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The Structure of Ion Plated Films in Relation to Coating Properties

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ABSTRACT

Ion plating is an ion assisted or glow discharge deposition technique, where ions or energetic atoms transfer energy, momentum and charge to the substrate and the growing film in a manner which can be controlled to favorably modify surface, subsurface chemistry, and microstructure. The glow discharge energizing effects from the initial nucleation stages to the final film growth are discussed. As a result, adherence, coherence, internal stresses, density and morphology of the coatings are significantly improved, over the conventional (nonion-assisted) techniques which in turn favorably affect the surface initiated failures caused by friction, wear, erosion, corrosion and fatigue. Ion plated films because of their graded coating/substrate interface, fine, uniform, densely packed film structure also induce a surface strengthening effect which improved the mechanical properties such as yield, tensile strength, and fatigue life. Since a uniform, continuous film can be obtained at lower nominal film thickness, this effect is of great importance in solid film lubrication and in corrosion protection. The glow discharge intensification on the structural zone model is explained, how a typical columnar grain structure can be modified to a more dense, equiaxed structure without increasing the substrate temperature.

ION PLATING is an ion assisted or glow discharge deposition technique, where ions or energetic atoms transfer energy, momentum and charge to the substrate and the growing film, in a manner which can be controlled favorably to modify surface, subsurface chemistry, and microstructure. It is important to recognize that the majority of material failures are surface initiated by surface processes such as wear, friction, corrosion, erosion, and fatigue and can be controlled or mitigated by the proper structure/property relationship produced by an ion plated coating. Ion plating offers a great flexibility and control

in modifying and tailoring the structural and chemical properties of the coating. Interrelationships between film formation, structure and properties is strictly controlled by the parameters of ion plating and substrate condition. The object is always to obtain an adherent, coherent film with dense, homogeneous growth morphology.

Glow discharge energizing during ion plating favorably modifies the nucleation and growth sequence and the coating/substrate adherence. As a result, adherence, coherence, density, stoichiometry, internal stresses, morphology and defects in the coatings can be significantly improved, which in turn favorably affect the surface initiated failures. Plasmas generated in the conventional dc-diode ion plating system have a low degree of ionization, less than 0.1 percent and are primarily used for the deposition of the lower melting point materials. However, to achieve high densification of the coating structure for the high melting point materials such as ceramics (carbides, nitrides) a higher ionization efficiency has to be achieved than offered by the diode-system, and has to be performed in the reactive mode. Extensive investigations are presently being conducted to enhance the ionization efficiency, basically either to increase the number of ionizing electrons or making their trajectories longer, primarily for the purpose to synthesize and ion plate ceramics.

The object of this discussion is to describe the structure/property relationships of dc-diode ion plated soft, elemental metallic films (Au, Ag, Pb) which are used as solid film lubricants. These lubricating, metallic films reduce friction and/or wear on sliding or rotating surfaces, and are finding increased applications in areas where combination of high vacuum, temperature and radiation preclude the use of conventional lubricants such as oils and greases. These soft coats, confine friction losses to a thin, low shear strength film interposed between the contacting surfaces. These ion plated lubricating films because of their superior adherence, crystalline structure, and very thin thickness (2000 Å) display low

coefficients of friction, reduce wear rate and increase the endurance lives.

GLOW DISCHARGE CONSIDERATIONS

In ion plating the plasma or glow discharge generated in a low pressure argon gas consists of a melange of ions, atoms, atomic ions in various stages of excitation, electrons, photons, etc. which make the plasma particularly reactive. Plasma energizing has basically two effects in a deposition process: (1) the physical aspect, no matter what gas is used it is always present and (2) the chemical aspect present only when reactive gases are used. In this paper only the physical aspects of the glow discharge and its profound effects on nucleation and growth kinetics will be discussed.

During ion plating the energizing is provided by the gas discharge and in principle it combines (1) the energetic impingement of ions and activated atoms of the sputtering process, (2) the high throwing power of electroplating and (3) the high deposition rates of thermal evaporation. The impingement of the ions and neutrals contributes to the excellent adherence and modified structural growth of the film, and the high throwing power provides for three-dimensional coverage to coat complex, intricate surfaces. The basic ion plating system consists of a dc-diode configuration, where the specimen is made the cathode of the high voltage dc-circuit with the evaporation source the anode and is shown schematically and photographically in Fig. 1. The principles and operation of the process have been widely described in the literature (Refs. 1-6) and will not be reviewed here.

For ion plating the degree of glow discharge intensification in terms of ionization efficiency (the percentage of the evaporant atoms which are ionized) and the energies of the evaporant flux basically control the nucleation and growth kinetics. For instance, in a dc-diode plating system, the applied bias voltage directly influences the energy of the arriving ions or neutrals and the ion current. The ion current is controlled by the bias voltage and argon pressure. In the diode system these parameters are not independent, but depend on each other. The typical commercially used ion plating conditions are: voltage 3 to 5 kV, argon pressure 20 mTorr and cathode current density 0.3 to 0.5 mA/cm². It has been estimated that under these conditions the ions carry only 10 percent of the energy dissipated while the energetic neutrals carry 90 percent (Ref. 2). The energetic neutrals which are generated through charge transfer collisions (where a large part of the kinetic energy of the ions are transferred to the neutral atoms) constitute a very significant proportion of the energy carried. The ions and the activated neutrals may have a distribution of energies from thermal 0.2 eV up to the voltage applied to the discharge. It has been estimated that the average energies of the ions and neutrals are of the order of 100 eV (Ref. 2). More recent studies reveal that the average energy of the argon ions is

450 eV, and the average energy of the metallic ions during ion plating is 1100 eV (Ref. 8). It should be noted, that in this study the average energy of the ions of the deposited material is considerably higher (2 times) than that of the gas bearing the discharge.

