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LUBRICATION WITH SPUTTERED MoS_2 FILMS

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Abstract

Sputtered MoS_2 films (2000 - 6500 Å) were deposited on highly polished metal surfaces. These films have a low coefficient of friction (0.03 - 0.04) at speeds of 40 - 80 rpm and loads of 250 - 1000 grams. At loads of 250 grams the wear lives are over 0.5 million cycles, but at 1000 gram loads, it decreases to 38,000 cycles. Friction experiments and tensile tests have indicated that sputtered films have a strong adherence to metal surfaces. Electron transmission, diffraction and scanning electron microscopy show that these films have an extremely small particle size less than 30 Å in diameter and are very dense and free from observable pinholes. The high kinetic energy of these sputtered species, the submicroscopic particle size and the sputter etched substrate surface is responsible for strong adhesion and cohesion of the sputtered film.

Introduction

When solid film lubricants (Au, Ag, MoS_2, WS_2) are applied to surfaces by sputtering, very thin films of about 2000 Å thick are required to achieve effective lubrication. Friction experiments conducted in vacuum gave longer endurance lives and lower wear with sputtered MoS_2 and WS_2 films than was obtained with the same films applied by other more commonly used methods.(1) As a consequence, the method of application has been shown to have a direct effect on the performance of the film. The fact that sputtering provides higher arrival energies of the sputtered species has certain consequences with respect to film formation. The strong adherence between the sputtered film and the surface can be explained in terms of the high kinetic energies of the sputtered species and the sputter etched (cleaned) surface. The high arrival velocities of the sputtered species bring with them a certain activation energy for reacting with the surface.

When rf sputtering is used, all types of solid film lubricants (conductors, semiconductors, insulators) can be directly and accurately deposited. A controlled coating is always maintained in terms of film adherence, composition, thickness and uniformity when the experimental conditions are kept constant. The following types of solid film lubricants have been sputtered: (1) lamellar - MX_2 compounds (MoS_2, WS_2, $NbSe_2$), (2) soft metals (Au, Ag, Pb), and (3) plastics (PTFE and polyimides).(2)

The objective of this paper is to discuss rf sputtering of MoS_2 and illustrate the film formation characteristics and the behavior of such films during sliding friction experiments in vacuum. Sputtered, 2000 Å thin films were used and these films had an exceptionally strong adherence to highly polished (reflective 5×10^{-4} μm (~2 μin.)) metal surfaces. Strong adherence is shown by means of tensile test specimens coated with a sputtered MoS_2 film. The strength and durability of these films were tested in ultra-high vacuum friction experiments. A hemispherical metal rider was in sliding contact with the disk surface on which the film had been sputtered. The average coefficient of friction was about 0.03 - 0.04 over million cycles at speeds of 40 - 80 rpm using loads of 250 - 1000 grams with a 4.75 mm radius hemispherical rider sliding on a flat. Electron microscopy, electron diffraction and scanning electron microscopy were used to characterize and analyze these films for particle size, orientation effects, film roughness and density. Actual wear tracks after friction experiments were analyzed by scanning electron microscopy.

APPARATUS

Ultrahigh Vacuum Friction Apparatus

The vacuum friction apparatus shown in Fig. 1 was used for determining the coefficient of friction and the durability of the sputtered coatings. The basic components of the apparatus are the specimens, a 6.35 cm diameter flat disk, and a 4.75 mm radius rider. The disk specimen was mounted on the end of the rotatable horizontal shaft in the vacuum chamber. A 4.75 mm hemispherical rider specimen was loaded against the disk. The rider was supported by a bellows-sealed, rigid arm which projects through a port in the side of the vacuum chamber. A removable gimbal assembly containing a strain gauge measuring device was used to load the rider against the disk surface and to monitor the frictional force. The friction tests were conducted at various speeds of from 40 - 80 rpm using loads of 250 - 1000 grams in a vacuum of 10^{-11} torr.

RF Sputtering System With DC Bias

The sputtering apparatus is a rf-diode mode with a superimposed dc-bias. The system is shown schematically in Fig. 2(a) and photographically during sputtering with the dc-bias in Fig. 2(b). The apparatus consists of a water cooled metal electrode to which the MoS_2 target material is bonded. The bonded MoS_2 target is a circular disk about 0.63 cm thick and 12.7 cm in diameter. The system consists of 3 electrodes, the target to which the rf potential is applied, the specimen which is at a negative dc potential and the metal screen which has a positive dc potential. This system is capable of sequential substrate cleaning or etching, followed by rf sputter deposition or simultaneously etching while sputtering. To clean the specimen by sputter etching a negative potential (2 - 5 kv) with respect to the screen is applied to the specimen. A glow discharge is immediately established and sputter etching of the surface begins. After the surface is pre-cleaned the rf power source (1 kw capacity) to the target is energized and film deposition by rf sputtering begins. During rf sputtering once the surface is precleaned the dc voltage can be turned off or the potential reduced to the specimen so that the reverse dc sputtering rate is smaller than the forward rf sputtering rate. A rotatable shutter is placed in front of the target during dc sputter etching of the specimen to prevent the sputtered material from contaminating the target.

