feasible process, using two coating steps in the deposition of the films. Lewis personnel consulted with and provided expertise to RCA personnel in the coating application process.

VIDEO RECORD PREPARED BY SPUTTERING

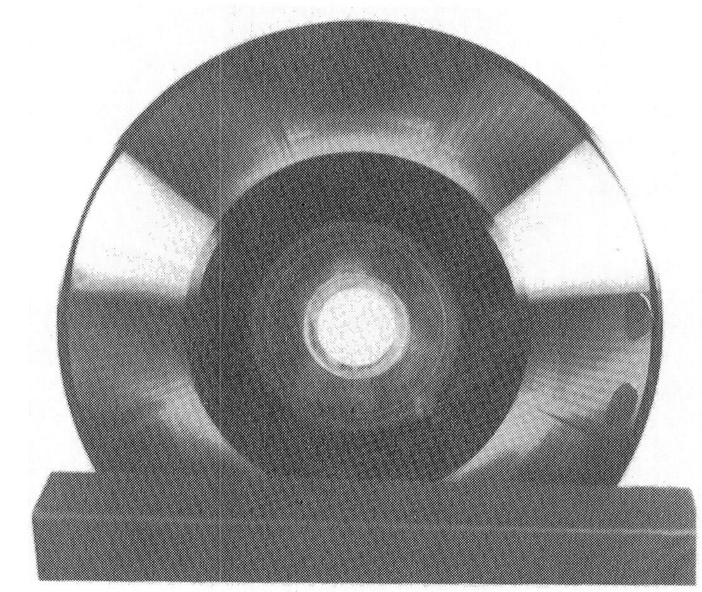

Figure 10

Coating Thickness

While these processes, both ion-plating and sputtering, are used primarily for depositing thin films for corrosion protection, lubrication, decoration, and catalysis, they can be used, particularly the sputtering process, for the deposition and formation of free-standing bodies. Figure 11 is a photograph of a shroud, actually a cylinder, that was formed completely by sputtering. The film thickness was built up enough to form a free-standing body.

Hard Face Coatings

In our own laboratory, one of our current interests in the sputtering process is to develop very hard-face, wear-resistant coatings. Throughout this country and abroad, there is a considerable amount of research effort (in fact, millions of dollars are being spent) to find good, wear-resistant coatings for use in the tooling, drilling, and machining industries. Such coatings would eliminate the need for solid carbide bodies for machining and cutting operations. The use of inexpensive steels with very hard refractory-type carbide coatings would greatly reduce equiment costs.

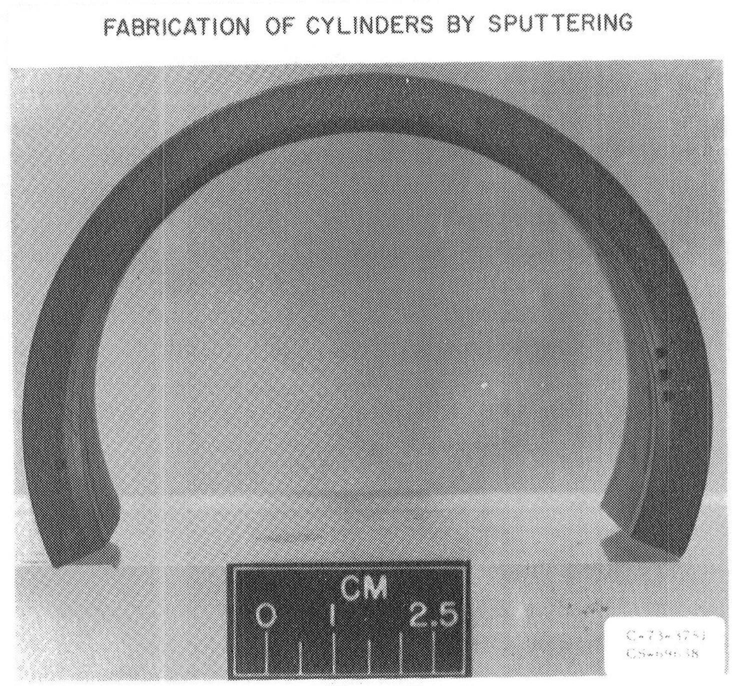

Figure 11

The problem that confronts everyone, however, is getting good adhesion of these hard-face coatings to the substrate. The coating material generally has markedly different mechanical properties from the substrate, and these differences cause considerable stress at the interface. As a consequence, the interface is weak and the coating easily fractures or falls off the substrate.

Researchers here at Lewis, as well as at a number of other places, are exploring ways of improving the adhesion of the hard-face coating to the substrate. One technique that we have developed is the use of an interfacial or transition layer between the substrate and the coating. One suitable transition layer material was discovered to be ordinary oxides. A buildup of selected oxides on the substrate surface before applying a hard-face coating (e.g., refractory metal carbides such as molybdenum, tungsten, titanium) improves adhesion considerably.

Now this is just the opposite of what we discussed earlier. In the deposition of lubricating and corrosion protective film, for example, sputter cleaning and ion-bombardment promote better adhesion. But with hard-face coatings, we deliberately oxidize for the same reason.

In the course of our experimental work, we are interested in the friction and wear of these coatings, and how well do they stand up in mechanical applications. Figure 12 presents some data on a titanium diboride (TiB_2) coating on a 440 C steel substrate. Plotted in figure 12 are the friction coefficient and the wear for the material in four cases: (1) uncoated 440 C, (2) uncoated and oxidized 440 C, (3) coated and etched 440 C, and (4) coated and oxidized 440 C. The best performance was obtained with the coated and oxidized material.

