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**COATINGS FOR WEAR AND LUBRICATION**

by Talivaldis Spalvins  
Lewis Research Center  
Cleveland, Ohio 44135

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# COATINGS FOR WEAR AND LUBRICATION

by Talivaldis Spalvins

National Aeronautics and Space Administration  
Lewis Research Center  
Cleveland, Ohio 44135

## ABSTRACT

This paper reviews the recent advances in the tribological uses of rf-sputtered and ion plated films of solid film lubricants (laminar solids, soft metals, organic polymers) and wear resistant refractory compounds (carbides, nitrides, silicides). The sputtering and ion plating potentials and the corresponding coatings formed are evaluated relative to the friction coefficient, wear endurance life and mechanical properties. The tribological and mechanical properties for each kind of film are discussed in terms of film adherence, coherence, density, grain size, morphology, internal stresses, thickness and substrate conditions such as temperature, topography, chemistry and dc-biasing. The ion plated metallic films in addition to improved tribological properties also have better mechanical properties such as tensile strength and fatigue life.

# COATINGS FOR WEAR AND LUBRICATION

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Lewis Research Center

## INTRODUCTION

E-9555

In order to prevent tribological failures of interacting mechanical component surfaces in sliding, rotating, rolling, or oscillating motion, friction and wear has to be minimized and proper lubrication maintained. What really happens when two contacting surfaces are in relative motion depends on material characteristics, environmental conditions and the nature of the contact itself. Friction may be described as a result of surface asperity deformation and shearing (adhesive theory),<sup>1,2</sup> whereas wear is a gradual removal of discrete particles from one or both surfaces as a result of mechanical action.<sup>3</sup> When faced with a wear problem, the first step is to decide the type or types of wear involved. Burwell<sup>4</sup> recognizes four principal types of metallic wear: adhesive, abrasive, corrosive, and surface fatigue or pitting wear. The above wear mechanisms may be operative singularly or in combinations in a particular mechanical operation. The final step is to minimize these tribological failures by proper application of lubricating coatings to the contacting surfaces.

It is convenient to divide the lubricating coatings into two main groups based on their chemical, physical, and mechanical properties. First, the hard wear resistant coatings (carbides, nitrides, silicides, etc.) and second, the soft lubricating coatings with low shear strength (graphite,  $\text{MoS}_2$ , Au, PTFE, etc.).



The effectiveness of a wear resistant or lubricating coating, regardless of the specific application, depends primarily on the coating technique selected, since the tribological properties and characteristics are affected primarily by the coating adherence, coherence, and morphology. The degree of adherence is directly related to the surface pretreatment and type of interface formed,<sup>5</sup> but the morphological growth (nucleation and growth) is directly affected by the surface finish, cleanliness and the evaporation flux. These aforementioned factors determine the mode of coating wear and durability.

When discussing the lubricating coatings or treatments, it is possible to divide the coating techniques into two classes. The first class involves the formation of wear resistant films on a substrate without a change in chemical composition (flame hardening, induction hardening, and shot peening) or by high temperature diffusion treatments (carburizing, nitriding, etc.). The second class covers the direct application of coatings (burnishing, spraying, flame spraying, dipping, electroplating, physical and chemical vapor deposition, sputtering, ion plating, ion implantation, etc.). Each of these techniques has its strong and weak points. Since it is impossible to discuss all the surface treatments and coating techniques which have been proposed to combat wear, it was decided to limit the discussion in this paper to the more recent deposition techniques such as physical rf-sputtering and ion plating. These techniques are rapidly gaining more acceptance and use in the field of tribology.

The objective of this paper is to illustrate and evaluate the sputtered and ion plated soft lubricating and hard wear resistant films in terms of friction, wear and film durability. It also evaluates the manner in which such coating characteristics as adherence, coherence, density, thickness, internal stresses, growth morphology, and substrate conditions such as surface temperature, topography, and chemistry affect the coating behavior.

#### SPUTTERING POTENTIALS AND THE TECHNIQUE IN TRIBOLOGY

The growing interest of sputtering in tribology originates from the fact that virtually any coating can be stoichiometrically sputter deposited without a binder, with strong adherence, and with a controlled thickness on curved and complex shaped surfaces such as retainers, races, balls, and gears. In addition, the sputtering technique is not limited by thermodynamic criteria, and it therefore offers a great flexibility to form coatings with graded interface compositions, laminated layers, dispersion strengthening, and other desirable additives. This technique allows one to tailor film properties in ways not available with the other deposition methods. This results from the availability of the many sputtering modes and configurations and the ability to prepare the sputtering targets in any desired chemical ratio by powder metallurgy techniques.

RF or dc diode sputtering systems with rf or dc substrate bias are the most widely used configurations for depositing solid lubricating coatings. A typical rf sputtering system with dc bias is shown in Figure 1. The apparatus has been described in detail in

reference 6. Planar sputtering targets are the most commonly used configurations, with an rf power density of 2 to 5 w/cm<sup>2</sup> for inorganic lubricants and about 2 w/cm<sup>2</sup> for organics such as PTFE at a frequency of 13.56 MHz and argon pressure of  $2 \times 10^{-2}$  torr. The component surfaces are cleaned by sputter etching prior to sputter deposition. Irregular, complex surfaces such as bearings and gears can be coated with the lubricant. Bearing balls can be uniformly sputter coated when placed in a screen pan (insert Fig. 1) and the pan is kept in constant vibration so that the balls are in a continuous motion.

#### CHARACTERISTICS OF SPUTTERED SOLID FILM LUBRICANTS

##### Solid Lubricant Classification

Solid lubricants can be classified as follows:

##### 1. Inorganics:

- (a) Laminar solids: MoS<sub>2</sub>, WS<sub>2</sub>, NbSe<sub>2</sub>, MoSe<sub>2</sub>, BN, graphite
- (b) Nonlaminar solids: PbO, CaF<sub>2</sub>
- (c) Soft metals: Au, Ag, Sn, Pb, In, Cd

##### 2. Organics

- (a) Polymers: PTFE, polyimides
- (b) Fats, soaps, waxes

All the above inorganics and the organic polymers PTFE and polyimide have been sputtered as thin lubricating films. From the above sputtered lubricants MoS<sub>2</sub> films have been investigated in more detail relative to their lubricating and morphological properties than any of the others. Sputtering technology in depositing

solid lubricants, particularly  $\text{MoS}_2$  is however, relatively new. Despite this newness the technique has moved very quickly from the research laboratory into practical industrial use to meet new application requirements.<sup>7-10</sup>

Layered solids such as  $\text{MoS}_2$ ,  $\text{WS}_2$ , etc. must meet two requirements in order to function as a lubricant: (1) intercrystalline slip and (2) adhesion to the substrate. Generally, sputtered  $\text{MoS}_2$  films have strong adherence and this is assisted by the fact that only thin films of the order of 2000 Å in thickness are required for effective lubrication. A low coefficient of friction (0.04) and long endurance lives (over million cycles) have been obtained with such films, as previously reported.<sup>11</sup>

An interrelation exists between sputtered film properties and tribological behavior.  $\text{MoS}_2$  film adherence, morphological growth, chemical composition, thickness, substrate temperature, topography, and chemistry are observed to affect friction, wear, and lubricating endurance lives.