Sputtering Procedure

At the start of the sputtering process the argon pressure of 15 - 17 μ is established. A high voltage of (2 - 5 kv) is applied to the specimen to be plated which establishes a glow discharge, thereby sputter etching the specimen. After a predetermined period of sputter etching which depends on the material used, the high voltage dc is turned off and rf power applied to the target. The most important power requirement in rf sputtering is to match the output of the power supply to the load properties of the plasma. A matching network serves this purpose, to control and adjust the proper power requirements. The forward and reverse power is monitored by power read-out meters.

The following rf sputtering parameters were used for depositing MoS_2 films: rf frequency 7 MH_z, argon pressure 15 - 17 μ, power input 400 w, reflected power about 2 w, dc input 500 v, target voltage AC 1.2 - 1.3 kv, target to specimen distance 2.54 cm, sputtering rate about 150 Å/min. The specimen temperature was monitored by a thermocouple and during the above power levels, the specimen temperature was about 90° C.

An interesting and useful phenomena was observed during rf sputtering when the specimen is located about 7.6 cm from the target and floating, and exposed from all sides to the plasma sheath; under these conditions the specimen is completely coated from all sides. Utilizing this phenomena, MoS_2 was sputtered on a number of ball bearing components (cages and races). Figure 3 shows the coated ball bearing components which were completely coated including the ball pockets of the cages. The potentials used during sputtering and the distance between the target and the specimen is very critical to the film uniformity of the components.

Results and Discussion

Characterization of Sputtered MoS_2 Films as Deposited

The sputtered MoS_2 films were qualitatively and quantitatively analyzed by chemical and spectrographic methods for any change in stoichiometry. The quantitative analyses of the bulk and sputtered MoS_2 material are shown in Table 1. The analysis of the dc and rf sputtered MoS_2 films show a very small compositional change from the bulk material. The table illustrates that during sputtering the lubricant film can be directly transferred onto a surface while retaining the same composition. Such films are not usually attainable by ordinary coating techniques. To examine and evaluate the film formation characteristics of these sputtered films formed under high energy conditions electron transmission and electron diffraction microscopy were utilized. The object was to determine the film structure and any orientation effects. MoS_2 films about 500 Å thick were sputtered on nickel, glass and mica surfaces under identical experimental conditions. Sputtering was performed on the three different substrates during the same run, eliminating all possible operational variables. The substrate temperature was monitored by a thermocouple before and during sputtering and the temperature under these conditions was 90° C. Bright and dark field micrographs were taken of randomly selected areas of the sputtered film on each of the three substrates.

In dark field, crystals normally show up as bright spots.(2) These transmission micrographs were taken at a magnification of 154,000 x. In all cases the micrographs, irrespective of the substrate, had an identical appearance and a typical micrograph of sputtered MoS_2 film is shown in Fig. 4. This micrograph illustrates that the film had a continuous, structureless appearance. It does not reveal any visible grains or grain boundaries. Figures 5(a) and (b) are typical micrographs at 250,000 x and 500,000 x and again does not show any degree of texturing. Previous investigations have shown that in a dark field one can image crystals as small as 30 Å in diameter. The dimensions of these sputtered species are close to the limit of resolution of the microscope, therefore the exact size and distribution could not be determined. It is concluded however, that the particle size is less than 30 Å in diameter. Electron diffraction patterns of the sputtered MoS_2 on nickel, glass and mica were also very similar in appearance. Typical diffraction micrographs are shown in Figs. 6(a) and (b). In both cases a broad, dispersed ring was obtained which failed to indicate any crystallinity in the film.

Transmission electron micrographs also showed that pinholes, greater than 30 Å in diameter were absent in the films. This indicates that the density of the sputtered films is very close to the density of the bulk material. Formation of pinholes generally is interpreted as resulting from poor adhesion. These transmission micrographs have prove that the sputtered film has a submicroscopic particle size possibly of an amorphous nature, and the films are of high density.

The sputtered film in all instances was rougher than the original substrate surface. When solid film lubricants are applied by the most commonly used methods to surfaces, the surface always has to be roughened to obtain a longer wear life. The wear life is extended due to an increased surface concentration of the lubricant. In contrast the sputtered films were deposited on highly reflective surfaces (5×10^{-4} μm). Such highly polished surfaces are not used for best results when a solid lubricant is applied by the conventional methods. With the highly polished surface, surface roughness still exists, but it is on the atomic or molecular scale. The submicroscopic particle size of the sputtered species and the high velocity of these particles are responsible for providing an adherent, dense lubricating film. The microscopic depressions can be easily penetrated by the energetic submicroscopic species.

