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# The XPS Depth Profiling and Tribological Characterization of Ion-Plated Gold on Various Metals



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# The XPS Depth Profiling and Tribological Characterization of Ion-Plated Gold on Various Metals

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## ABSTRACT

An investigation was conducted to examine, by XPS analysis and depth profiling, the atomic nature of such tribological properties as friction and microhardness of ion-plated gold. Friction properties were measured with 1) a gold film, 2) the graded interface between gold and nickel substrate, and 3) the nickel substrate. All sliding was conducted against hard silicon carbide pins in two processes. The first is the adhesive process in which friction arises primarily from adhesion between sliding surfaces, and the second is a non-adhesive process, namely abrasion, in which friction occurs as a result of the hard pin sliding against the film, indenting into it, and plowing a series of grooves. The other substrates used in this study included copper and 440 C stainless steel. Reference experiments were also conducted with vapor-deposited gold on the substrates. A vacuum environment is used in order to maximize the adhesion effect, while oil is used to minimize the adhesion effect. The results of the investigation indicate that the friction related to adhesion as well as the friction related to abrasion are influenced by coating depth. The trends in friction behavior as a function of film depth are, however, just the opposite. The graded interface exhibited the highest adhesion and friction, while the graded interface resulted in the lowest abrasion and friction. The coefficient of friction due to abrasion is inversely related to the hardness. The greater the hardness of the surface, the lower is the abrasion and friction. The microhardness in the graded interface exhibited the highest hardness

due to an alloy hardening effect. Almost no graded interface between the vapor-deposited gold film and the substrates was detected.

## 1. Introduction

In order to understand the reaction mechanism for adhesion and interfacial formation and to improve tribological properties of thin film coatings on different substrates, it is important to know the composition and its variation in the film and at the interface between the film and substrate. Depth profiling is actually a very favorable technique that can be used in conjunction with any of the analytical methods, such as X-ray photoelection spectroscopy, Auger electron spectroscopy, secondary ion mass spectroscopy, and ion scattering spectroscopy.

The present authors have conducted X-ray photoelectron spectroscopy (XPS) and depth profiling studies on ion-plated gold on nickel and iron surfaces to determine the composition profiles of the graded interfaces (ref. 1). The gold and nickel in the graded interface can form an alloy. The gold in the graded interface with iron was primarily atomically dispersed in the iron and formed a physically bonded interface.

The present investigation was conducted to examine such tribological properties as friction and hardness of; 1) the ion-plated gold film, 2) the graded interface, and 3) the substrate. The friction properties were determined with flat specimens containing the film, the graded interface, and the substrate sliding against silicon carbide pins in two processes. The first is an adhesive process in which friction arises primarily from adhesion between sliding interfaces, and the second is a non-adhesive process such as abrasion in which friction occurs as a result of the silicon carbide sliding against the film indenting into it, and plowing a series of grooves. Various substrates examined include copper, iron, nickel and 440 C stainless steel. Reference experiments for friction and hardness were also conducted with vapor-deposited gold on the above substrates.

## 2. MATERIALS

Gold of 99.99 percent purity was the plating material. The copper substrate was 99.999 percent pure, and the nickel and iron were 99.99 percent pure.

The rider specimen that was made to slide on the coating surface was single-crystal silicon carbide (99.9 percent pure). The mineral oil used for lubrication was a pharmaceutical grade that had been degassed.

## 3. APPARATUS

### 3.1. Coating

The ion plating chamber used in this study is shown in figure 1. The chamber is evacuated by a mechanical-oil and diffusion pumping system and a liquid-nitrogen trap. An alternative pumping system was also used to eliminate any possible external contamination, such as oil backstreaming during the pumping cycle. The mechanical and diffusion pumps were isolated from the chamber, and the pumping was performed directly by two vacsorb pumps. The chamber shown in figure 1 was also used for vapor-deposition of gold.

### 3.2. Friction

The two apparatuses used in this investigation are shown schematically in figure 2. They were basically a pin (rider) sliding on a flat. One was a vacuum system capable of measuring adhesion, load and friction. The apparatus also contained X-ray photoelectron spectroscopy for surface analysis. The ion gun shown in figure 2(a) was used for ion sputter-etching (depth profiling). The second apparatus was a system capable of measuring friction in oil. The load is applied by placing dead weights on a pan which rests on top of the rod containing the pin or rider specimen.

## 4. EXPERIMENTAL PROCEDURE

### 4.1. Coating and XPS depth profiling

The ion-plating and XPS depth profiling procedures are described in reference 1.