The discharge intensity has a direct effect on the nucleation, morphological growth and densification of the film. An increase of bias voltage is equivalent to an increase of the substrate temperature. It is well known that when film deposition is carried at low and intermediate substrate temperatures, a columnar film grain structure results. Therefore it is common practice to heat substrates at high temperatures to form the favorable dense, equiaxed structure. However, the densification of the film structure can be obtained by increasing the discharge intensity in the diode system, without additional substrate heating. The amount of increased energetic input to produce dense coating structures is related to the melting point of the coating material. The highest ionization enhancement is required to produce dense coatings of ceramic materials in the reactive mode.

A diverse range of modifications have been introduced to the diode system to increase the ionization efficiency. The various system designs are schematically summarized in Fig. 2. All of these designs basically consist either of increasing the number of ionizing electrons, or making their trajectories longer. For instance, the multicathode technique aims to increase ionization with the emission of thermal electrons from hot tungsten filaments placed in the evaporation area. Or a very simple way to increase the length of electron trajectories consists in placing a third electrode between the substrate and the evaporation source and positively biasing it with respect to ground. These above configurations are generally referred to as triode ion plating. In these systems the ion current can be controlled independently of the bias voltage. As a result, low voltages, very high discharge current intensities can be obtained which allow the use of lower pressures (1×10^{-3} Torr). The ionization ratio can be increased by a factor of 10 and ion current density can be in excess of 1 mA/cm².

ADHERENCE AND GRADED INTERFACE

Strong adherence between the coating and the substrate is of paramount importance for any successful application. The interface or transition from the substrate material to the coating usually forms a break in the normally uniform crystallinity and/or composition. This abrupt disparity or mismatch is reflected in the coefficient of thermal expansion, thermal conductivity and hardness. The objective is to reduce or eliminate this abrupt disparity by inducing a graded or fused interface between the coating and the substrate. The process of ion plating provides a gradual composition or graded interface. This effect is illustrated by experimental results by analyzing ion plated gold films on nickel and iron surfaces by x-ray photoelectron spectroscopy (XPS)

depth profiling as shown in Figs. 3(a) and (b). Compositions of surface (at %) for gold films ion-plated on nickel and iron were obtained as functions of the sputtering removal time from XPS analysis. The composition of gold did not change in the first 20 min. of sputtering and thereafter gradually decreased with increasing sputtering time. However, the nickel and iron content increased with increased sputtering times. The graded interface for gold on nickel was approximately 6 μm thick; that for gold on iron was approximately 1.5 μm thick. The deeper graded interface between gold and nickel is due to the continuous solid solubility between the two metals. Since gold and iron has a very limited solid solubility (1.5 at % at 850 °C) (Ref. 9) the interface is reduced and is basically produced by implantation and atomistic mixing and atomically dispersed (Ref. 10). On the other hand, XPS depth profiles for gold vacuum deposited on nickel and steel surfaces are shown in Fig. 4, where the composition of gold rapidly decreased with increasing sputtering time, thus forming an abrupt interface.

The interface formation was also investigated by Micro-Vickers hardness measurements where indentation hardness depth profiles were established for the ion plated and vacuum deposited gold films on nickel substrates and are shown in Figs. 5(a) and (b). The microhardness of the ion plated gold film, graded gold-nickel interface and nickel substrate as a function of depth from the surface is shown in Fig. 5(a). The gold films were gradually removed by argon ion sputtering for microhardness measurements. Initially, the microhardness of the gold film is relatively low, but gradually increases in the interface region and finally decreases again as it reaches the nickel substrate. The higher hardness in the interface region is due to alloying effects. The vapor deposited gold film on nickel substrates shown in Fig. 5(b) exhibits a constant hardness, which indicated the lack of a graded interface.

The XPS and microhardness depth profiles experimentally verify the formation of a graded-fused interface which is responsible for the excellent adherence. The controlling reaction mechanisms which contribute to the formation of this graded interface are schematically shown in Fig. 6. These contributing factors can act separately or most likely in various combinations depending on the film/substrate compatibility and the energetics of the evaporated flux.

The graded interface not only provides excellent adherence, but also induces a surface strengthening effect which improves the mechanical properties such as yield strength, tensile strength, fatigue strength as shown in Figs. 7(a) and (b). The surface-subsurface strengthening may arise from solid-solution alloying, dispersion of mobile interstitial or substitutional atoms which act as barriers to the egress of dislocations.

NUCLEATION AND GROWTH MORPHOLOGY

NUCLEATION - During ion plating the evaporant flux of energetic ions and neutrals transfers

energy, momentum and charge to the substrate and the depositing film surface. These effects produce several unique nucleation characteristics as determined by transmission electron microscopy (TEM). Typical TEM micrographs of ion plated Pb films in the initial stages of nucleation are shown in Fig. 8. The examination of these microstructures reveal that the nucleation of the ion plated films, unlike the conventional films, exhibit a very distinct behavior. The size of the nuclei is considerably smaller (200 Å), they remain rounded, are uniformly distributed over the entire surface and the density of the nuclei is very high. As deposition continues the nuclei remain rounded with slight increase in size, but the formation of new nuclei continues to be a major growth mechanism. Consequently, continuous films are obtained at lower nominal thicknesses usually in the 250 Å thickness range, with high packing density and a minimum degree of lattice misfit.

Typical TEM micrographs of 400 Å thick ion plated and vapor deposited gold films are compared in Figs. 9(a) and (b). The ion plated gold films in Fig. 9(a) have fine, uniform crystallite structure, but the vapor deposited gold films shown in Fig. 9(b) display a high degree of nonuniformity in the crystallite size and shape.