Tensile Testing

To evaluate the adherence of these sputtered MoS_2 films, tensile testing was selected. A number of 2.5 cm gage length nickel, inconel and 52,000 tool steel specimens were coated with sputtered MoS_2 films with various thicknesses from 2000 - 10,000 Å. After coating the specimens, they were tensile tested. Figure 7 shows the appearance of typical nickel and inconel specimens before and after breaking. The broken (uncoated and coated) specimens in Fig. 7 show a "roughening effect" on the surface due to the plastic flow of 38 percent elongation and 81 percent reduction in area. The surface topography of the elongated sections of the uncoated broken specimens is similar to sections of the sputtered ones showing no scaling or peeling effects. The sputtered film on the broken elongated section of the specimen is intact, and the film plastically flows with the bulk material. This strong adherence can be basically attributed to the relatively high arrival energies (15 - 60 ev) of the sputtered species, the submicroscopic particle size and the sputter etched surface. These energetic, submicroscopic sputtered species have certain activation energies which favorably affect surface adherence and also increase the cohesion between the particles. The strong particle to particle cohesion is responsible for the formation of high density films.

MoS_2 sputtered onto Ni, Au, Ag, Co, Mo, W, Ti, Al, a number of steels (e.g., 440C, 52100), glass, plastics, etc., did not show any stress induced peeling within the film. The thickness range changed from 2000 - 10,000 Å for the above substrates. Stress induced peeling becomes important for films thicker than 15,000 Å. Therefore, the MoS_2 films considered in this study are free of stress peeling effects. Other factors contributing to the low stress are the low temperature which was maintained during sputtering and the relatively low sputtering rate (150 Å/min). Generally it has been observed that the strongly adherent films do not exhibit inherent stresses as readily as poorly adherent films. One exception was observed in respect to MoS_2 adherence; it did not adhere to copper or bronze surfaces. The film had a tendency to blister and peel even during the sputtering process. A typical sputtered MoS_2 film on copper surface is shown in Fig. 8.

Evaluation of Sputtered Films During Friction Experiments

In all instances MoS_2 was sputtered on highly polished (5×10^{-4} μm) metal surfaces. Before sputter coating the metal surfaces, they were cleaned by sputter etching. The deposited film thickness was between 2,000 - 6,500 Å thick as measured by an interference microscope. It was determined that a 2,000 Å thick MoS_2 sputtered film was sufficient to provide effective lubrication when tested in ultra high vacuum.

The rf sputtering parameters were kept constant (rf - frequency, 7 MH_z; argon pressure 15 - 17 μ; rf power input 400 watts, reflected power about 2 w; dc input 500 v; target voltage AC, 1.25 - 1.35 kv; target to specimen distance about 2.5 cm). Friction tests in ultra high vacuum were conducted on these sputtered films. A typical friction curve in the initial state is presented in Fig. 9. The data of Fig. 9 was obtained with a 440C rider sliding on a sputtered MoS_2 film (2,000 Å) deposited on a 440C disk at an applied load of 250 grams and speed of 50 rpm. The coefficient of friction at the beginning of the friction test was 0.06 which was somewhat higher than the steady state value. During the first few minutes or until 100 revoluations had been reached, the coefficient of friction continuously dropped until a value of 0.03 - 0.035 was reached. With continued sliding the coefficient of friction reached a steady state friction value of 0.04. Once this value was reached, the endurance life was over 0.5 million cycles.

When the initial load selected was 1000 grams and the speed was 50 rpm, the coefficient of friction started at even a lower value and the average friction coefficient was 0.02 (Fig. 10). The endurance life, however, with this high load was considerably shortened and the film failed after 38,000 cycles. A comparison of the coefficient of friction is shown in Figs. 11(a) and (b), where the experiments are conducted at two different speeds. The speeds were 40 rpm and 80 rpm and the loads were changed from 250 - 1000 grams. Figure 11(a) illustrates that the coefficient of friction at a 250 gram load is about 0.04 while at 1000 grams, it is 0.025. Figure 11(b) shows similar results except at a higher speed (80 rpm). At 250 grams load, the coefficient is again about 0.04 but at 1,000 grams load, it drops to 0.03. These friction curves indicate that at the lower loads and speeds (250 grams and 40 rpm, respectively) the average coefficient is 0.04 and the wear lives are over 0.5 million cycles. At the heavier loads (1000 grams) and higher speeds (80 rpm) the average coefficient is the lowest (about 0.02) but the wear life is considerably reduced (38,000 cycles).