The same ion-plating experimental configuration was used for the vapor deposition of gold films. Before vapor deposition the substrates were dc sputter cleaned for about 10 minutes, and subsequently the chamber pumped to a pressure of $6.7 \times 10^{-4}$ pascal ($5 \times 10^{-6}$ torr), at which pressure the gold evaporation was performed.

4.2. Friction experiments

In situ friction experiments were conducted with a load to 0.2 N applied to the pin-flat contact. The radius of the silicon carbide pin specimen was 0.79 mm. To obtain consistent experimental conditions, the time in contact before sliding was kept constant at 30 seconds. The frictional force was continuously monitored during a friction experiment. The sliding velocity was $5 \times 10^{-2}$ mm $S^{-1}$ with a total sliding distance of about 3 mm. All in situ experiments were conducted in a vacuum of 30 nPa. The pin specimens were also sputter cleaned in the vacuum system.

In the oil experiments a 0.025 mm radius silicon carbide pin was used. The surfaces of the pin specimen were polished with 3 - micrometer - diameter diamond powder, and 1 - micrometer - diameter aluminum oxide ($Al_2O_3$) powder. Both the silicon carbide and ion-plated gold surfaces were rinsed with absolute ethyl alcohol before use. The friction experiments were single pass over a total sliding distance of 3 to 10 millimeters at a sliding velocity of 0.7 millimeter per second. They were conducted in mineral oil. All experiments were conducted at 25° C.

The vacuum environment was used to maximize the adhesion effect, while the oil was employed to minimize the adhesion effect. The 0.79 mm radius silicon carbide pin was used to lower the plowing effect on friction, while the 0.025 mm radius silicon carbide pin was used to raise the plowing effect.

## 5. RESULTS AND DISCUSSION

### 5.1. Adhesion and Friction

XPS survey spectra of the ion-plated gold surface on the substrates obtained before sputter cleaning revealed a carbon peak due to atmospheric contamination as well as an oxygen peak, as typically shown in figure 3. There is a layer of adsorbate on the outermost surface, which consists of water vapor or hydrocarbons from the atmospheric environment that may have condensed and become physically adsorbed to the gold. The spectra of the surface which were sputter cleaned for 5 min revealed that the XPS peaks for gold on the surface of the ion-plated gold had an absence of the contamination peaks from the spectrum, as shown in figure 3(b). After subsequent sputter etching, peaks associated with the substrate were seen in the XPS spectra, as has already been discussed in reference 1. Elemental depth profiles for the ion-plated gold surfaces on nickel and iron substrates as a function of sputtering time indicated that a graded interface between the ion-plated gold and the substrate was present (ref.1).

Single-pass sliding friction experiments were conducted with the surfaces of the clean ion-plated gold, the graded interface between gold and nickel and the nickel substrate sliding against the clean 0.79 mm radius silicon carbide spherical pin in vacuum at a pressure of 30 nPa. Friction force traces resulting from sliding in vacuum were generally characterized by stick-slip with fluctuating behavior. Figure 4 presents the coefficients of friction as a function of film depth of the ion-plated gold on a nickel surface. The results of XPS elemental analysis and depth profiling are also schematically summarized in figure 4 with a structural model. The coefficient of friction for the clean ion-plated gold surface is generally lower than that for the surface, which is ion-etched about 0.5 μm from the ion plated surface. With ultra thin gold films of the order of 0.1 μm thick or less on nickel, high friction is associated with a local break through of the gold film in the contact area. Breakthrough of the film will induce direct contact of the silicon carbide pin with the graded interface of gold and nickel. Inspection of the ion-plated gold after single-pass sliding contact with silicon carbide under high adhesive conditions in vacuum clearly revealed that the sliding friction resulted in wear and transfer of gold to the mating surface (ref. 1).

At the graded interface the coefficient of friction generally increases with the presence of substrate element relative to that obtained for the ion-plated gold film itself. The high friction is associated with high adhesion at the graded interface. This may be due to the raising of the Peierles stress and an increase in lattice friction stress, by nickel atoms of the substrate. This results in resistance to the shear fracture of the cohesive bonding in the alloy of the graded interface. The present observation is consistent with the authors' earlier work (ref. 2).

In the nickel substrate region, the coefficient of friction differs considerably from that for the graded interface. The coefficient of friction generally decreases markedly with the absence of the ion-plated gold.

## 5.2. Abrasion and Friction

### 5.2.1. Indentation Hardness

Micro-Vickers hardness measurements were conducted in air at atmospheric pressure on both ion-plated and vapor-deposited gold film on nickel substrates.