MORPHOLOGY - Films deposited on non-biased substrates (without a glow discharge environment) at ambient temperatures exhibit the typical columnar grain structure, with the axis of the columns along the direction of growth. The columns are generally separated by porosity, so that the packing density is less than unity. However, the desirable morphological structure is the one which exhibits the equiaxed, dense grain structure which can be obtained only at relatively high substrate temperatures. It is well recognized that the films prepared by ion plating and sputtering also show a wide range of microstructures as the substrate temperature increases. As a result the structure zone model (SZM) has been developed, which consists of four zone structures shown in Fig. 10. This model is based on the ratio of the surface temperature (T) to the melting point of the deposited material (T_m). The structural T/ T_m dependence is affected by the surface diffusion process and the bulk process that characterize the recovery and recrystallization (Ref. 11). The coating in zone one has the columnar structure, has a high degree of porosity and therefore does not withstand high stresses and loads. Coating in zone T (transition) region still consists of fibrous grains but more densely packed. In zone two the structure has columnar grains separated by distinct, intercrystalline boundaries. Finally in zone 3 bulk diffusion has predominant influence on the final structure of the coating and consists of equiaxed dense, recrystallized grains. Consequently the structural densification increases with a higher T/ T_m ratio. Using the SZM model, substrate temperatures in excess of 1300 °C would be required for the deposition of high melting point materials such as ceramics (carbides, nitrides, etc.) in the reactive mode. This places severe constraints on

the specimens such as steels and tool steels which are coated, since the mechanical properties of the specimens would be unfavorably affected at these high temperatures. Instead of increasing the bulk temperature, the zone boundaries can be shifted to lower temperatures by intensifying the glow discharge during ion plating. Basically an increase of the bias voltage is equivalent to an increase of the substrate temperature in the SZM diagram. However, diode ion plating generally gives improved grain structures, but still tend to be columnar as the film thickness increases.

Primarily for the deposition high melting point materials the triode system is used which utilizes ionization enhancement, where the structure from coarse columnar (zone 1) through fine columnar (zone 2) finally to a dense equiaxed (zone 3) can be formed. The equiaxed structure obtained under the ionization enhancement conditions is primarily due to intense ion bombardment, which continually cause recrystallization and growth of zone three type structure even when the bulk temperature is low. The formation of the coarse columnar structure can be associated with higher glow discharge pressures and low current densities and the dense, equiaxed structure at lower pressures and high current densities.

It has been reported that high energy (>500 eV) ion bombardment can suppress the formation of a distinct columnar structure (Ref. 5). The high rate of nucleation tends to form a uniform, fine grained, high-packing density film which contributes to an increased cohesive strength. This increased cohesive strength improves the film's integrity, thereby reducing the likelihood of lamination or separation within the film.

FRICTIONAL CHARACTERISTICS OF SOFT

METALLIC FILMS

Of the soft, metallic films (Au, Ag, and Pb), gold and lead have found extensive uses in space-born bearings of satellite mechanisms such as solar array drives, despin assemblies and gimbals. These ion plated lubricating thin films 0.2 μm thick are very effective in improving the frictional and wear characteristics and increasing the endurance lives (Refs. 12-16). For instance, during sliding conditions in a pin and disk tribotester, the normal load is supported by the real area of contact under pressure p , whereas the tangential force will be governed by the shear strength s of the thin, soft metallic film. As a result the friction coefficient is defined as $\mu = s/p$. The extent to which the coefficient of friction can be lowered depends primarily on film adhesion, shear strength, thickness, surface roughness, and the deposition technique. Typical friction curves for ion plated and vapor deposited gold films 2000 \AA in respect to testing time in a pin and disk tribotester under vacuum conditions are shown in Fig. 11. The ion plated film had three distinct improvements over the vapor deposited one: (1) increased endurance life, (2) lower coefficient of friction, and (3) avoidance of

catastrophic failure. The reasons for the increased endurance life are attributed to the superior adherence, the lower coefficient of friction due to the dense, cohesive small crystalline size and thin film thickness, and the gradual increase in the coefficient of friction after the film has been worn off to the formation of the graded interface.

In thin film lubrication the film thickness has a very pronounced effect on the coefficient of friction as shown in Fig. 12 with ion plated Au and Pb films. The effective or minimum film thickness for gold films was about 2000 to 3000 \AA , and for lead films 1800 to 2500 \AA with the lowest coefficients of friction of 0.1 and 0.085 respectively.

The variation in the friction coefficient with the film thickness is shown schematically in Fig. 13. It is divided into two regions, namely the ultrathin and the thin film regions, with the effective or critical film thickness at the lowest coefficient of friction. In the ultrathin region the increase in the friction coefficient is associated with a breakthrough in the film by mating asperities. In the thin film region, as the film thickness increased, the load-carrying capacity of the substrate surface decreased and an increase in the apparent area of contact leads to a higher friction coefficient.

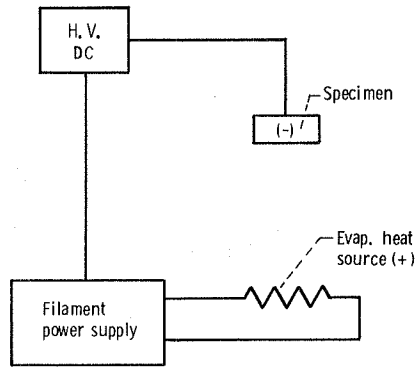
CONCLUDING REMARKS

In ion plating the energetics of the plasma plays a fundamental role and can be favorably controlled and used to improve coating/substrate adherence and precision tailor desirable morphological coating structures. The interrelationships between film formation, structure and resultant properties is strictly controlled by the parameters of ion plating and the substrate condition. The excellent adherence and coherence, improved morphological growth to form dense, cohesive, equiaxed grain structures, all of which have a tendency to improve the structure/property relationships primarily when used on surface initiated failure processes such as wear friction and corrosion. The basics of glow discharge and the characteristics of ion plating should be understood in order to exploit their capabilities to generate preferred morphological and compositional structures. The disadvantage of this process and the resultant coatings lies mainly in its newness; that is, the best coating structures and the optimum processing designs and parameters have yet to be established.

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(a) SCHEMATIC.