A typical wear track of sputtered MoS_2 film on Ni-Cr disk which did not fail after running 5.8×10^5 cycles is shown in Fig. 12. It was observed in these experiments and shown in Fig. 12 that the sputtered MoS_2 film which is worn off tends to agglomerate at the edges of the wear track and around the rider. A typical appearance of the scraped sputtered MoS_2 film is shown in Fig. 13. A tendency for agglomeration is evident. This might be interpreted as being due to the submicroscopic size of the sputtered material. Particles of this submicroscopic size (amorphous nature) have a tendency to build up an electrostatic charge, which would enhance the tendency for agglomeration. It has been shown that certain semiconductor compounds like CdS and group III-V compounds exhibit a polar nature with respect to certain crystallographic faces.[3]

Scanning electron microscopy was used to determine the general surface topography of MoS_2 sputtered coatings as received and the surface of the coating which had been friction tested. Figures 14 and 15 provide a comparison of representative scanning electron micrographs obtained from both areas at 1000 x and 5000 x magnifications. Figure 16 shows again the appearance of several wear tracks taken randomly. These micrographs of the wear track substantiate the tendency for agglomeration of the wear debris. The wear particles have a spherical or elliptical shape rather than a flake-like one with sharp edges. The large number of the small spherical wear particles which have a tendency to agglomerate might be instrumental in prolonging the wear life because they can enter the load carrying area more freely as a result of their shape and size.

Torque Test Evaluation of Sputtered and Bonded MoS_2 Ball Bearings

Three sets of ball bearings were rf sputtered with a 3500 Å thick MoS_2 film and another set coated with sodium silicate-bonded MoS_2. Low speed torque measurements at 4.5 kg thrust loads were made with each bearing running at 88 rpm for periods to 2 hr or until a steady state torque condition was reached.[4] The rf sputtered MoS_2 films gave the lowest torque, while the bonded MoS_2 gave the most consistent performance. Stylus profilometry showed that the sputtered MoS_2 films were smoothest, and as a result they gave the best torque performance and less degradation within the run-in condition.

Summary of Results

Thin (2000 - 6500 Å) sputtered MoS_2 films on highly polished (5×10^{-4} μm) metal surfaces gave low average coefficients of friction 0.04 and long wear lives, over 0.5 million cycles at loads of 250 grams. The coefficient of friction generally decreased with higher loads (1000 grams) to 0.3 but had a decreased wear life of only 38,000 cycles.

Friction experiments and tensile tests have indicated that sputtered films have a strong adherence to metal substrates. Electron transmission, diffraction and scanning electron microscopy was used to characterize these films. It was found that these films are of an "amorphous" nature, particle size less than 30 Å in diameter. These films are very dense, and without observable pinholes and the particle to particle cohesion is strong. The strong adhesion to the surface and the strong cohesion between the particles is explained as being due to the high energy of the sputtered species, the submicroscopic size of these species and the sputter etched character of the substrate surface.

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4. Flom, D. G. and Snediker, D. K., "Evaluation of Vacuum Deposited Solid Lubricant Coatings on Angular Contact Bearings Using Power Spectral Density Analysis," Final Report (Contract No. NAS3-13485), General Electric Co., Philadelphia, Pa, Aug. 1970.

CHEMICAL COMPOSITION OF DC AND RF SPUTTERED MoS_2 FILMS

EXPT NO.	COMPOSITION OF ORIGINAL MoS_2, WT %	COMPOSITION OF DC SPUTTERED FILM, WT % (EXP COND: 3.5 kV, 20 MA, 20 μAr)	COMPOSITION OF RF SPUTTERED FILM, WT % (EXP COND: 400 W 15 μAr)
1	Mo 58.60 S 39.44 Fe .12	Mo 58.23 S 38.90 Fe .11	Mo 58.8 S 40.3
2	Mo 58.90 S 39.44 Fe .12	Mo 58.55 S 38.65 Fe .10	Mo 60.3 S 38.6
3			Mo 61.10 S 39.20