Figure 5(a) presents the microhardness of the ion-plated gold on nickel as a function of depth from the surface of the film. The gold coating film on nickel was gradually etched by argon ion sputtering. The hardness is influenced by the depth from the coating surface and is also related to the composition gradient between the ion-plated gold and the substrate. As one might expect, the microhardness increased with increasing depth from the coating surface, because the load borne by the hard graded interface and substrate increases as the film becomes thinner, and deformation accordingly decreases during indentation, (ref. 3).

Furthermore, in the graded interface, the hardness increased slightly with increasing depth. The graded interface exhibited the highest hardness. Below a certain depth (about 3 μm in figure 5(a) in the graded interface, the hardness decreases with an increase in depth and gradually approaches the hardness of the nickel substrate. The trend and behavior of hardness in the graded interface is due to an alloy hardening effect (refs. 4 and 5).

Figure 5(b) presents the microhardness of the vapor-deposited gold on nickel as a function of depth from the gold surface. The hardness of the gold surface was the lowest hardness value obtained. The hardness increases with an increase in depth from the vapor-deposited gold surface. The hardness of the substrate, where the gold film was removed by argon ion sputtering, is almost the same as that of the bulk nickel substrate. Almost no graded interface between the vapor-deposited film and substrate is seen in figure 5(b).

5.2.2. Plowing Friction

Sliding friction experiments were conducted with both ion-plated and vapor-deposited gold on nickel substrates in contact with a 0.025 mm - radius, spherical silicon carbide pin with a mineral oil lubricant at loads of 0.05 N and 0.1 N. The sliding action resulted in permanent grooves in the coating films and in the metal substrates, with deformed metal piled up along the sides of the grooves. Under these conditions, the friction is due primarily to plowing of the coating film and the substrate. The friction-force traces obtained in this investigation were characterized by randomly fluctuating behavior with no evidence of stick-slip.

Figure 6(a) presents the coefficients of friction for ion-plated gold surface, the graded interface, and the nickel substrate in contact with the silicon carbide pin lubricated with mineral oil. The coefficients of friction decreases as the depth from the gold coating surface increases. The coefficient of friction of the gold coating was the highest value obtained, while the graded interface resulted in the lowest coefficient of friction. In the substrate region, the coefficient of friction increases slightly. The trend of this data indicates that the coefficient of friction is inversely related to the hardness, and directly related to the apparent contact area during sliding. The greater the hardness of the metal surface, the lower the coefficient of friction. This is consistent with the authors' earlier work (ref. 4).

Figure 6(b) presents the coefficients of friction for vapor-deposited gold on nickel and the nickel substrate as a function of the depth from the gold surface at a load of 0.1 N. Again, the coefficient of friction is inversely related to the hardness, namely the load carrying capacity of the vapor-deposited gold surface and the substrate.

In order to examine the influence of hardness on friction with various substrates, sliding friction experiments were conducted with ion-plated and vapor-deposited gold films on copper, nickel and 440 C stainless steel substrates in contact with the 0.025 mm radius spherical silicon carbide pin with a mineral oil lubricant. The coefficients of friction are presented as a function of hardness measured at a normal load of 0.1 N in figure 7 (a). The coefficients of friction correlate with the hardness of the gold film on substrate, and the relationship is a linearly decreasing one. The coefficient of friction data were reexamined as a function of hardness of the substrate measured at loads of 1 N and 3 N. The results are presented in figure 7 (b).

This figure clearly indicates that the coefficients of friction correlates with the hardness of the substrate itself.

## 6. CONCLUSION

The following conclusions are drawn from the data presented herein.

1. The friction related to adhesion as well as the friction related to abrasion are influenced by the depth from the surface of the film, but the trend of friction behavior as a function of the depth is just the opposite.

The graded interface between gold and nickel exhibited the highest adhesion and friction, while the graded interface resulted in the lowest abrasion and friction.

The coefficient of friction due to abrasion is inversely related to the hardness. The greater the hardness of the surface, the lower is the abrasion and friction.

2. The microhardness in the graded interface exhibited the highest hardness due to an alloy hardening effect.

3. The behavior of friction and hardness for vapor deposited gold on various substrates is similar to that with ion-plated gold, but there is almost no graded interface between the gold and the substrate.