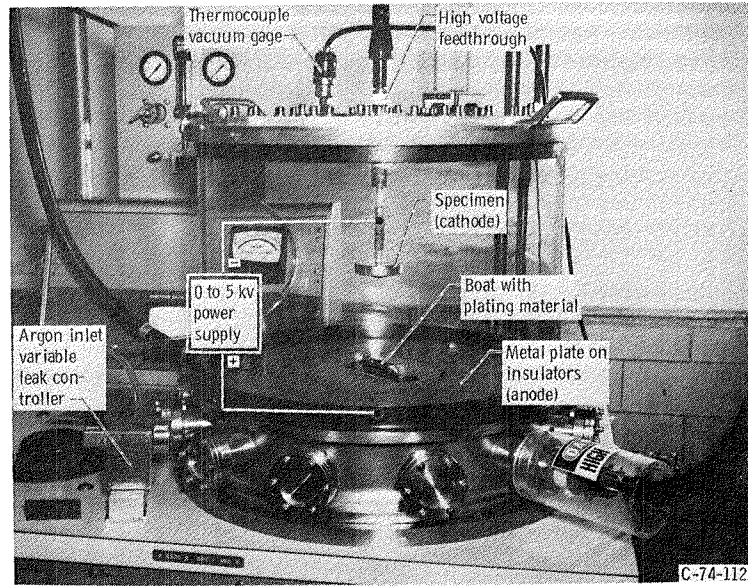


Figure 1. - Ion plating system.

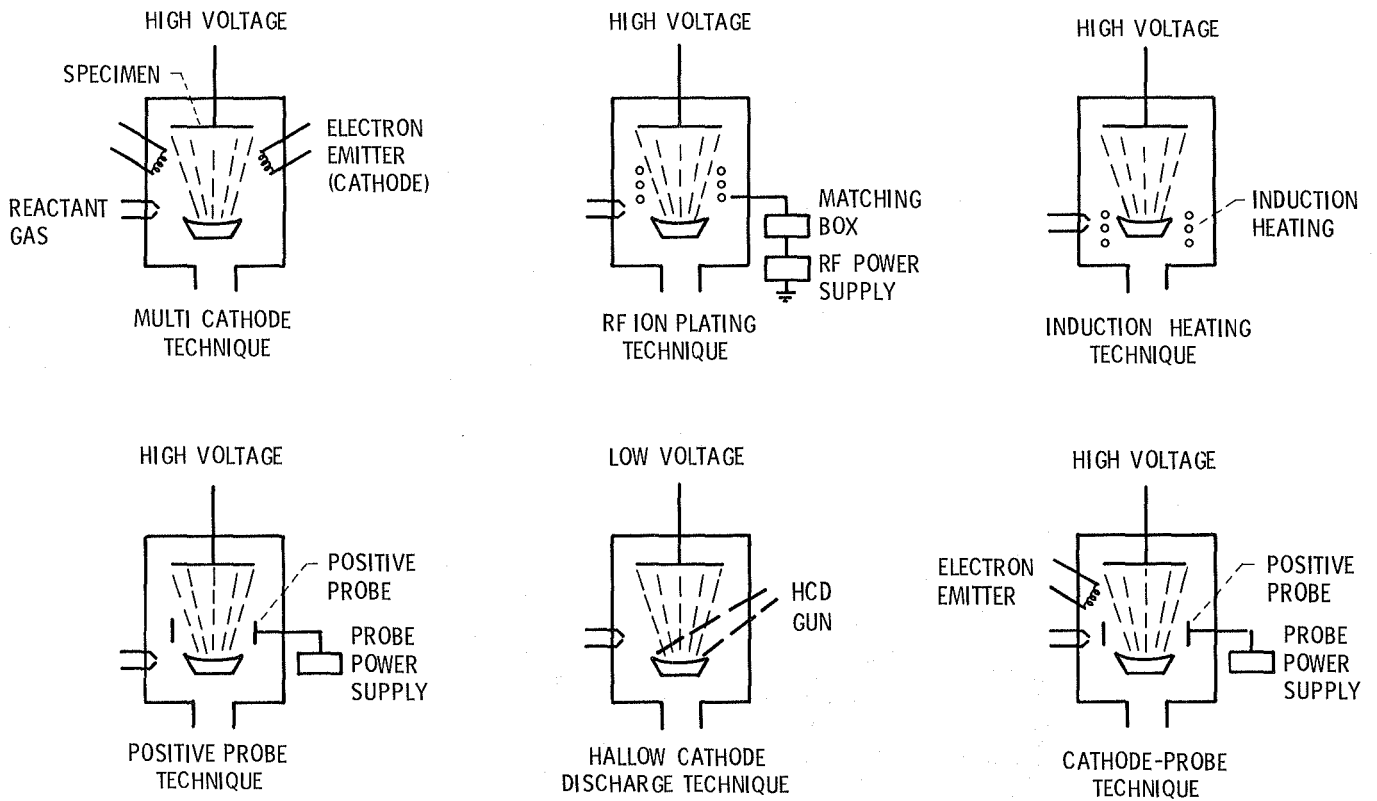


Figure 2. - Enhanced ionization techniques of ion plating.