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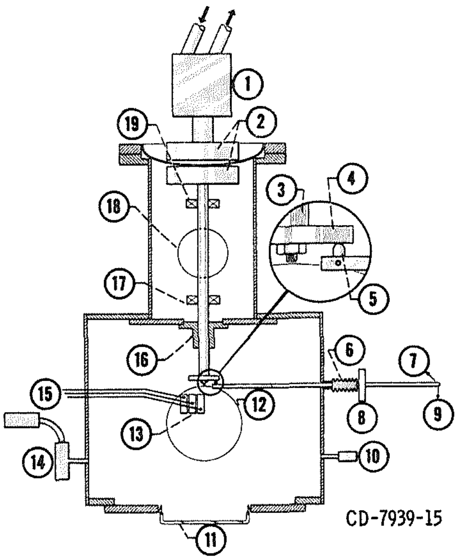
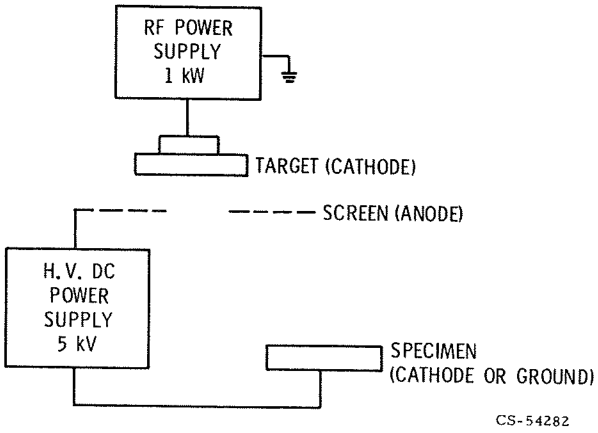
Table 1

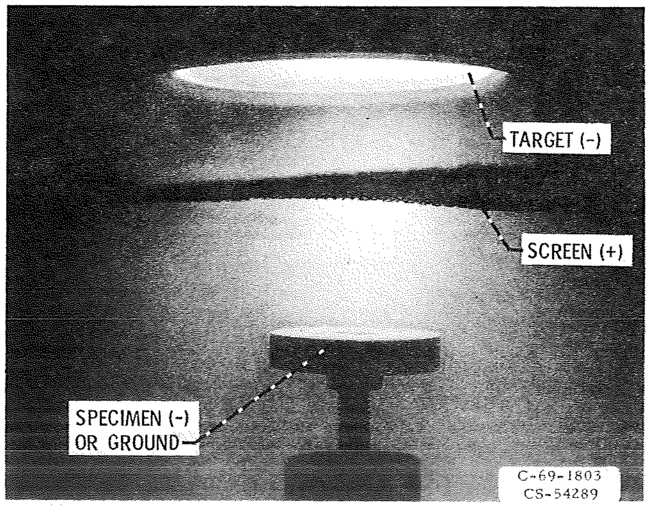


1 HYDRAULIC DRIVE MOTOR
2 MAGNETIC-DRIVE ASSEMBLY
3 SHAFT
4 DISK SPECIMEN
5 RIDER SPECIMEN
6 BELLOWS
7 FRICTIONAL FORCE
8 GIMBAL ASSEMBLY
9 LOAD
10 TRIGGERED DISCHARGE VACUUM GAGE
11 GLASS WINDOW
13 ELECTRON GUN WITH TUNGSTEN FILAMENT
14 MASS SPECTRO-METER ASSEMBLY
15 POWER SUPPLY
16 MOLECULAR FLOW SEAL
17 WATER-COOLED SUPPORT BEARING
18 TO ION PUMP AND MECHANICAL PUMPING SYSTEM
19 WATER-COOLED SUPPORT BEARING

Figure 1. - Ultra-high-vacuum friction apparatus.



(A) RF SPUTTERING SYSTEM WITH DC BIAS.



(B) RF WITH DC BIAS DURING SPUTTERING.

Figure 2.

BALL BEARING ASSEMBLY COMPLETELY COATED WITH MoS_2 FILM BY RF SPUTTERING

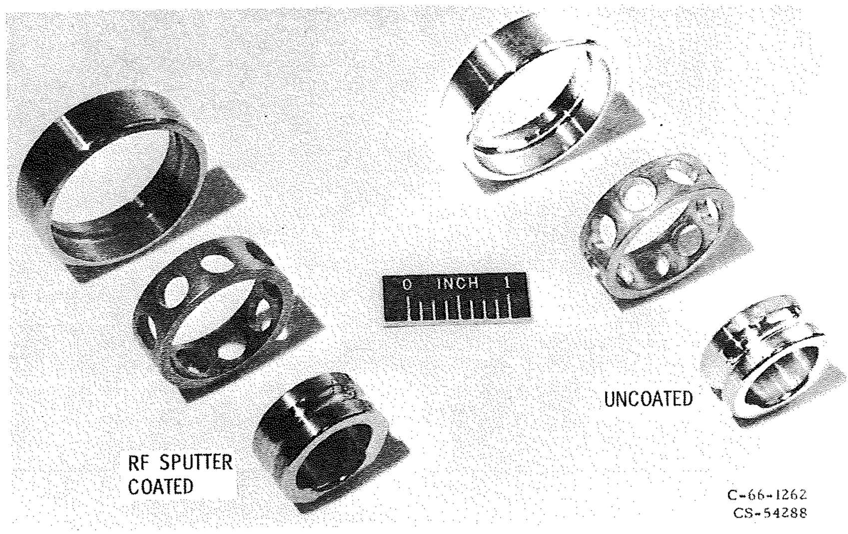
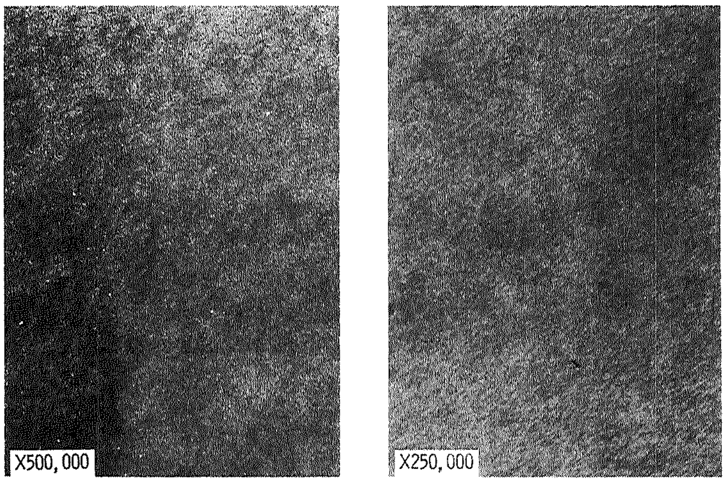