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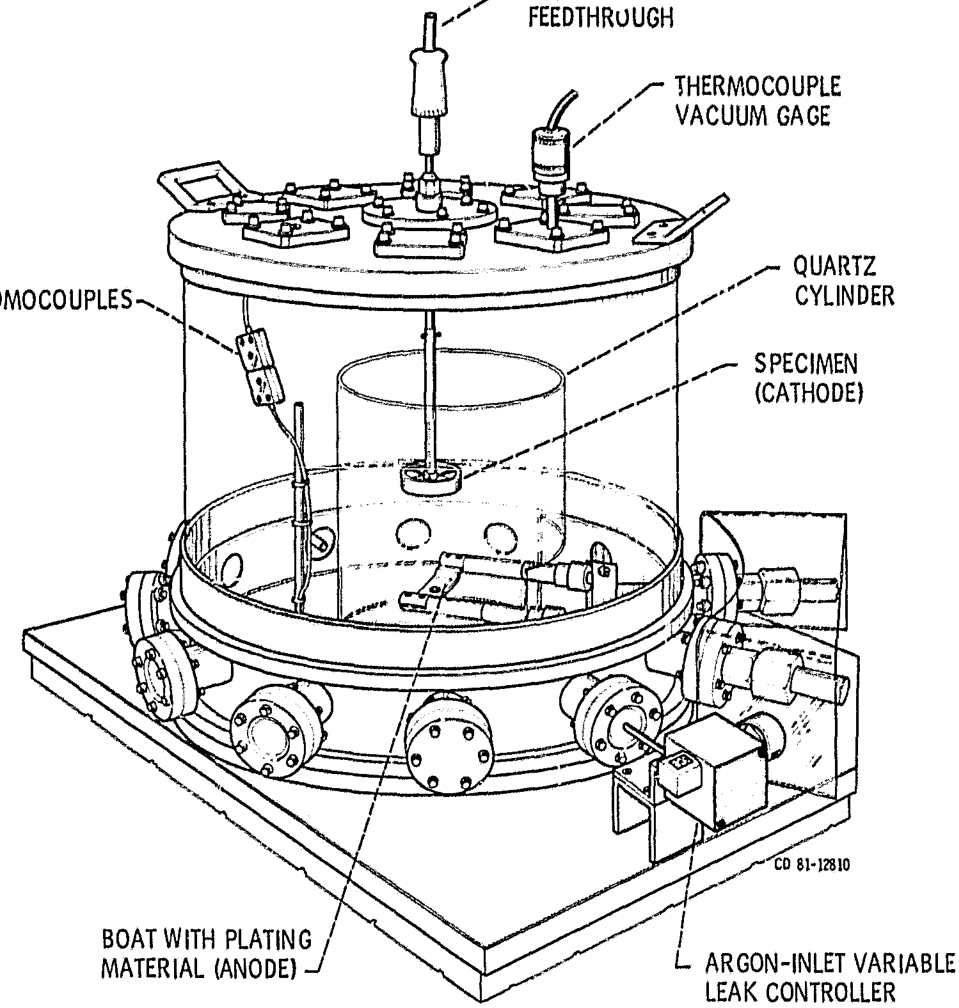