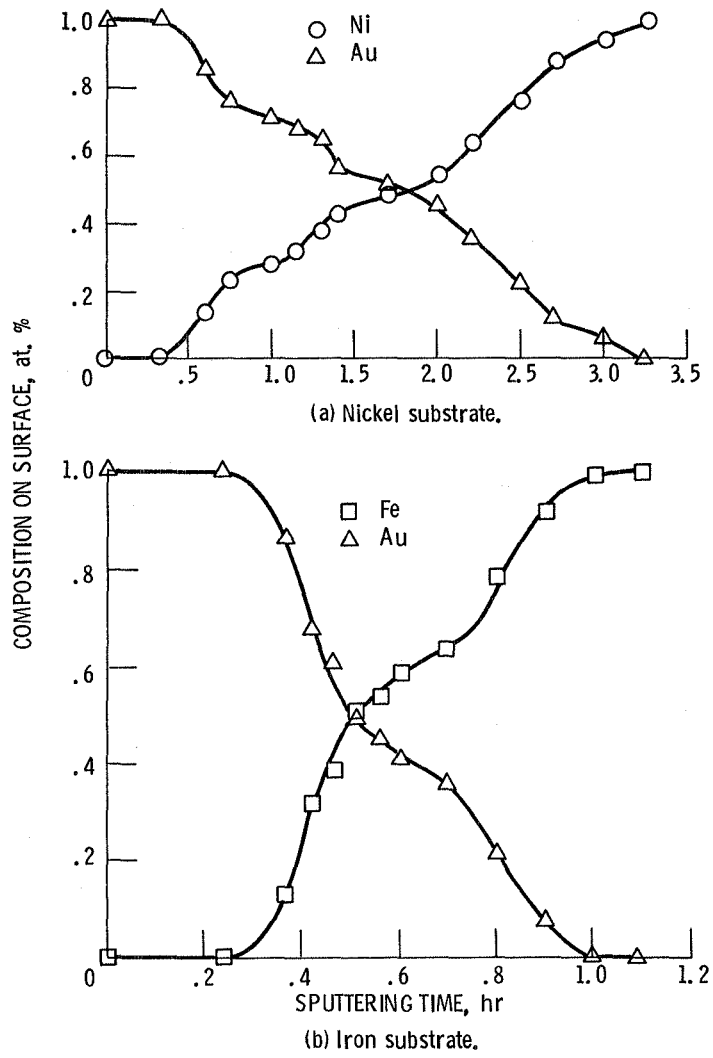


Figure 3. - Elemental depth profiles for gold ion plated on nickel and iron. Film thickness, 0.6 μ m.

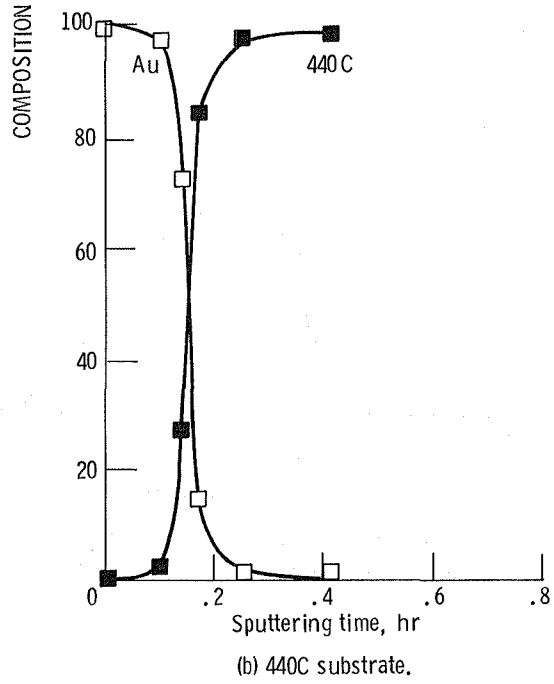
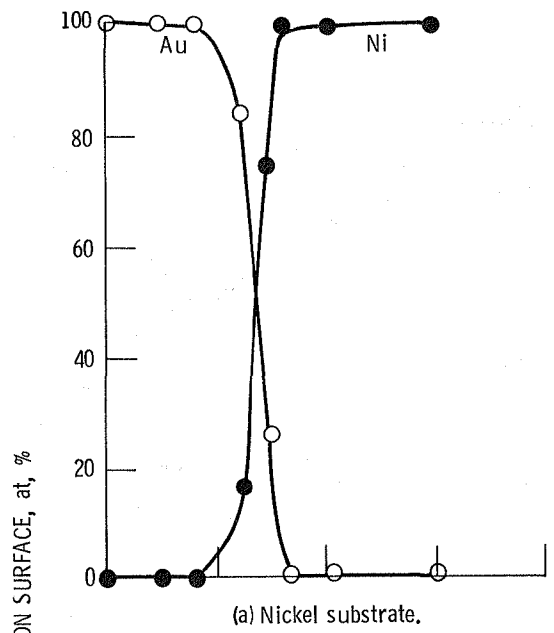
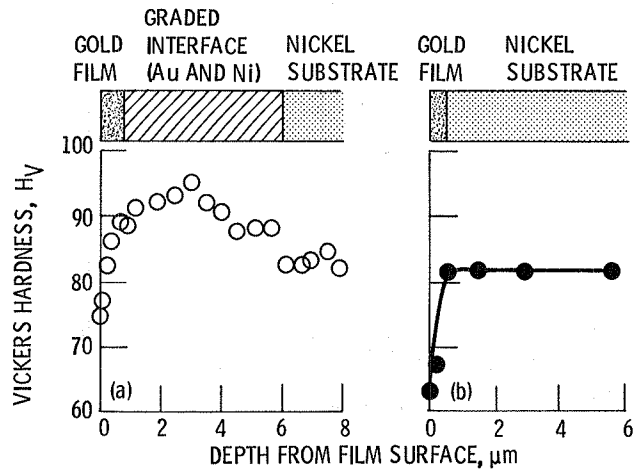


Figure 4. - Element depth profiles for gold vapor deposited on copper, nickel, and 440C stainless steel. Film thickness, 0.3 μm.



(a) Ion-plated gold film.
 (b) Vapor-deposited gold film.