Adherence and surface chemistry. - Thin, sputtered  $\text{MoS}_2$  films about 2000 Å thick, generally exhibit strong adherence not only to bearing metallic surfaces such as 440 C and 52100 steels, but also to ceramics, glass and polymer surfaces. Several exceptions have, however, been observed. These include copper, silver, and bronze surfaces where very poor adherence is noted and the film flakes.<sup>12</sup> When  $\text{MoS}_2$  is sputtered onto a sputter-etched copper surface, typical reaction islands form in the initial stages of film formation and these are shown in Fig. 2. With continued sputtering the isolated

reaction islands tend to combine by enlarging in size and finally a complete lifting of the film occurs as indicated in Fig. 3. Similar effects were also observed with silver and bronze surfaces.

The reaction products, of the sputtered  $\text{MoS}_2$  film which have a dark blue color in comparison to the usual grey  $\text{MoS}_2$  color, were analyzed by energy dispersive X-ray analysis (EDAX). From the foregoing analysis it was concluded that a chemical reaction has occurred between sulfur and the metal (e.g., Cu or Ag) surface. It should be pointed out that the sputtered  $\text{MoS}_2$  species are in a highly energetic state and are very prone to chemical adsorption and reaction. A noticeable increase in crystalline size up to  $200 \text{ \AA}$  of the Cu- $\text{MoS}_2$  reaction products were determined by electron reflection and diffraction.

When the same copper, silver, and bronze surfaces were oxidized and were not sputter cleaned prior to  $\text{MoS}_2$  sputter deposition adherent films were formed. These results indicate that the selection of substrate material is of great importance when sputter-depositing  $\text{MoS}_2$  films.

Substrate temperature. - Variation of the substrate temperature during  $\text{MoS}_2$  sputtering results in changes in the nucleation and growth characteristics as well as in particle size. The substrate temperature effects from  $-195^\circ$  to  $320^\circ \text{ C}$  on sputtered  $\text{MoS}_2$  films  $300$  to  $400 \text{ \AA}$  thick were investigated by transmission micrographs and electron diffractograms.<sup>13</sup> The interrelation between the substrate temperature, film morphology, grain size, and the coefficient of

friction is shown in Fig. 4.

At low temperatures the film was amorphous while at elevated temperatures it was crystalline. When the sputtered MoS<sub>2</sub> film thickness at the low substrate temperature is increased to 2000 Å, and friction tested in vacuum, the coefficient of friction is high (0.4) and the film does not exhibit lubricating properties. These films are relatively brittle.

MoS<sub>2</sub> films sputtered on substrates at ambient temperatures (25° C) and up to 320° C have distinct ridges (black lines) in the matrix. The diffractograms are characterized by sharp diffraction rings and the mean particle size increases up to 100 Å. The transition region from amorphous to crystalline has not been fully established. However, there is a clear trend in the transition region with the coefficient of friction decreasing from 0.4 for the amorphous film to 0.04 for the crystalline film.

Distinct differences in growth morphology of MoS<sub>2</sub> films sputtered at low and at elevated temperatures are also observed. These are observed in cross section by SEM and are shown in Fig. 5. At the elevated temperatures the coating has the typical "feathery" lamellar structure, where at cryogenic temperatures the lamellar structure cannot be identified.

Substrate biasing and film stoichiometry. - The excellent lubricating properties of sputtered MoS<sub>2</sub> films are attributed to their strong adherence. Substrate biasing has a tendency to re-sputter the adsorbed or weakly adhered material, thus promoting film adherence. In the case of the layer solid lubricants,

particularly  $\text{MoS}_2$ , it has been shown that the friction coefficient is very sensitive to the amount of bias applied to the substrate during  $\text{MoS}_2$  sputter-deposition. The friction coefficient of the film increases steeply with a bias over  $-150$  V dc and the lubricating properties of the film are completely lost at  $-350$  V dc as indicated in the data of Fig. 6. This increase in friction is due to the depletion of sulfur in the film.

All  $\text{MoS}_2$  sputter deposition has been therefore performed on sputter-cleaned surfaces at ground potential. Under these conditions the stoichiometry of the film is maintained as analyzed by chemical techniques<sup>11</sup> and by Auger spectroscopy.<sup>14</sup>

Other laminar solids. - Laminar ( $\text{MX}_2$ ) compounds other than  $\text{MoS}_2$  having lubricating properties have not as yet attracted any great interest for deposition by sputtering. However, very limited investigations have been performed with  $\text{WS}_2$  and  $\text{NbSe}_2$  sputtered films. Typical wear tracks of sputtered  $\text{WS}_2$  films are shown in Fig. 7. In vacuum, sputtered  $\text{WS}_2$  films have a low coefficient of friction (0.05) and display endurance lives over million cycles with lubricating properties very similar to sputtered  $\text{MoS}_2$ . When the same film was tested under identical experimental conditions in atmosphere the coefficient of friction immediately increased to 0.22 and film failure occurred after only 1500 cycles. This premature failure of the sputtered  $\text{WS}_2$  film under atmospheric conditions is due to the formation of  $\text{H}_2\text{SO}_4$  which results from the reaction of sulfur and sulfur dioxide in the film with moisture of the atmosphere.

Organic polymers. - PTFE (polytetrafluoroethylene) and the polyimides are the only organic lubricants which have been sputtered as thin films for tribological applications.<sup>16</sup> Sputtered PTFE films display excellent adherence and uniformity and are pin-hole-free not only on metal substrates but also on glass, wood, and paper surfaces.

A yellow color is common to all polymers prepared in glow discharge and is probably due to disorder or cross-linking.<sup>17-19</sup> All sputtered PTFE films also exhibit a yellowish color in appearance. At low rf power input just above the level where the glow discharge is self-sustaining, the sputtered PTFE films are usually clear and transparent with only a slight yellowish tinge. As the power input is increased darkening of the color occurs. At the higher power levels and with increasing sputtering rates the percent composition of carbon increases while that of fluorine decreases.<sup>16</sup>

Electron transmission micrographs and diffractograms of sputtered PTFE films show an amorphous type of structure. Preliminary results with sputtered PTFE films indicate that the coefficient of friction is comparable to that of the original PTFE, which may vary from 0.08 to 0.2.<sup>20</sup> The coefficient of friction for PTFE depends on the load, sliding speed, and film thickness. When the thickness of the sputtered film dominates the frictional behavior, the coefficient of friction decreases markedly with increase in load for any given thickness.<sup>20</sup>

PTFE lubricating films have been found to be useful in practical systems requiring lubrication. Sputtered PTFE films for example, have been applied to surgical needles (cataract operations)



where they have to function as a lubricant to reduce the friction during the insertion and removal.<sup>21</sup>

## CHARACTERISTICS OF SPUTTERED WEAR RESISTANT FILMS

### Tribological Parameters

Sputtering is essentially the only deposition technique which offers a high degree of operational flexibility and does not depend on the melting point and vapor pressure of refractory compounds (carbides, nitrides, silicides, and borides). Films of these compounds can be directly sputtered onto surfaces without the alteration of the desirable properties in the bulk. Only very recently, however, has activity developed in sputter-deposition of the hard wear resistant films of carbides: TiC,<sup>22-24</sup> WC,<sup>25,26</sup> Cr<sub>3</sub>C<sub>2</sub>,<sup>27</sup> silicides: MoSi<sub>2</sub>,<sup>27-29</sup> Cr<sub>3</sub>Si<sub>2</sub>,<sup>27</sup> CrSi<sub>2</sub>,<sup>30</sup> and borides: CrB<sub>2</sub>,<sup>28</sup> TiB<sub>2</sub>,<sup>29</sup> on friction and wear surfaces. These wear resistant films, because of their hardness and brittleness, are highly sensitive to surface conditions and the mode of application. Further, these wear resistant coatings must be able to absorb a large amount of energy during friction and wear without fracturing.