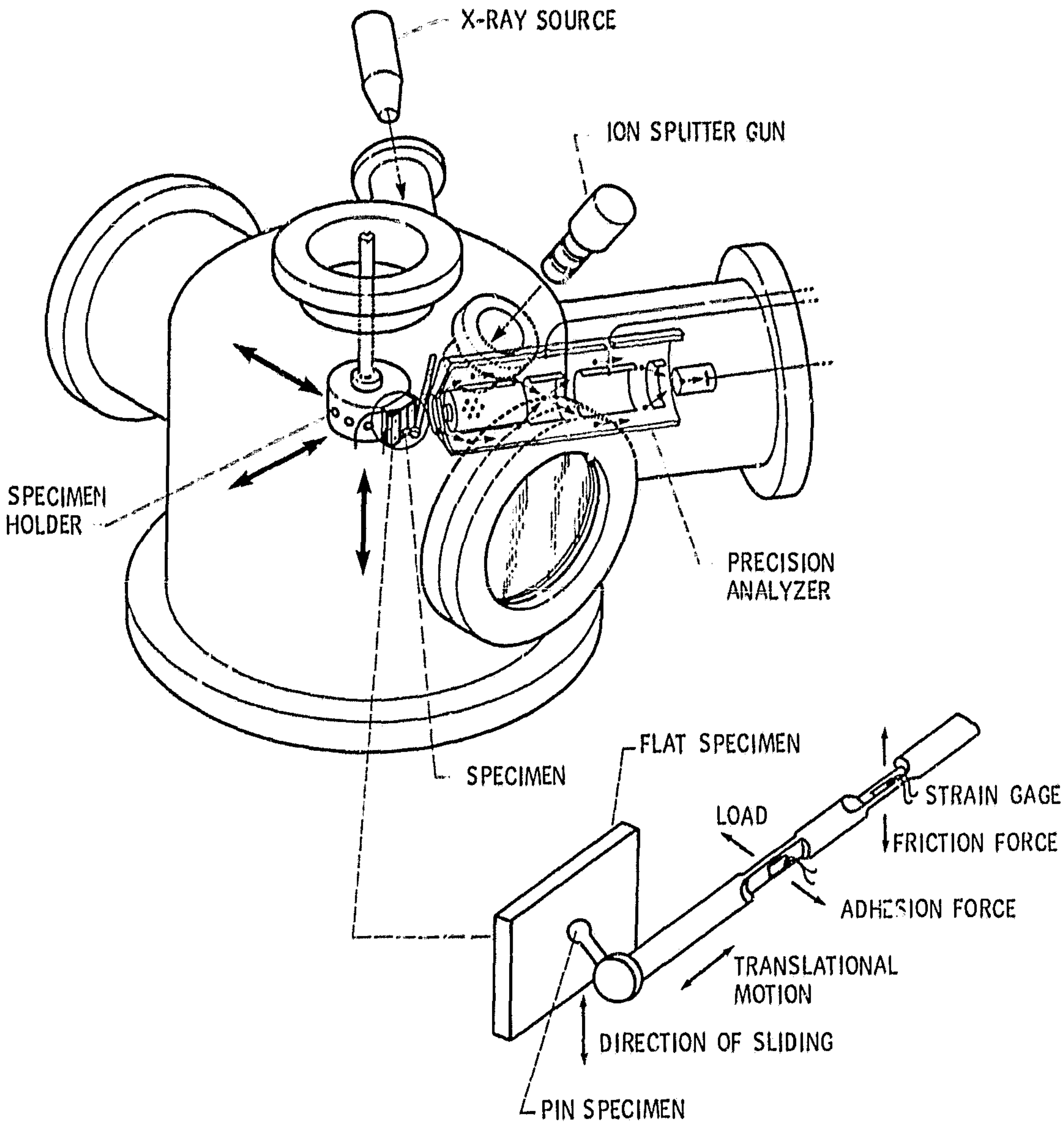
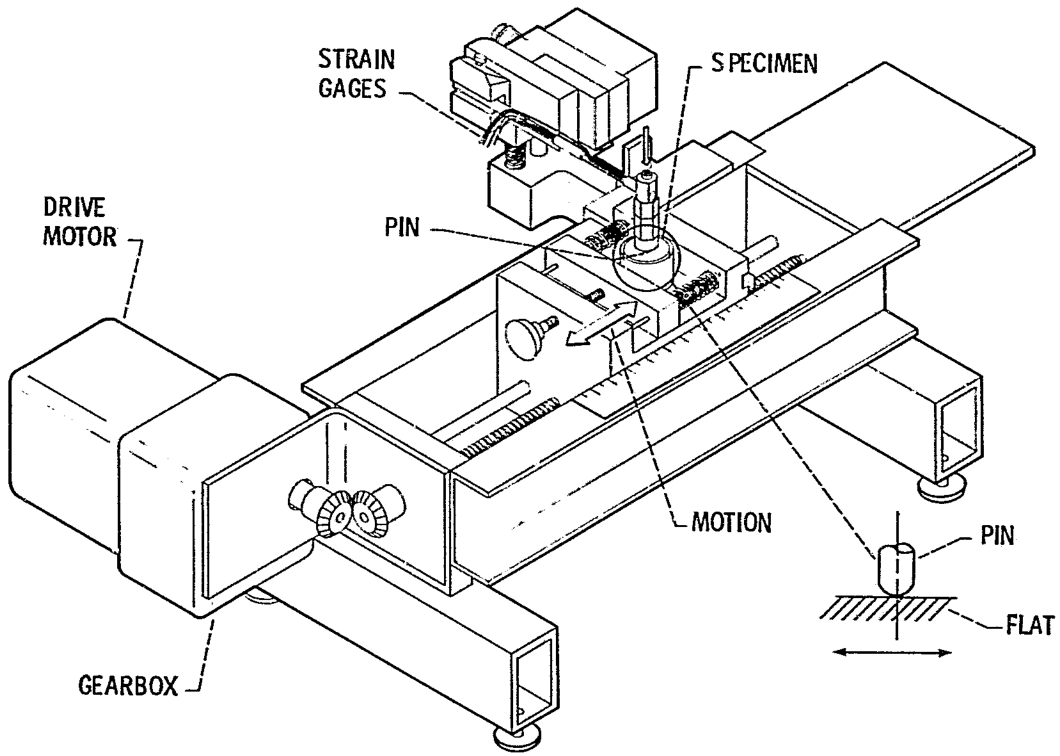