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

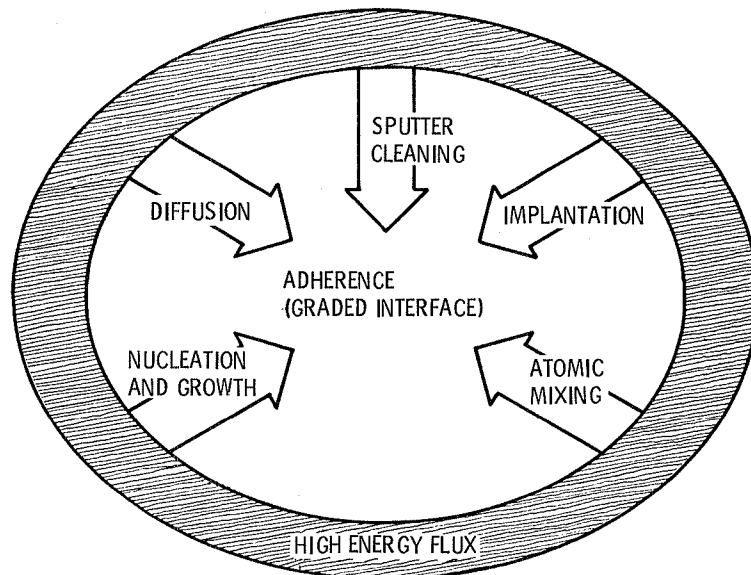
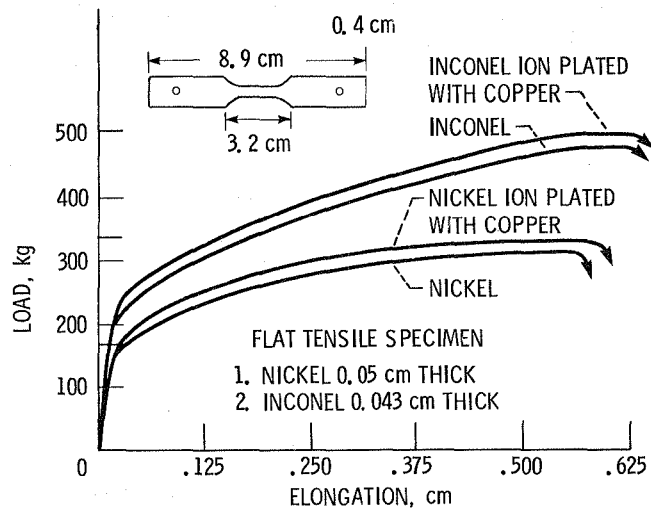
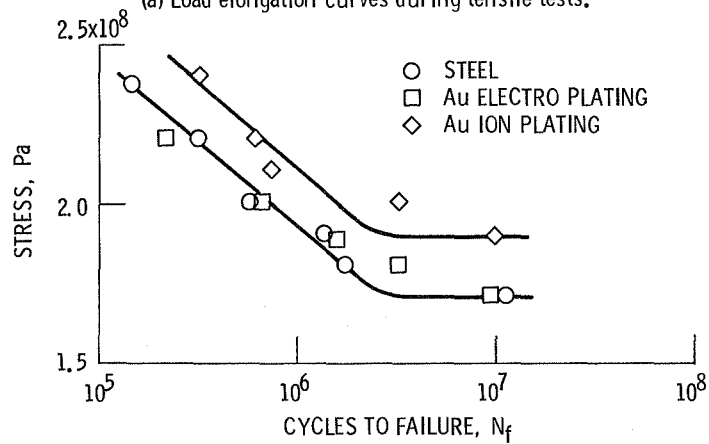


Figure 6. - Illustration of the factors which influence adherence and interface formation during ion plating.



(a) Load elongation curves during tensile tests.



(b) Effect of ion plating on fatigue property of low carbon steel.

Figure 7. - Surface strengthening effects on mechanical properties.