The refractory compound coatings are intrinsically very strong, but in practice this strength is not achieved because of the inevitable presence of residual or internal stresses or surface defects at which stress concentrations arise when external stress is applied. In order to increase the mechanical strength and toughness of the coating to resist premature fracture from the high stresses generated during friction and wear, special cermet sputtering targets

such as WC-Co have been prepared. When these cermet films are sputter-deposited and subjected to loads, any crack formed within a hard particle is arrested when it meets the surrounding soft cobalt matrix which prevents further crack extension since it deforms easily and thereby relaxes the local stresses. In addition to the structural effects, compositional effects also control the properties of the film. Since the refractory compound sputtering targets without metallic binders are generally prepared by hot pressing, they may be quite porous and during sputter-deposition produce appreciable outgassing with the result that the films may be contaminated or partially or completely oxidized.

The factors affecting film adherence and coherence which should be recognized and carefully controlled, are: target preparation, type of interface formed, residual or internal stresses, film thickness, internal and surface defects. All these factors contribute to premature failure of the film, and the coating may not wear by normal, relatively slow attrition but rather by a more accelerated wear mechanism such as spallation or delamination. The wear debris formed under these accelerated wear conditions could act in an abrasive manner, thereby accelerating the wear process.

Target preparation. - The carbide, nitride, silicide, and boride sputtering targets are generally prepared by hot pressing and are usually quite porous ranging from less than 60% to about 95% of theoretical density.<sup>31</sup> Some of the targets such as  $\text{Si}_3\text{N}_4$  are very difficult to prepare in high density form without using binders, and they

average particle size between 15 and 45 Å.<sup>24</sup> The particle size is such that the film is of an amorphous nature. This extremely small particle size is important in the compactability and high density of the film as well as its strength. Film strength is related to the final grain size: the smaller the grain size, the tougher and stronger the film.

Film thickness and stresses. - Coatings that are sputter-deposited on surfaces are usually in a state of mechanical stress, and this effect becomes even more pronounced with hard wear resistant surface coatings (such as carbides and silicides). Internal stresses are present to various degrees in all films deposited, and they can be as large as  $10^8$  to  $10^{10}$  dynes/cm<sup>2</sup> and often larger than the yield strength of the bulk material. Film stresses vary also with film thickness and it has been observed that thicker films produce greater shear stresses at the interface.<sup>32</sup> Whenever the shear stress is greater than the yield stress of the interface region, the film separates from the surface. By using this particular condition wherein the shear stress exceeds the yield stress as the critical value for determining the thickness of the film, the optimum thickness can be predetermined. Using films of less than the optimum thickness will prevent separation of the film from the substrate.

Sputtered  $\text{Cr}_3\text{Si}_2$ ,  $\text{MoSi}_2$ ,  $\text{TiC}$ , and  $\text{Cr}_3\text{C}_2$  films adhere strongly to both metal and glass substrates. Because of this strong adherence, film separation occurs within the coating as it increases in thickness. Figure 8 shows this effect where film delamination occurs in a sputtered  $\text{Cr}_3\text{C}_2$  film about 3.5  $\mu\text{m}$  thick.

The critical thickness effect for sputtered TiC was determined during sliding friction experiments (pin-on-disk) at different loads by Green and Cook<sup>23</sup> and their results are presented in Fig. 9. For films less than a critical thickness, the coefficient of friction was dependent on the applied normal load and was in the range of from 0.2 to 0.3. For coatings thicker than the critical value, the coefficient of friction was between 0.6 and 0.8.

Surface topography. - It is practically impossible to prepare surfaces which are atomically smooth over an appreciable area and therefore surface microdefects and imperfections cannot be completely eliminated, thus imposing limitations for obtaining the most controlled surface. As a result, defect-induced nucleation and growth is of great concern in wear resistant coatings. Unusual crystallographic growth defects are observed by SEM.<sup>33</sup> Nodular, crater type and runaway localized growth features are the most commonly observed as shown in Figs. 10(a) to (c). All these defects act as stress raisers by initiating cracks in the coating or producing cavities. For very thin films the nodules are very small and their effects are not seriously detrimental. In thick coatings, however, these effects multiply as the size of the nodule increases. The concentration of this defect formation during sputtering can be reduced by improving the surface finish.

Duplex films. - A series of angular contact stainless steel bearings (races and cages) were sputter coated with a 1000 Å thick MoS<sub>2</sub> film. These two sets of bearings were tested for film endur-

ance at speed of 1750 rpm, thrust load of 137.9 newtons in high vacuum.<sup>34</sup> Figure 11 presents a comparison of the endurance lives of the duplex films and the MoS<sub>2</sub> films. The endurance life with the Cr<sub>3</sub>Si<sub>2</sub> underlayer was over 1000 hours, compared to 187 hours for the directly sputtered MoS<sub>2</sub> films. The increased endurance life is probably due to the Cr<sub>3</sub>C<sub>2</sub> film acting as a barrier to the movement of dislocations during asperity deformation, thus having a tendency to hinder direct metal-to-metal contact which otherwise could occur and lead to metallic seizure.

WC-Co cermets. - To improve coating adherence and toughness, and reduce the internal stresses in the film WC-Co, cermet targets with Co content between 4 and 25% have been prepared. Structural and compositional characteristics of sputtered WC + 6% Co films and their frictional properties have been reported.<sup>25,26</sup>

#### ION PLATING AND ITS POTENTIALS IN TRIBOLOGY

Ion plating is the only plasma deposition technique where a direct potential (3 to 5 kV) is applied directly across the specimen to be coated and the evaporation source. The specimen to be coated is made the cathode of the high voltage dc circuit and the evaporation source is made the anode. A conventional ion plating apparatus is shown in Fig. 12, and the details of ion plating are reported in the literature.<sup>35-38</sup> This technique differs from the other vacuum deposition processes in that the plating material is partially ionized and it strikes the specimen as charged or excited atoms rather than as neutral atoms.

The ion plating process has two outstanding characteristics associated with it; (1) flux of high energy ions and neutrals and (2) high throwing power. These two features of the process make this technique far superior to any other deposition technique in terms of adherence and ability to coat uniformly complex irregular surfaces, inside cavities and around corners.

The excellent adherence of ion plated films is due to a formation of a graded-fused interface, where a gradual transition between the film and the substrate is formed, thereby reducing the damaging residual stress gradients. This type of interface provides not only a superior adherence but it also contributes to improved mechanical properties. Because of these two unique features ion plating has great potentials in plating soft metallic films as has been reported.<sup>39-42</sup> Au, Ag, Pb, In, Sn, and Cd have been ion plated as thin lubricating films. Other tribological type materials (compounds), because of their chemical nature, cannot be readily ion plated, because in ion plating the material is thermally evaporated. In sputtering it is removed from the target by impact evaporation. With high melting point materials, alloys, compounds, etc. deposition by dc or rf bias sputtering is therefore preferred.