We have in our laboratory analytical surface tools that assist us in what we call depth-profiling, or analyzing, these films. We can start, for example, with X-ray photoelectron spectroscopy (XPS) and analyze the chemistry of the film at the outside surface. Then we can ion-bombard with argon ions knocking away the coating to expose the interface region, and analyze the interfacial region and its chemistry. Going on further through the interfacial region and into the substrate, we can determine the chemistry of the material at any point. We have done this for a number of these hard refractory carbides using the oxide interface.

Figure 13 presents some results for a series of molybdenum compound coatings. The substrate is 440 C bearing steel, represented in the figure by Fe (iron). The coating materials are molybdenum carbide (Mo_2C), molybdenum boride (Mo_2B_5), and molybdenum silicide ($MoSi_2$). Between the substrate and coating material are the deliberately formed oxide layers.

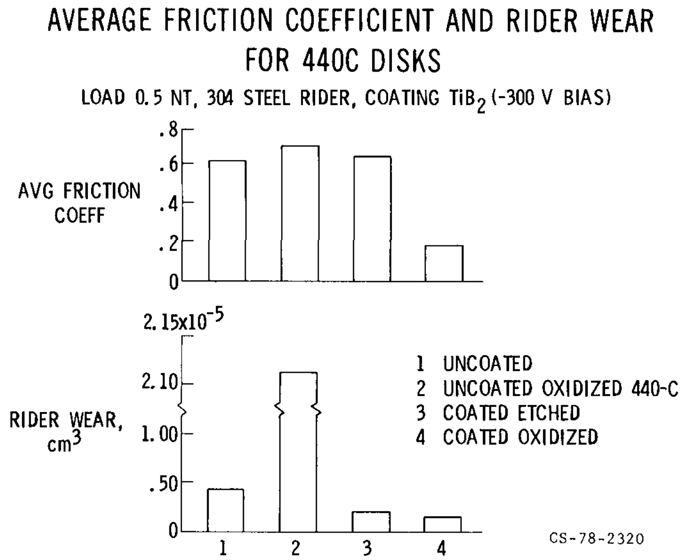

Figure 12

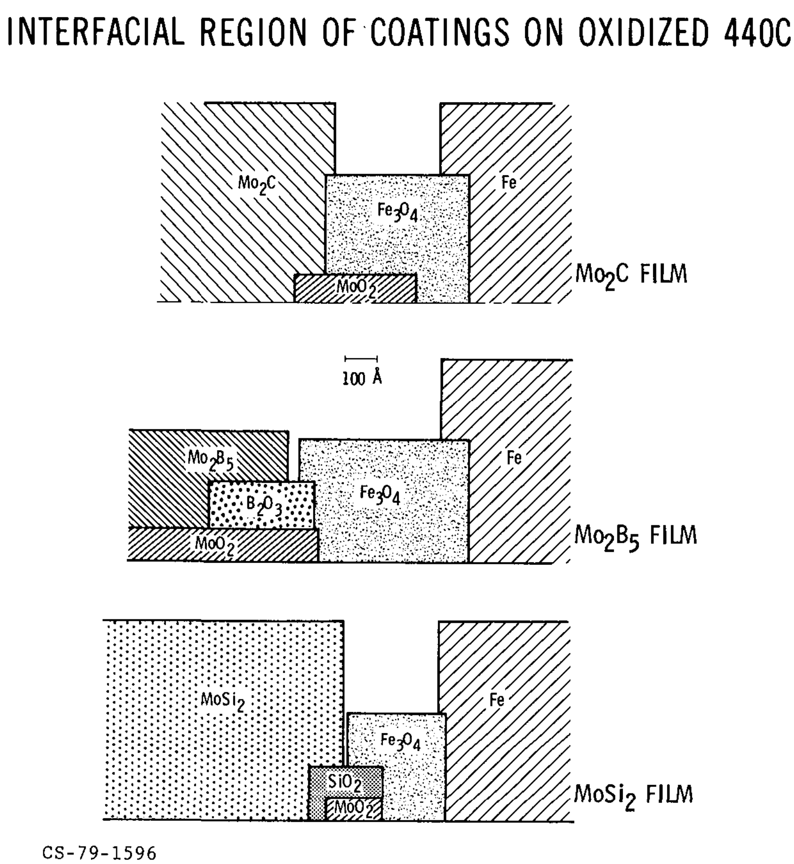

Figure 13

X-ray photoelectron spectroscopy reveals first the molybdenum coating, then the molybdenum oxides, the iron oxides, and finally the iron substrate. (The same thing is true with the boride and silicide, except one sees different oxide compositions.) What the oxides do, then, is key the coating material to the oxide and then the oxide to the substrate, thereby promoting good adhesion of the coating material to the substrate.

We have since found that other materials can be used to achieve the same type of bonding. For example, a layer of pure titanium metal sputter-deposited between the titanium alloy substrate and the coating material bonds very strongly to the oxide of a titanium-base alloy substrate and, for example, very strongly to the carbon of a carbide coating.

Recactive gases, such as acetylene, can also be usd to promote the formation of interfacial carbides. These carbides perform the same keying function as oxides, in that they promote the adhesion of the hard, refractory coatings to the substrate.

Conclusions

Sputtering and ion-plating are very useful techniques for applying dense, tenacious films to a variety of surfaces. The distinct advantage of the ion-plating process is the diffuse, or graded, interface it produces; that of sputtering is the wide variety of coating materials that can be deposited on a wide variety of substrates. Both processes have applications in a number of areas, including a catalytic corrosion, protective, decorative and lubrication films.