Figure 3.

Figure 4. - Dark field transmission micrograph of MoS_2 film. X154 000.



(a) (b)

Figure 5. - Electron transmission micrographs of r-f sputtered MoS_2 film of nickel.

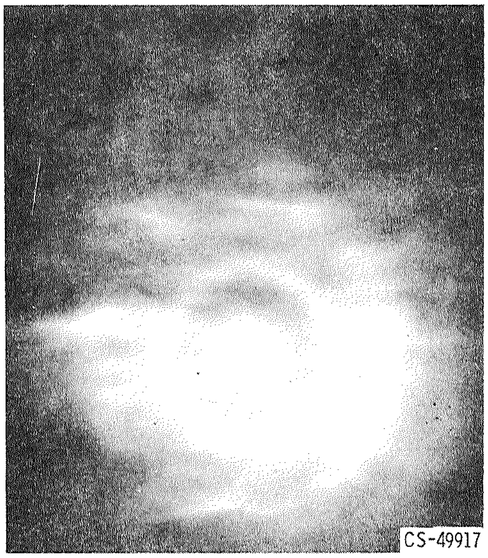


Figure 6(a). - Electron diffraction pattern of sputtered MoS_2 film.

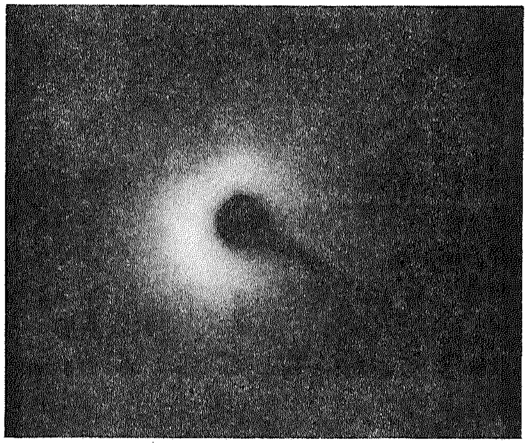


Figure 6(b). - Electron diffraction pattern of sputtered MoS_2.

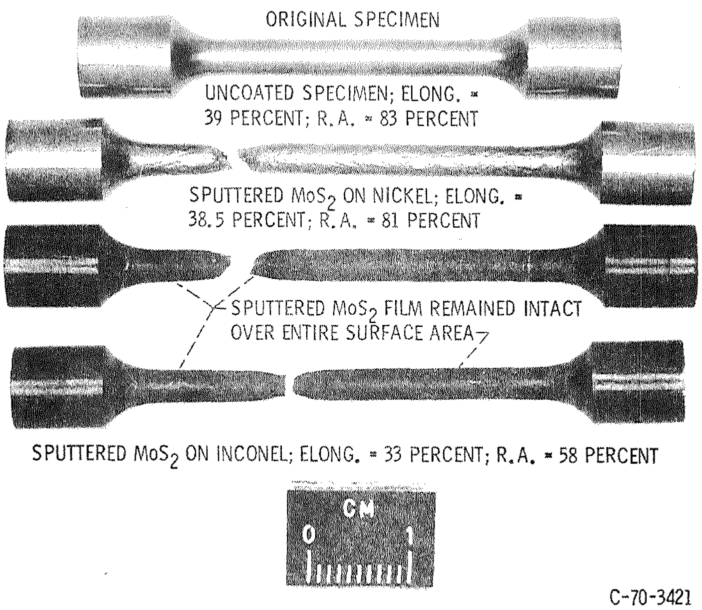


Figure 7. - Comparison of uncoated and rf sputtered MoS_2 on nickel and inconel tensile specimens after fracture.