In addition to the soft film deposition other metals such as Al have been ion plated on Ti-surfaces. Such films produce hard wear resistant surfaces.<sup>38</sup>

#### CHARACTERISTICS OF ION PLATED METALLIC FILMS

Adherence. - All the soft metallic films, Au, Ag, Pb, In, Sn, and Cd when deposited by ion plating on metallic surfaces even where

the film and substrate materials are mutually incompatible produced dense, pin-hole-free, uniform films with a graded-fused interface. The exact reaction mechanisms for the formation of the strong adherence are not fully understood, but the controlling factors are sputter-etching of the substrate, and the high energy flux of the evaporant striking the surface which enhances diffusion and chemical reaction. All these mechanisms improve the physical, mechanical, and tribological properties of the lubricating film.

Tribological properties. - All the soft metallic films when ion plated on hard steel surfaces and evaluated in a pin-on-disk apparatus, display a lower friction coefficient less wear and longer endurance lives than do films applied by other vacuum deposition techniques and electroplating. Typical friction results are shown in Fig. 13 where friction experiments were conducted on 2000 Å thick ion plated gold and vapor deposited gold on Ni-Cr alloy surfaces in ultra high vacuum. The ion plated gold film had a lower coefficient of friction (0.18) and this low friction continued for almost twice the sliding distance observed for the vacuum evaporated films.

When the nature of the slopes of the two curves is compared after the film has been worn through, the friction coefficient for the ion plated film rises gradually as compared to the abrupt rise for the vacuum deposited film. Reasons for the gradual increase in friction coefficient are explained in terms of the graded interface. The lower friction coefficient is believed to be caused by surface hardening created by the alloying effects in the interface. Similar

results where ion plated gold films have longer endurance lives and lower friction coefficients than do sputtered and vacuum evaporated films on steel surfaces have been reported in the literature.<sup>43</sup> In addition ion plated In, Pb, and Ag films on steel surfaces are far superior to vacuum deposited films.<sup>42</sup>

Mechanical properties. - The impact which the graded interface exerts on the mechanical properties has been evaluated by tensile and fatigue tests. Nickel and Inconel tensile specimens were ion plated with 1500 Å thick copper and gold films. Typical load elongation curves for the specimens with and without a copper film are shown in Fig. 14. The ion plated specimens show an increase in yield and tensile strength from 5 to 8%. Similar results have been reported<sup>43</sup> where 316 stainless steel and tungsten wires were ion plated with Cu and Ti. The ion plated wires showed higher tensile strength than the bulk wire. The higher strength properties are explained in terms of the interfacial and surface effects which inhibit the motion of the slip planes during sliding. After fracture the ends of the broken specimens were analyzed by EDAX, and a typical X-ray dispersion micromap is presented in Fig. 15. The figure indicates a continuous distribution of the gold film at the point of fracture without any loss of the film, reflecting that during plastic flow the film flows with the bulk as an integral part thereof.

Fatigue life can also be extended by ion plating as shown in Fig. 16. Nickel and Inconel fatigue specimens plated with a 1500 Å thick gold and copper film had 23 to 27% increase in fatigue life,



respectively. Practically all fatigue failures start at the surface, therefore the increase in the fatigue life is attributed to solid solution strengthening and surface residual stresses induced during ion plating. Similar results have been reported<sup>43</sup> wherein steel fatigue specimens were ion plated and electroplated with gold, and then fatigue tested. The results obtained are presented in Fig. 17. The ion plated film increased the fatigue limit, while the electroplated film had no noticeable effects.

#### CONCLUDING REMARKS

To prevent tribological breakdown and mechanical failures the selection and the mode of application of the proper lubricant or wear resistant film is of paramount importance. Sputtering and ion plating offer great flexibility in the technique with respect to surface pretreatment and the unlimited potential to deposit any tribological material with the additional beneficial feature of being able to impose strict controls. The real impact of these techniques in applying tribological materials is yet unknown, however they offer two highly promising alternatives to existing coating technology.

#### REFERENCES

1. F. P. Bowden and D. Tabor, Friction and Lubrication of Solids, Clarendon Press, Oxford, vol. I, 1950, vol. II, 1964.
2. D. H. Buckley, Friction, Wear and Lubrication in Vacuum, NASA SP-277, 1971.
3. E. Rabinowicz, Friction and Wear of Materials, Wiley and Sons, Inc., New York, 1965.

4. J. T. Burwell, *Wear*, I (1957-1958) 119.
5. T. Spalvins and D. H. Buckley, Importance in Lubrication of Various Interface Types Formed During Vacuum Deposition of Thin Metallic Films, *Trans. Vac. Met. Conf.*, 9th., American Vacuum Society, 1967, 247, also NASA TM X-52305.
6. T. Spalvins, Lubrication with Sputtered MoS<sub>2</sub> Films, *Proceedings of the First International Conference on Solid Lubrication*, ASLE, 1971, pp. 360-370.
7. M. N. Gardos, *Lubr. Eng.*, 32 (1976) 463.
8. R. K. Christy and G. C. Barnett, Sputtered MoS<sub>2</sub> Lubrication System for Spacecraft Gimbal Bearings, Presented at ASLE Annual Meeting, Montreal, Quebec, May 1977.
9. B. C. Stupp, Sputtering and Ion Plating as Industrial Process, Presented at the SAE Automobile Eng. Meeting, Detroit, Michigan, May 1973, Preprint No. 730547, SAE.
10. C. E. Vest, *Lubr. Eng.* 34 (1978) 31.
11. T. Spalvins, *ASLE Trans.*, 14 (1971) 267.
12. T. Spalvins, Influence of Various-Surface Pretreatments on Adherence of Sputtered MoS<sub>2</sub> to Silver, Gold, Copper and Bronze, NASA TN D-7169, 1973.
13. T. Spalvins, *ASLE Trans.*, 17 (1974) 1.
14. D. H. Buckley, Examination of MoS<sub>2</sub> with Leed and Auger Emission Spectroscopy, NASA TN D-7010, 1970.
15. T. Spalvins, Friction Characteristics of Sputtered Solid Film Lubricants, NASA TM X-52819, 1970.
16. T. Spalvins, Friction Characteristics and Lubrication with Sputtered Solid Films, *Proceedings of Second German Sputtering School*, Munich, Germany, Sponsored by Materials Research Corp., Orangeburg, New York, May 1971.
17. S. M. Lee, *Insulation/Circuits*, 17 (1971) 33.
18. D. P. Morrison, *Thin Solid Films*, 15 (1973) 87.
19. T. Robertson and D. P. Morrison, *Thin Solid Films*, 27 (1975) 19.
20. R. Harrop, *Thin Solid Films*, 3 (1969) 109.
21. T. Spalvins, Engineering Design; Mechanical Failures Protection Group 25th Meeting, NBS Special Publication 487, T.R. Shives and W. A. Willard, eds., National Bureau Standards, Aug. 1977, pp. 324-337.