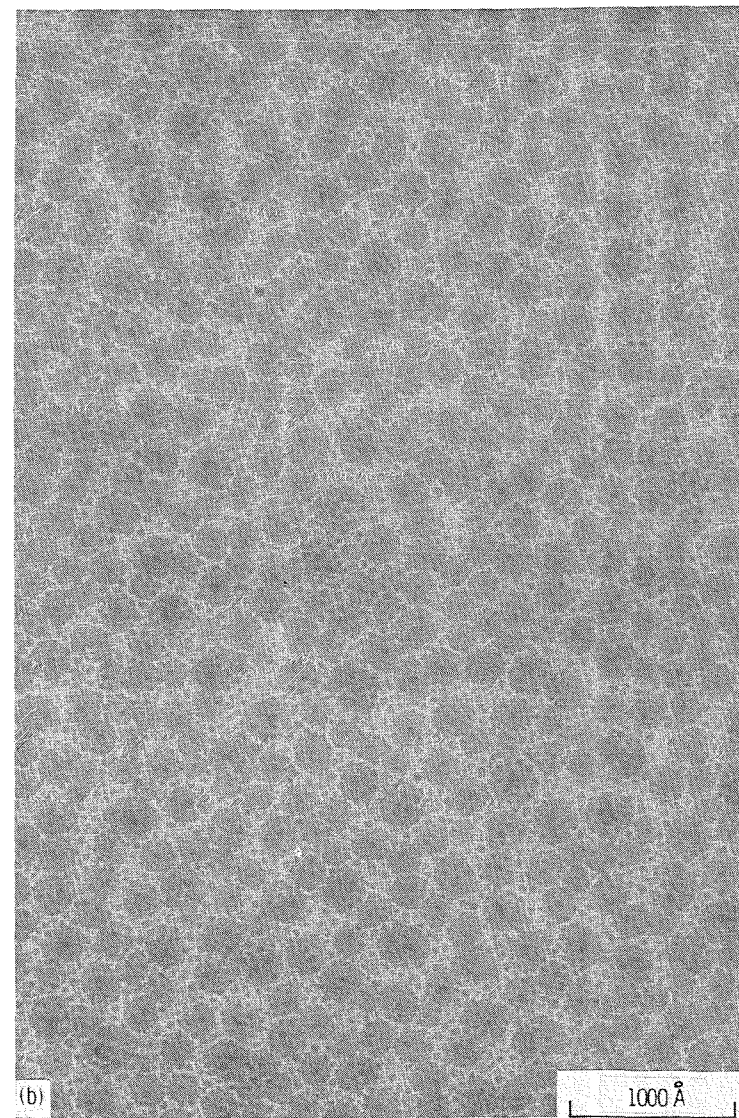
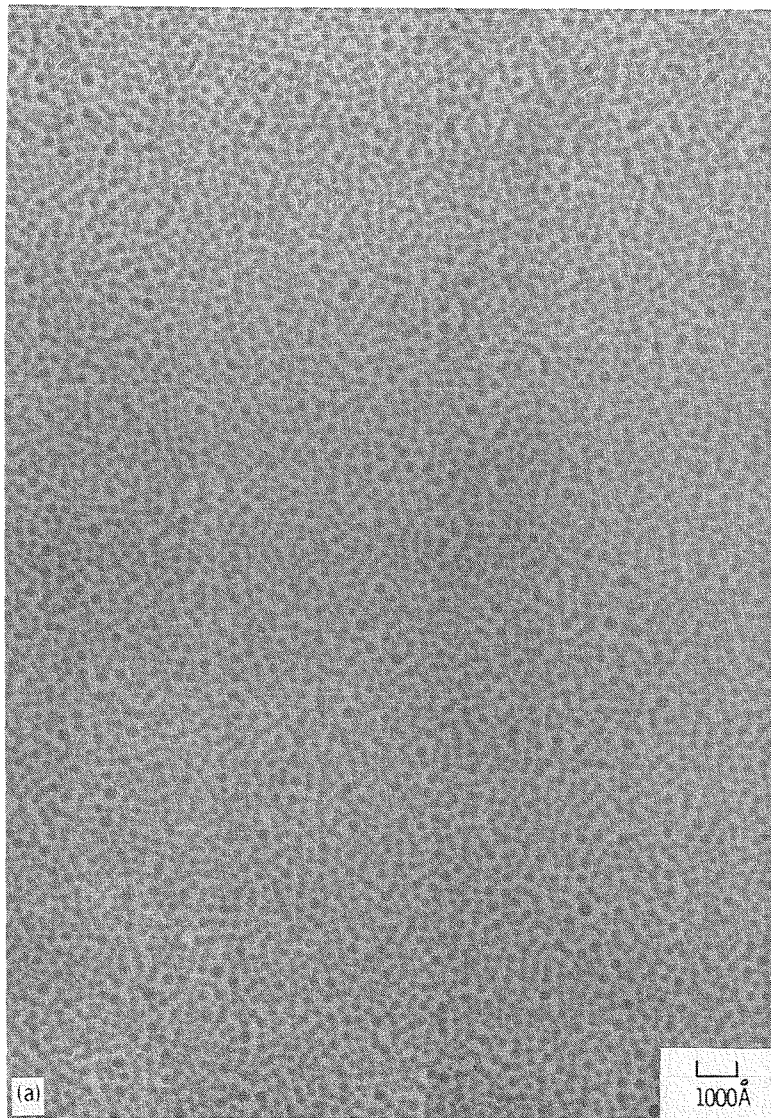
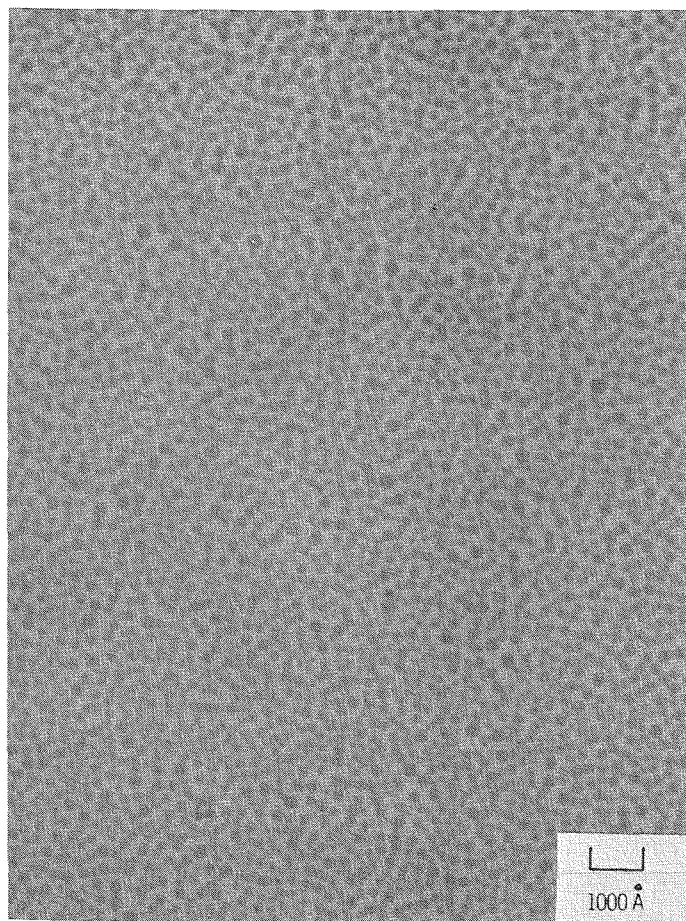
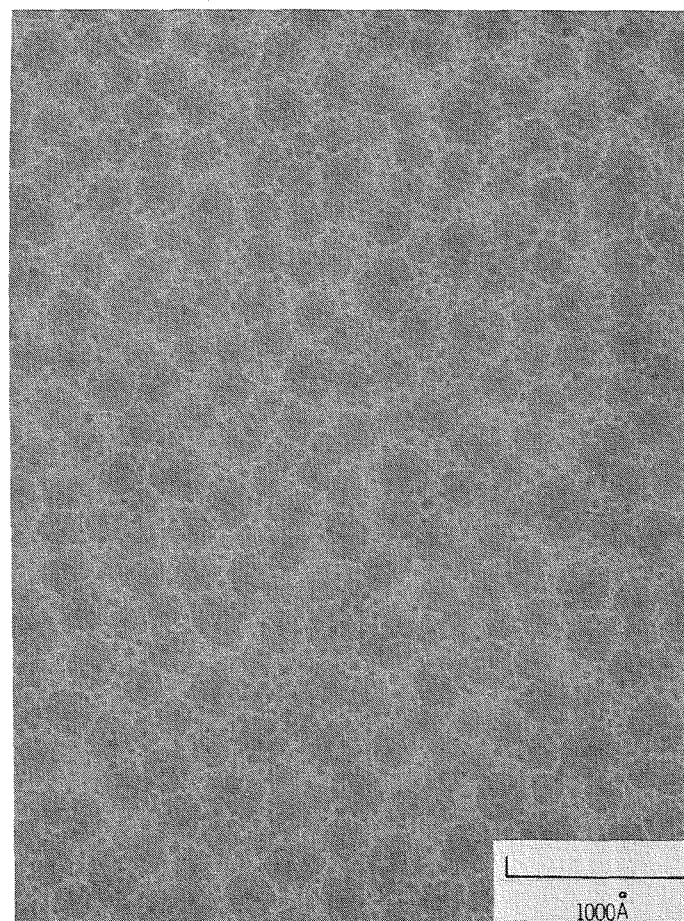


Figure 8. - TEM micrograph of ion plated lead film in the early stages of nucleation.