Figure 8. - Sputtered MoS_2 film on copper surface.

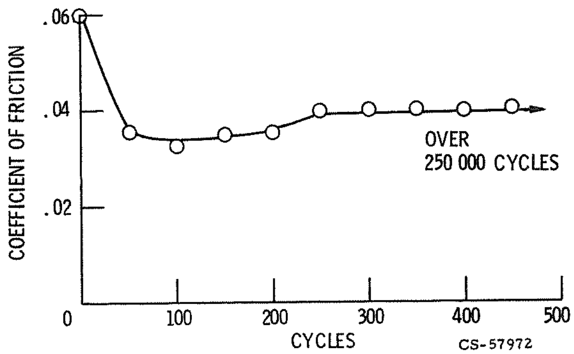


Figure 9. - Initial coefficient of friction of 440 C rider sliding on 440 C disk coated with rf sputtered MoS_2 (2000 Å) in vacuum (10^{-9} torr); load, 250 gms; speed 50 rpm, at ambient temperature.

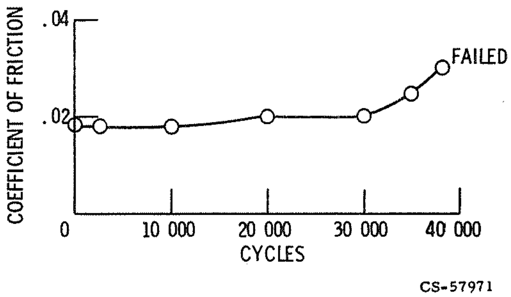


Figure 10. - Average coefficient of friction of 400 C rider sliding on 440 C disk coated with rf sputtered MoS_2 (6500 Å) in vacuum (10^{-9} torr); load, 1000 gms; speed, 80 rpm, at ambient temperature.

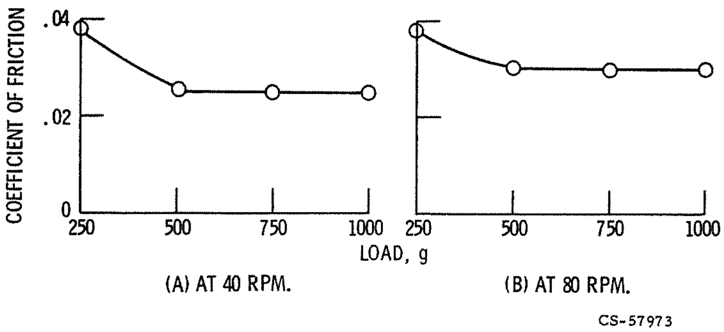


Figure 11. - Average friction coefficient of 440 C rider sliding on 440 C disk coated with rf sputtered MoS_2 (6500 Å) at speeds of 40 rpm and 80 rpm in vacuum (10^{-9} torr) at ambient temperature for 45 minutes.

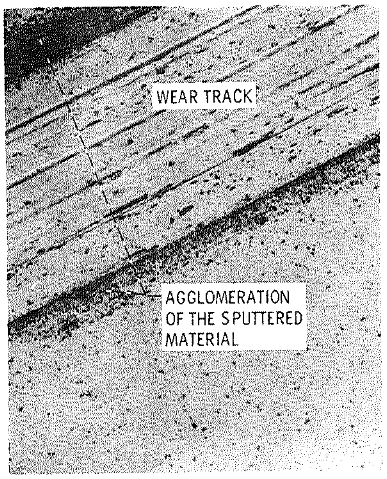


Figure 12. - Section of a wear track on (Ni-Cr disk with sputtered MoS_2 film before failure, sliding over 0.5 million cycles.

ELECTRON MICROGRAPH OF SPUTTERED MoS_2 POWDER

X27 000

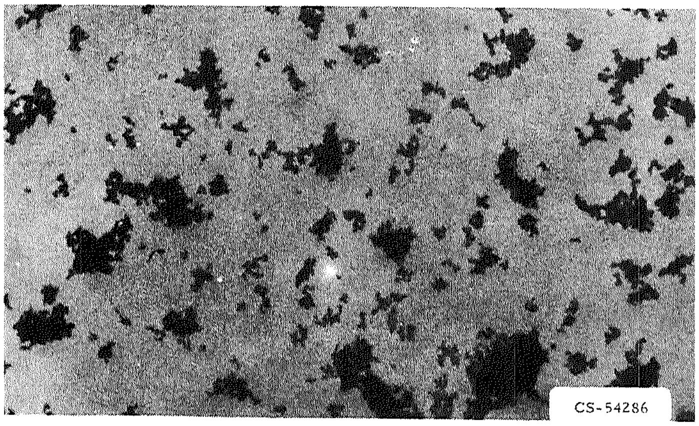


Figure 13.