22. L. C. Mukherjee, J. E. Wu, J. E. Greene, and M. E. Cook, J. Vac. Sci. Technol., 12 (1975) 850.
23. L. C. Wu, J. L. Zilko, J. L. Mukherjee, J. E. Greene, and J. E. Cook, Tribology, Chemistry and Structure of Bias Sputtered TiC Films on Steel Substrates, Wear of Materials, W. A. Glaeser, et al., eds., ASME, New York, 1977, pp. 364-371.
24. W. W. Carson, J. Vac. Sci. Technol., 12 (1975) 845.
25. K. A. Taylor, Structural and Compositional Characterization of Sputter Deposited WC + Co Films. Presented at 24 Symposium of the American Vacuum Society, Boston, MA, Nov. 1977.
26. K. A. Taylor, Friction and Wear Results from WC + Co Coatings by (-) Biased RF Sputtering in Helium Atmosphere, Ibid.
27. T. Spalvins, Microstructural and Wear Properties of Sputtered Carbides and Silicides, Wear of Materials, W. A. Glaeser, et al., eds., ASME, New York, 1977, pp. 358-363.
28. D. R. Wheeler and W. A. Brainard, X-Ray Photoelectron Spectroscopy Study of Radiofrequency Sputtered Chromium Boride, Molybdenum Disilicide and Molybdenum Disulphide Coatings and Their Friction Properties, NASA TN D-8482, 1977.
29. W. A. Brainard and D. R. Wheeler, X-Ray Photoelectron Spectroscopy Study of Radiofrequency - Sputtered Titanium Carbide, Molybdenum Carbide, All Titanium Boride Coatings and Their Friction Properties, NASA Tech. Paper 1033, 1977.
30. K. Gentner, Potential of Sputtered Films as Protective Coatings T-58 Engines, Report No. NADC-75038-30, Naval Air Development Center, May 1975.
31. J. L. Vossen, J. Vac. Sci. Technol., 8 (1971) 751.
32. D. G. Williams, The Adhesion of Vacuum Deposited Films, RFP-1690, Dow Chemical Co., Golden, Colo., July 1972.
33. T. Spalvins and W. A. Brainard, J. Vac. Sci. Technol., 11 (1974) 1186.
34. T. Spalvins, Bearing Endurance Tests in Vacuum for Sputtered MoS<sub>2</sub> Films, NASA TM X-3193, 1975.

35. D. M. Mattox, Sputter Deposition and Ion Plating, SLA-73-619, Sandia Lab., Albuquerque, N. Mex., 1973.
36. D. M. Mattox, Engineering Design; Mechanical Failures Protection Group 25th Meeting, NBS Special Publication 487, T. R. Shives and W. A. Willard, eds., National Bureau Standards, Aug. 1977, pp. 311-323, also SAND-76-5459 and CONF-761147-1.
37. T. Spalvins, Metals Finishing, 12 (1974) 38.
38. D. G. Teer, Tribology, 8 (1975) 247.
39. N. Ohmae, T. Nakai, and T. Tsukizoe, Ion Plated Thin Films for Anti-Wear Application, Wear of Materials, W. A. Glaeser, et al., eds., ASME, New York, 1977, pp. 350-357.
40. D. G. Teer, B. L. Delcea, and A. J. Kirkham, J. Adhes., 8 (1976) 171.
41. T. Spalvins, Lubr. Eng. 27 (1971) 40.
42. M. A. Sherbiney and J. Halling, Wear, 45 (1977) 211.
43. N. Ohmae, J. Vac. Sci. Technol., 13 (1976) 82.

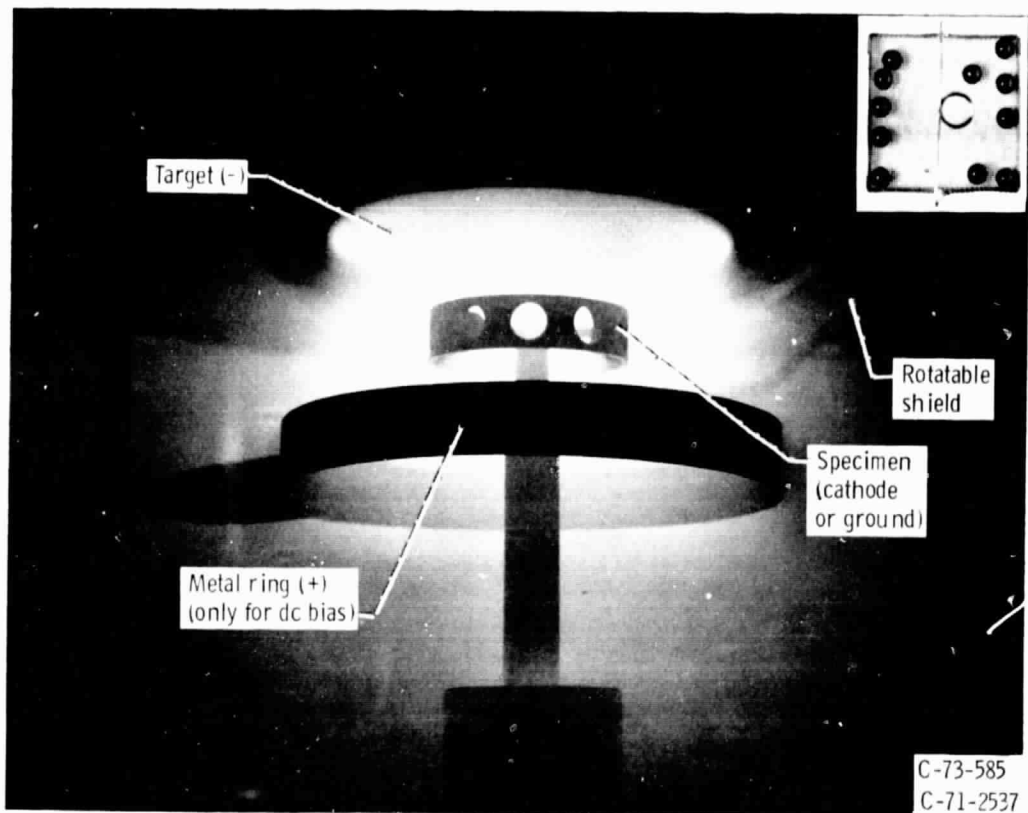


Figure 1. - Radiofrequency diode sputtering apparatus with direct-current bias.

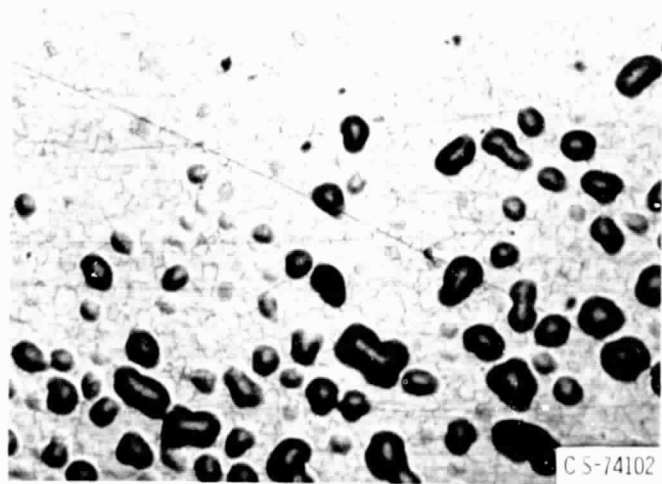


Figure 2. - Sputtered molybdenum disulfide on polycrystalline copper in the initial state of film formation, X80.

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Figure 3. - Sputtered molybdenum disulfide on polycrystalline copper in the final state of film formation, with blistering. X40.