Figure 1. - Ion-plating chamber.




(a) High vacuum apparatus.

Figure 2. - Friction and wear apparatus.




(b) Apparatus used for experiments in oil.

Figure 2. - Concluded.

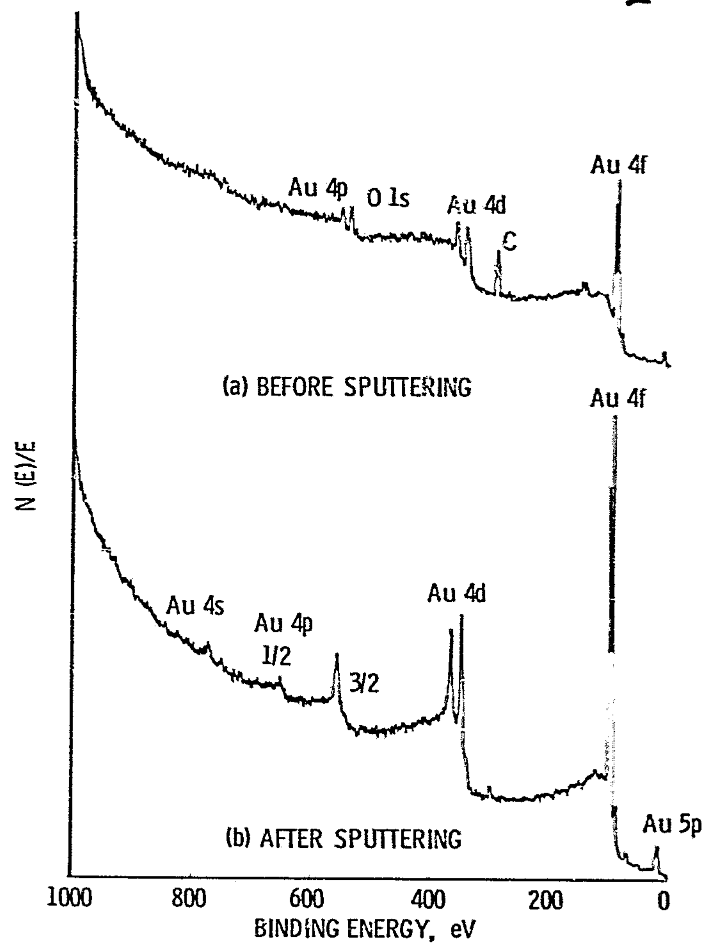



Figure 3. - Survey spectra of ion plated gold surfaces before and after argon ion sputtering. Sputtering time, 5 min; substrate, nickel.

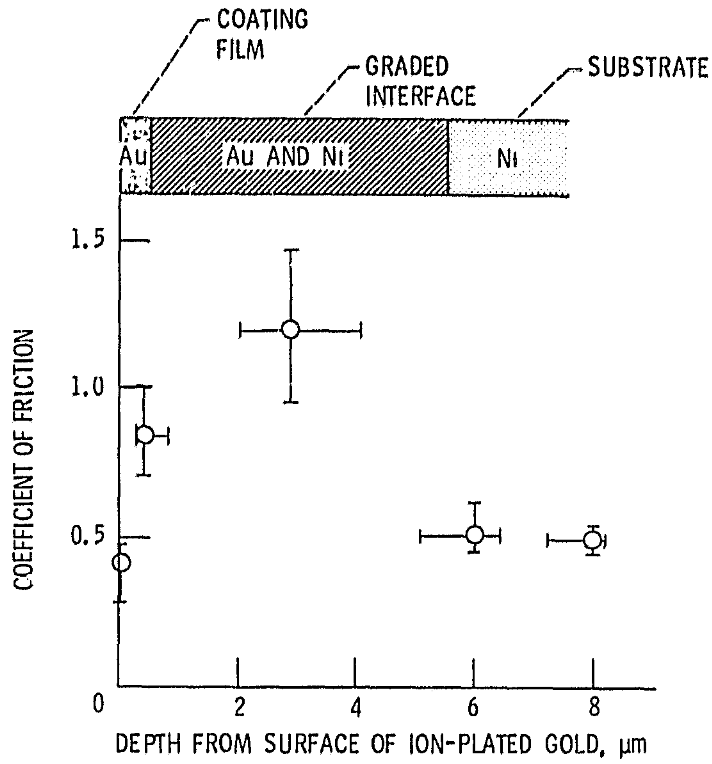



Figure 4. - Coefficient of friction as function of the depth of the ion-plated gold on nickel surface in ultra-high vacuum. 0.79 mm-radius spherical SiC pin sliding on the ion-plated gold surface and the argon ion etched surfaces. Load, 0.2 N; vacuum pressure, 30 nPa.