COMPARISON OF SCANNING ELECTRON MICROGRAPHS OF AS-SPUTTERED MoS_2 (2000Å) ON NICKEL SURFACE AND FRICTION WEAR TRACK AFTER SLIDING

AS-SPUTTERED MoS_2 FILM — WEAR TRACK AFTER SLIDING

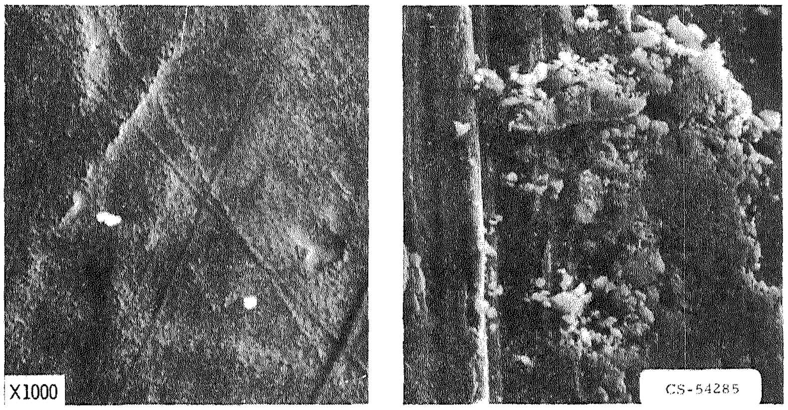


Figure 14

COMPARISON OF SCANNING ELECTRON MICROGRAPHS OF AS-SPUTTERED MoS_2 (2000Å) ON NICKEL SURFACE AND FRICTION WEAR TRACK AFTER SLIDING

AS-SPUTTERED MoS_2 FILM — WEAR TRACK AFTER SLIDING

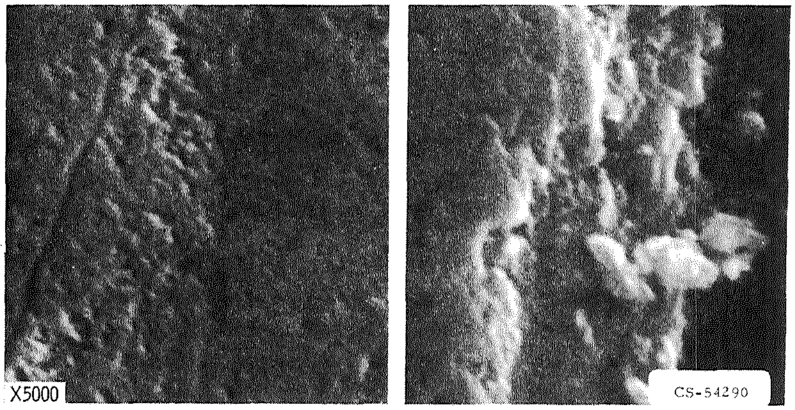


Figure 15

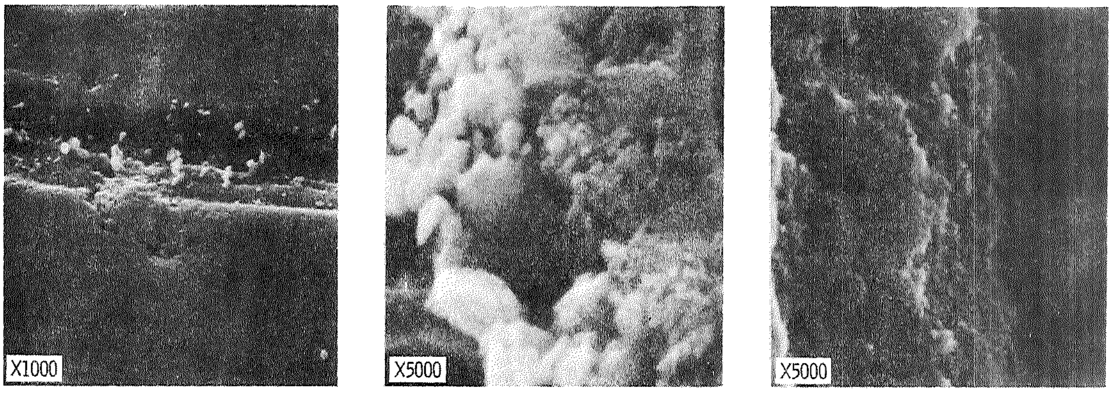


Figure 16. - Scanning electron micrographs of sputtered MoS_2 wear traces on nickel surface after sliding.