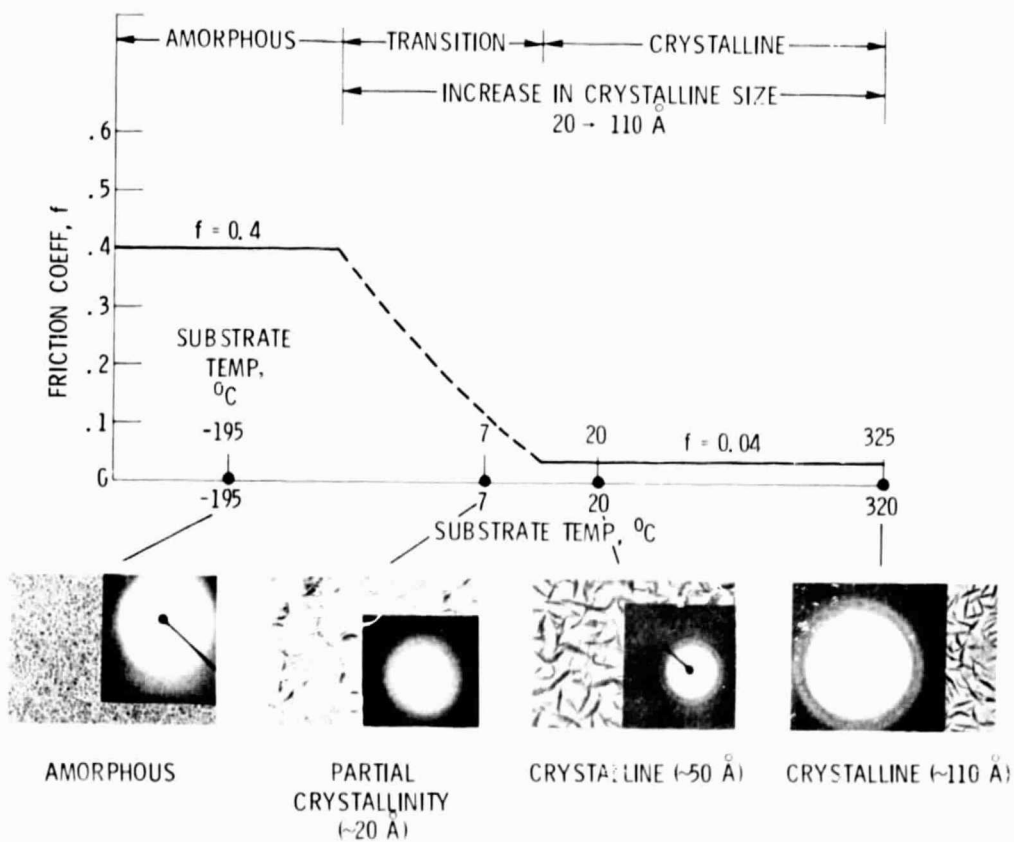
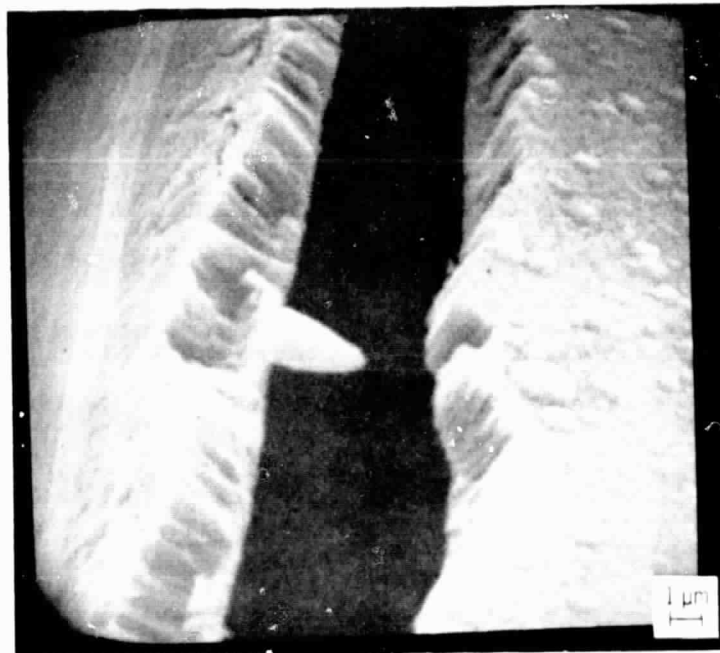


Figure 4. - Substrate temperature effects on MoS<sub>2</sub> film morphology and friction coefficient.

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(a) AT AMBIENT TEMPERATURE.



(b) AT CRYOGENIC TEMPERATURE (-195°C).

Figure 5. - Surface and cross sectional structure of sputtered MoS<sub>2</sub> on steel.

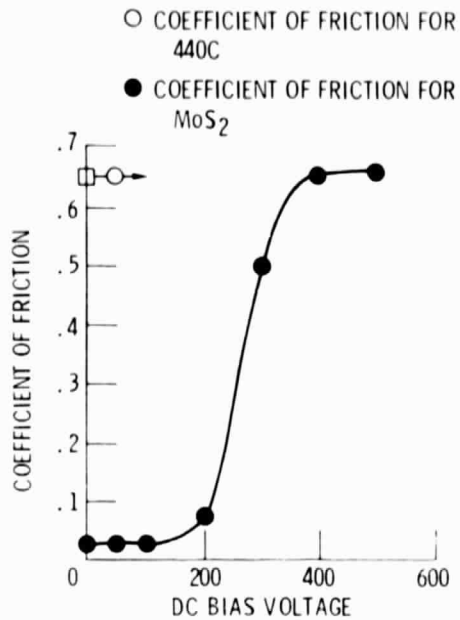
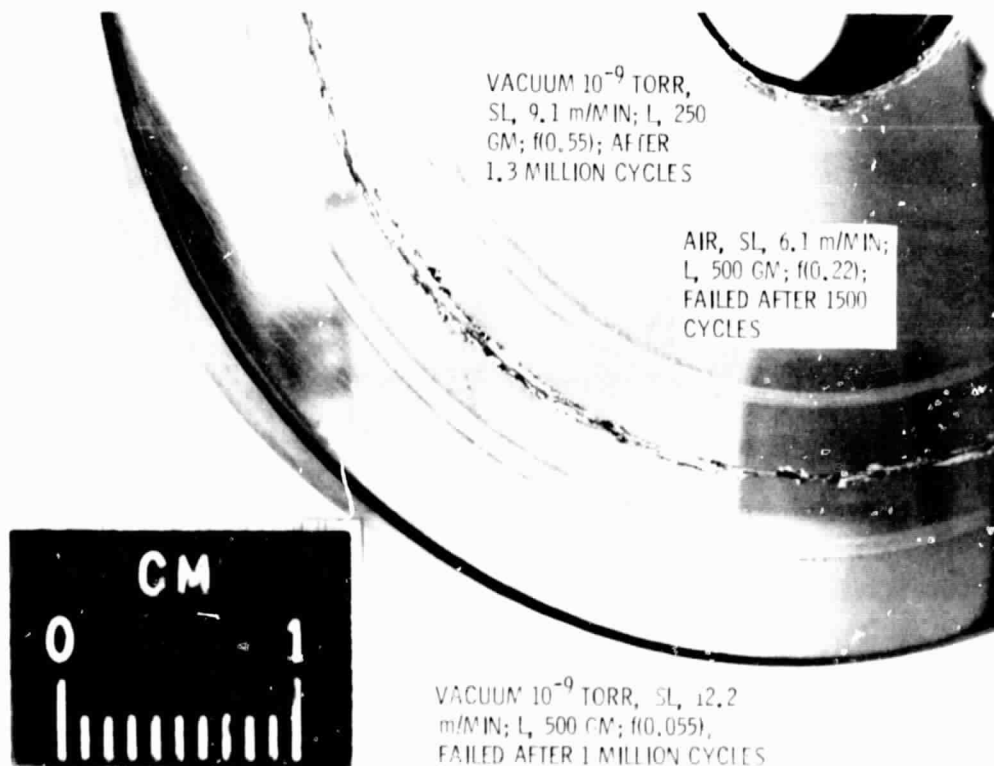


Figure 6. - Effect of negative DC bias on coefficient of sliding friction for sputtered MoS<sub>2</sub>. Load, 250 grams; speed, 40 rpm; substrate/rider, 440C/440C at  $1 \times 10^{-3}$  torr.