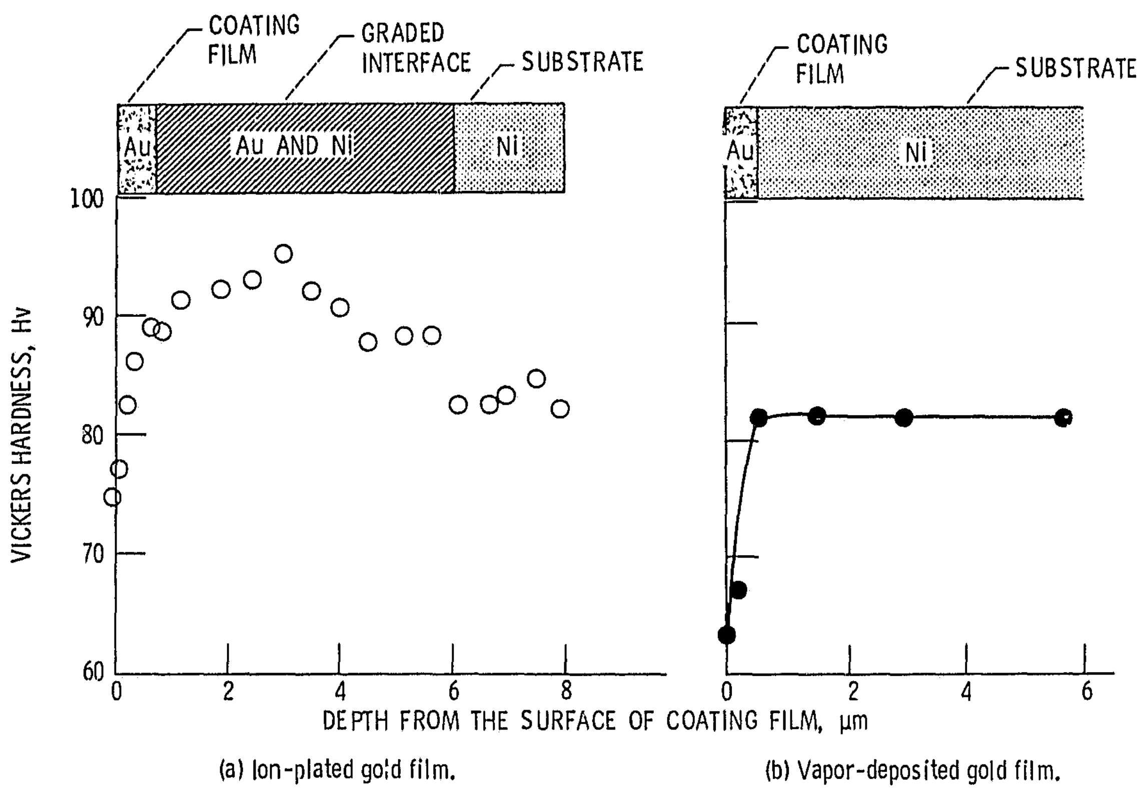
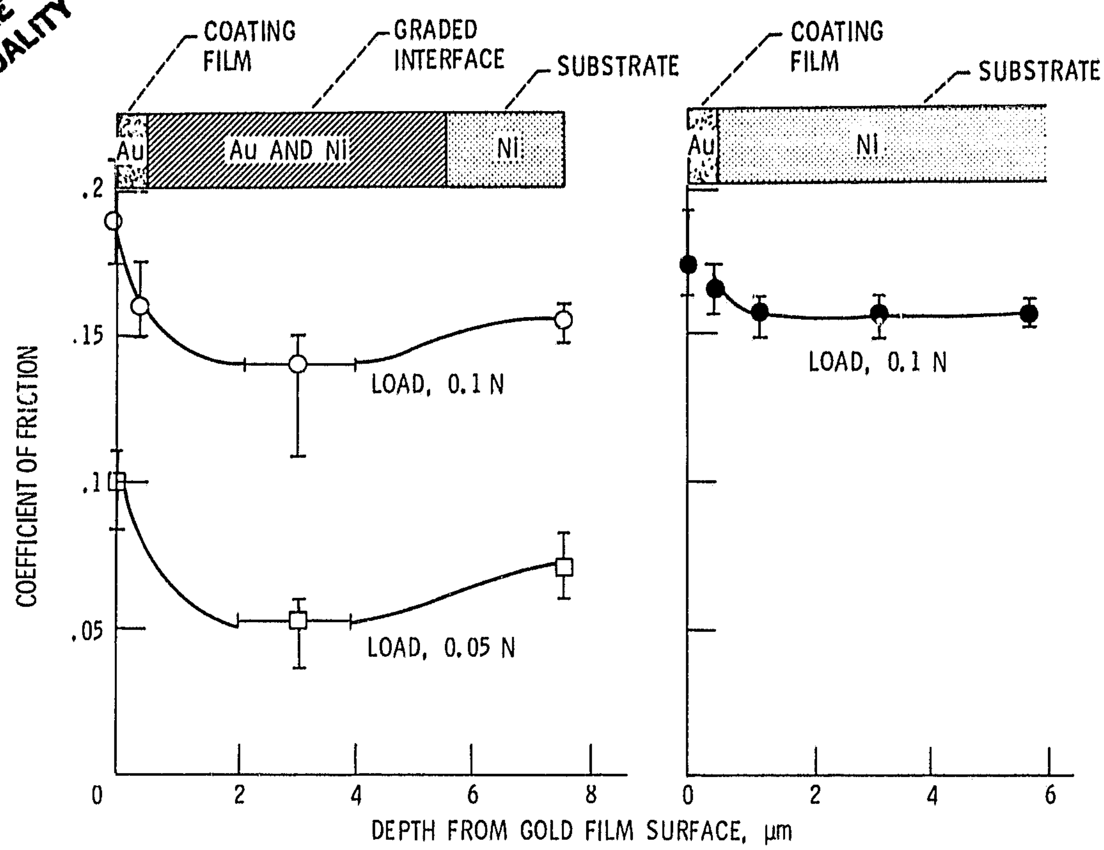