(a) ION PLATED GOLD.



(b) VAPOR DEPOSITED GOLD.

Figure 9. - TEM micrograph of the crystalline structure of gold film.

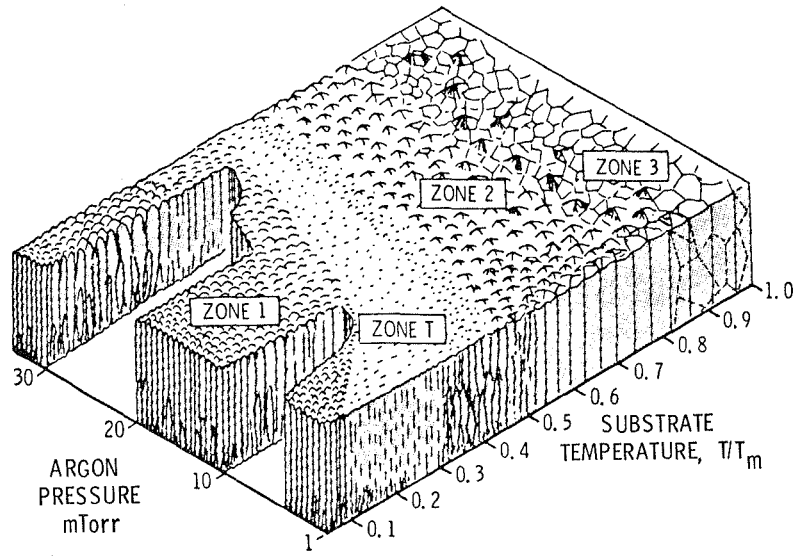


Figure 10. - Structure zone model representation of the influence of substrate temperature and argon working pressure on the structure of metal coatings. T is the substrate temperature and T_m is the melting point of the coating material in absolute degrees (ref. 11).

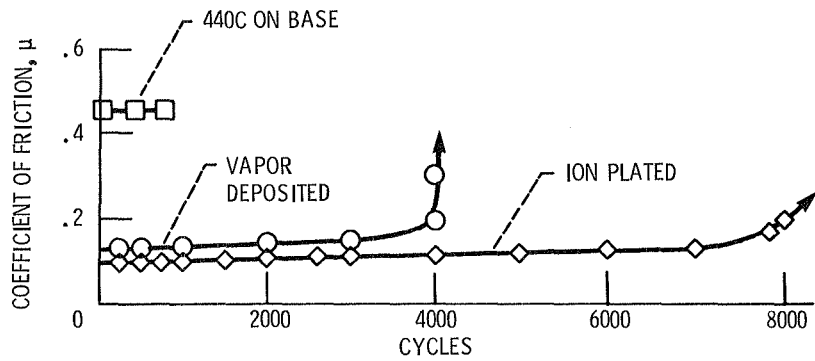


Figure 11. - Comparison of coefficient of friction of ion plated and vapor deposited gold film on 440C steel.

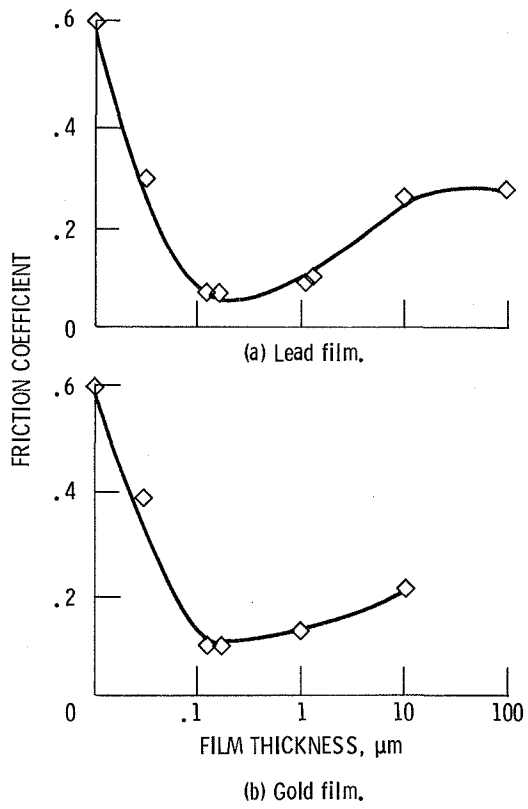


Figure 12. - The variation of friction coefficient with film thickness.

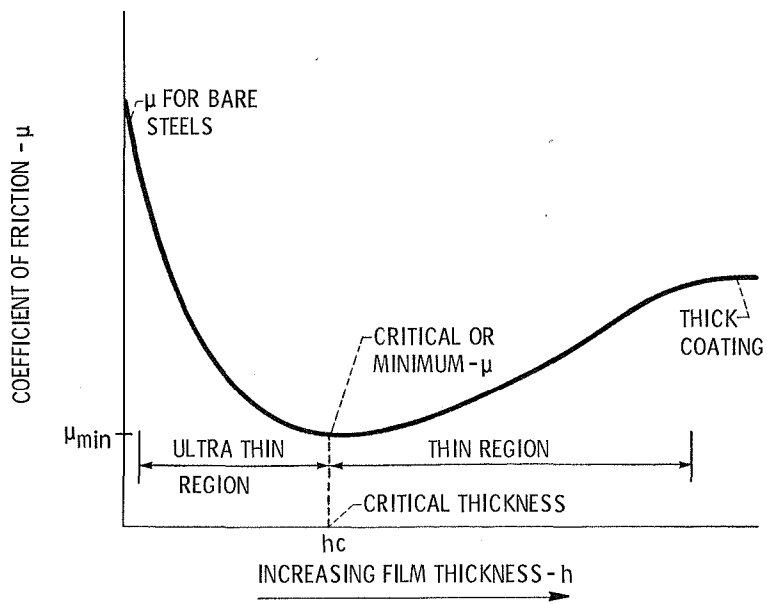


Figure 13. - Schematic representation of the effect of film thickness on the friction coefficient of low shear strength metallic films on steel.

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