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Figure 7. - Wear tracks on a (Ni-Cr) disk with sputtered WS<sub>2</sub> film (~2500 Å) after sliding against a 4.75 mm hemispherical nickel rider (SL, sliding velocity; L, load).



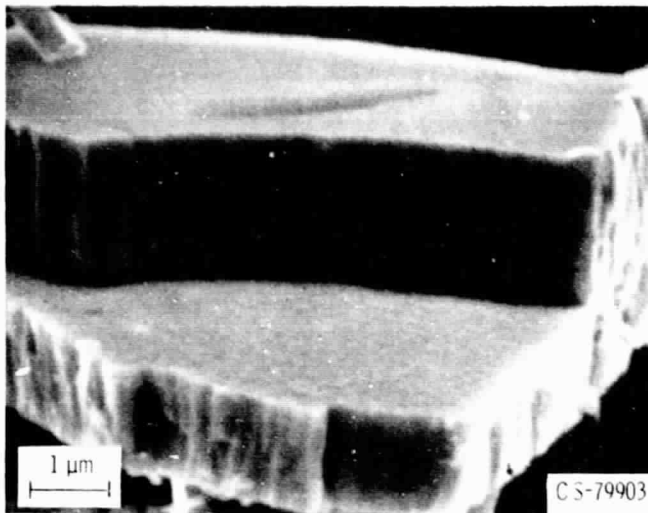


Figure 8. - Separation within a 3.5  $\mu\text{m}$  film of sputtered  $\text{Cr}_3\text{C}_2$ .

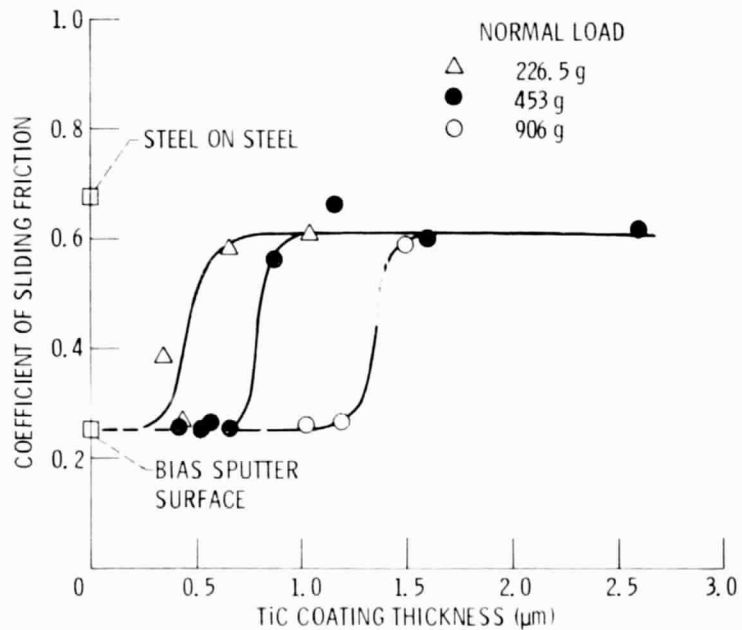
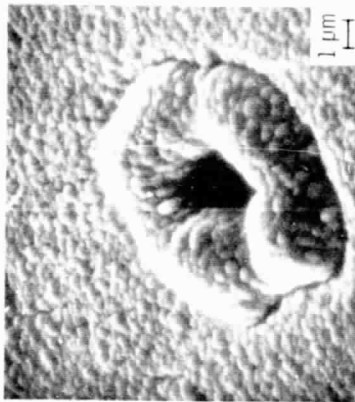


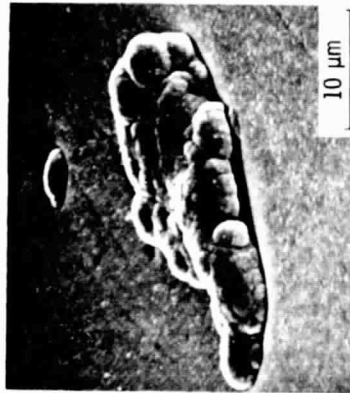
Figure 9. - Coefficient of sliding friction after 20 cycles for steel rider on sputtered TiC film as a function of film thickness (sliding speed was 1.5 cm/s)(Green and Cook - ref. 23).



(a) OVERLAPPING NODULE.



(b) CRATER TYPE DEFECT.



(c) EXTREME LOCALIZED OUTGROWTH.

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Figure 10. - Fracture cross section and surface view of sputtered MoSi<sub>2</sub>, WC and Cr<sub>3</sub>C<sub>2</sub> film.

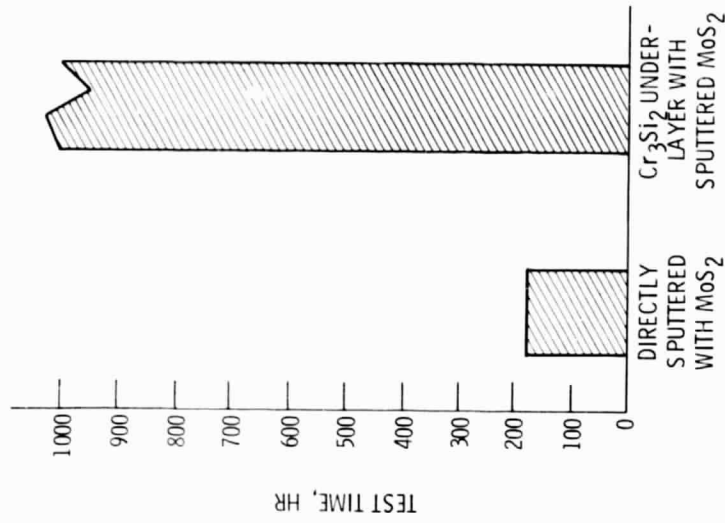


Figure 11. - Endurance lives of 44GC stainless-steel ball bearings with sputtered MoS<sub>2</sub> films on races and cage - with and without a Cr<sub>3</sub>Si<sub>2</sub> underlayer.



Figure 12. - Ion plating chamber.