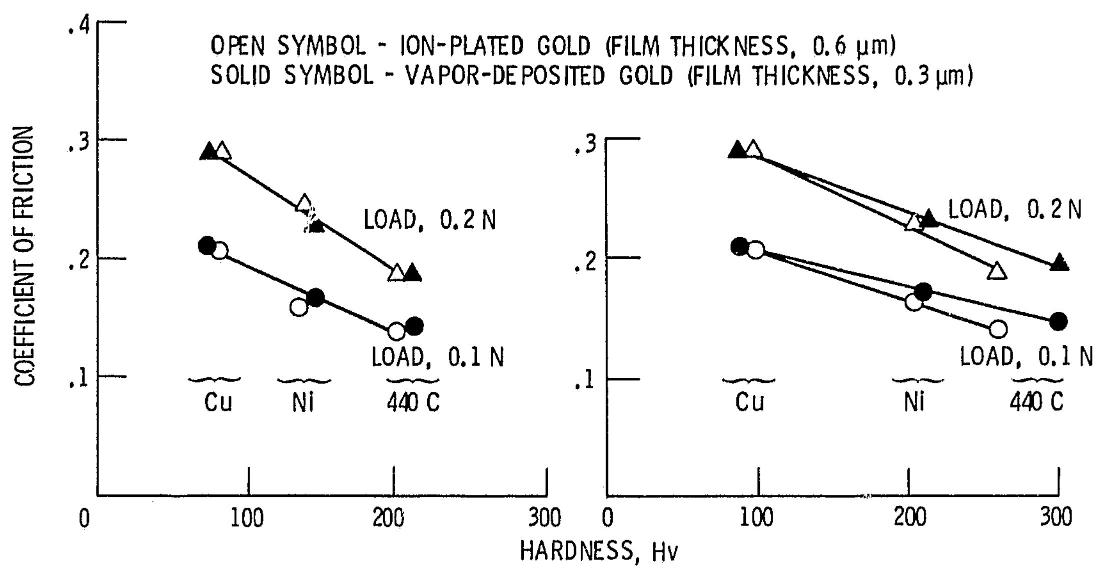

Figure 5. - Depth profiles of hardness for ion-plated and vapor-deposited gold on nickel substrate. Hardness measuring load, 0.1 N.




(a) Ion-plated gold film on nickel substrate.

(b) Vapor-deposited gold film on nickel substrate.

Figure 6. - Coefficient of friction as a function of the depth from the ion-plated and vapor-deposited gold surface. 0.025 mm-radius spherical SiC pin sliding.




(a) Friction vs hardness of Au on substrate (Measuring load of hardness, 0.1 N).

(b) Friction vs hardness of substrate (Measuring load of hardness, 3 N).

Figure 7. - Coefficients of friction for ion-plated gold and vapor-deposited gold on nickel, copper and 440 C stainless steel as function of hardness.