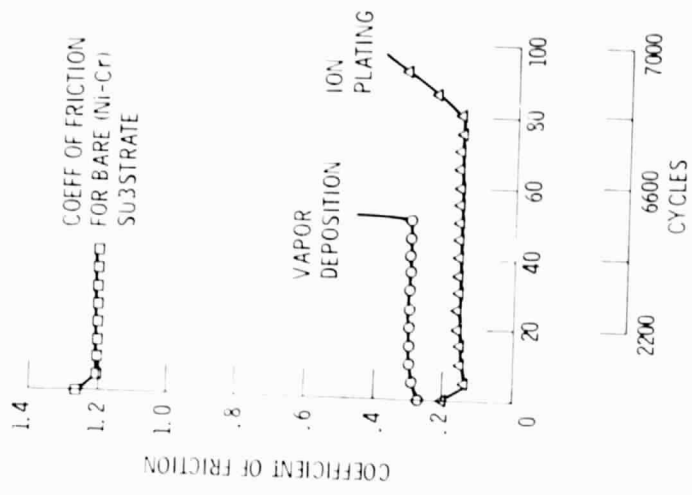


Figure 13. - Coefficient of friction of niobium sliding on (Ni-Cr) alloy with gold deposited by vapor deposition, and ion plating about 2000 Å thick (load, 250 g; speed, 1.52 m/min; ambient temp.  $10^{-11}$  torr).

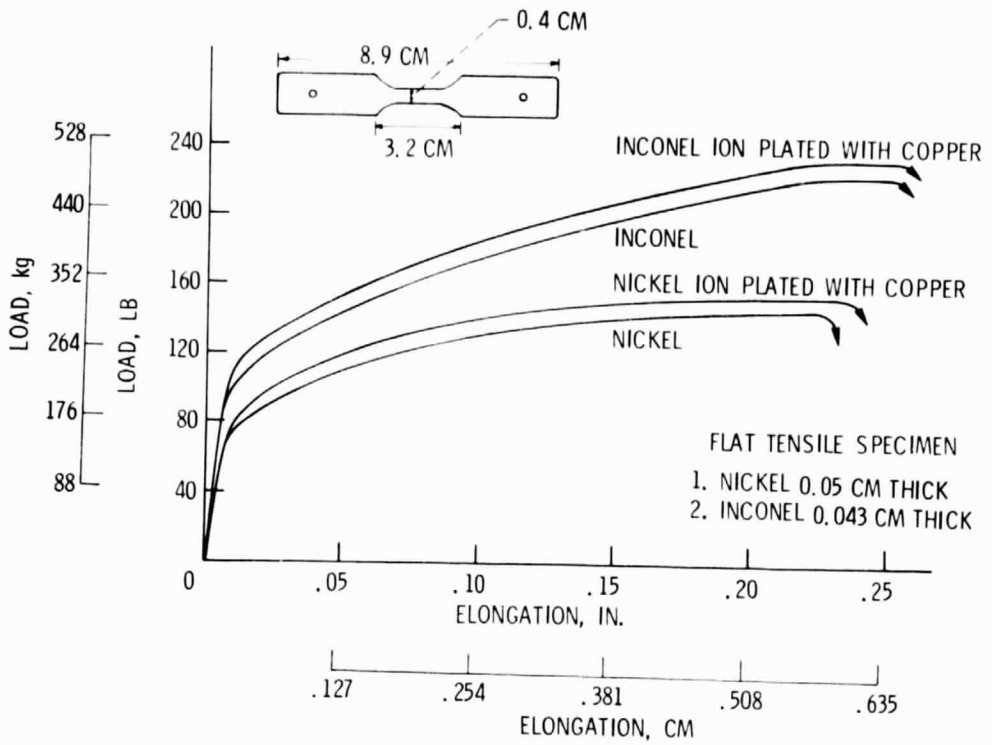


Figure 14. - Load elongation curves during tensile tests.

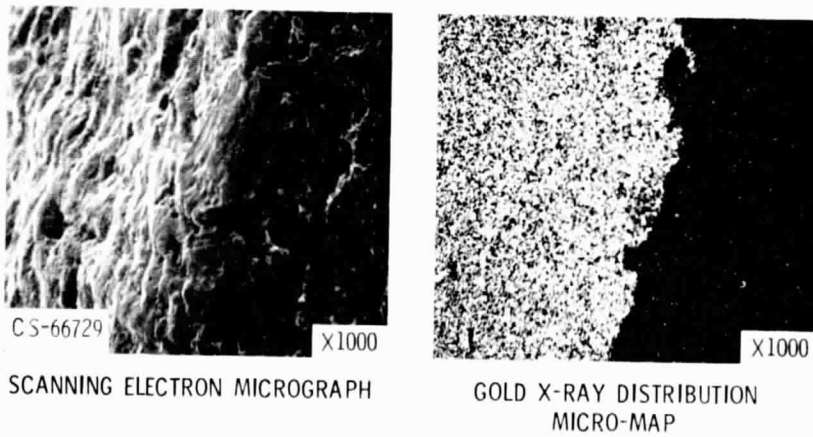


Figure 15. - Ion plated gold on nickel at fracture surface.

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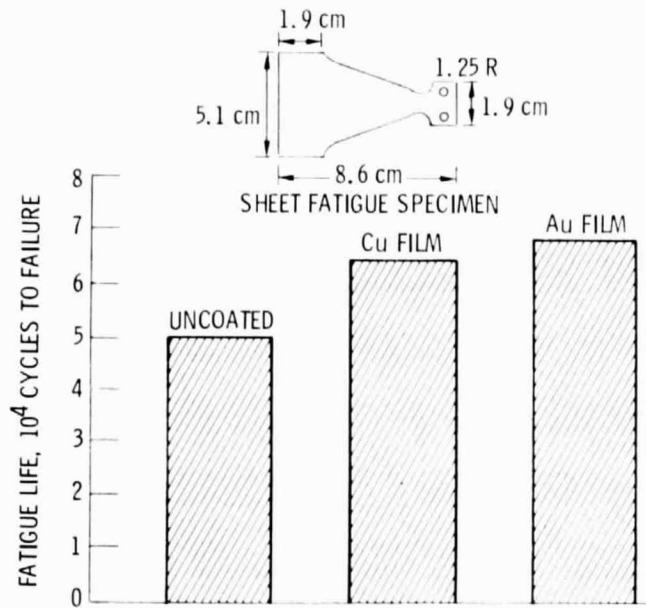


Figure 16. - Effect of copper and gold ion plated films (1500 Å) on the fatigue life of nickel.

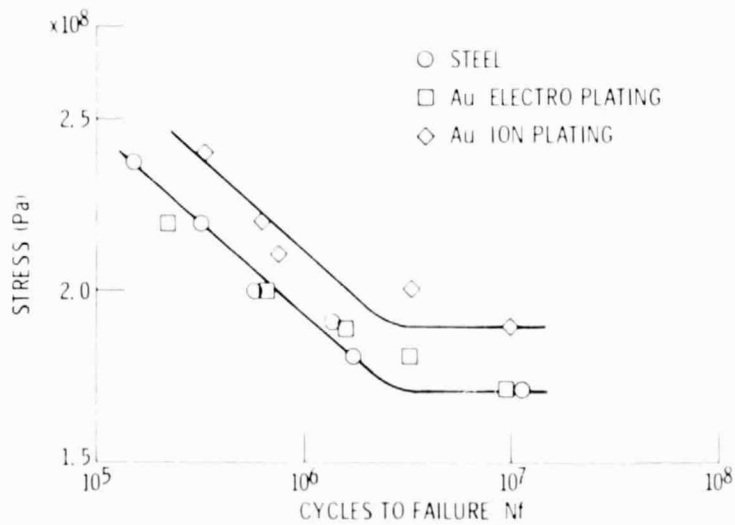


Figure 17. - Effect of ion plating on the fatigue property of low carbon steel (Ohmae, ref. 42).