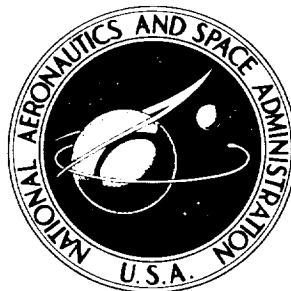NASA TECHNICAL NOTE

NASA TN D-4269

NASA TN D-4269

DEPOSITION OF SPUTTERED MOLYBDENUM DISULFIDE FILMS AND FRICTION CHARACTERISTICS OF SUCH FILMS IN VACUUM

by Talivaldis Spalvins and John S. Przybyszewski

Lewis Research Center
Cleveland, Ohio

DEPOSITION OF SPUTTERED MOLYBDENUM DISULFIDE FILMS AND

FRICTION CHARACTERISTICS OF SUCH FILMS IN VACUUM

By Talivaldis Spalvins and John S. Przybyszewski

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

DEPOSITION OF SPUTTERED MOLYBDENUM DISULFIDE FILMS AND

FRICTION CHARACTERISTICS OF SUCH FILMS IN VACUUM

by Talivaldis Spalvins and John S. Przybyszewski

Lewis Research Center

SUMMARY

Physical direct-current sputtering of molybdenum disulfide (MoS_2) is used to apply MoS_2 films as a solid lubricant for rotating and sliding components. This method does not use organic or inorganic binders or the process of burnishing. Friction experiments in vacuum (10^{-11} torr or 1.33×10^{-9} N/m^2) were conducted on these films. The coefficients of friction for the sputtered films were in agreement with the reported values in the literature. Stoichiometric films were obtained, and no dissociation was observed. There is a strong bonding (adherence) between the films and the substrate, as indicated by the long-endurance life of the lubricating films in friction experiments. The sputtered MoS_2 films had an accurate repeatability in terms of stoichiometry, adherence, thickness, and uniformity when the sputtering conditions were kept constant.

INTRODUCTION

Molybdenum disulfide (MoS_2) is frequently used as a solid lubricant not only in conventional lubrication situations but also in high-temperature and high-vacuum environments. Solid lubricants are preferred in high-vacuum environments because they generally have vapor pressures lower than 10^{-10} torr (1.33×10^{-8} N/m^2) as compared with the best conventional organic liquid lubricants, which have vapor pressures in the 10^{-6} torr (1.33×10^{-4} N/m^2) range. To be durable and effective, lubricant films of MoS_2 must be firmly bonded to the surface of the materials which require lubrication.

One of the primary problems concerning the use of MoS_2 as a lubricant is the method of application to the surface to obtain good film adherence. Previously, adherent MoS_2 films had been obtained either by utilizing binders (e.g., thermoplastic or thermosetting resins or sodium silicate) or by burnishing the substrate material with MoS_2 powder. There are applications where a bonding agent is undesirable or would be a disadvantage,

for example, where the performance of the film may be adversely influenced by certain chemical interactions, particularly those that would affect film adherence, such as decomposition of the binder. Burnished MoS_2 films leave much to be desired with respect to bonding of the MoS_2 to the surface, coefficient of friction, and uniformity of coating thickness. Further, the friction coefficient of burnished MoS_2 films (0.3, ref. 1) is higher than for most bonded MoS_2 films. Electron diffraction examinations of steel surfaces burnished with MoS_2 showed the surface film to be a complex mixture of iron and molybdenum sulfides (ref. 1). The presence of this mixture, rather than pure MoS_2, was considered to be responsible for the higher coefficient of friction.

Of the coating methods which presently are being intensively investigated for lubrication purposes, the various vacuum-deposition methods are of particular interest and show strong adhesion, long-endurance life, and controlled thickness. Although vapor deposition (thermal evaporation) is the simplest and most commonly used deposition technique, it cannot generally be used for alloys and compounds such as MoS_2. The differing vapor pressures of the constituent elements of MoS_2 during evaporation render unlikely the condensation of the vapor as a stoichiometric MoS_2 film.

This investigation was conducted to produce thin, uniform, adherent, stoichiometric lubricating films of MoS_2 (with a desired thickness) which could be used as lubricants with long-endurance lives. Molybdenum disulfide was deposited under controlled experimental conditions on two substrates, niobium (Nb) and nickel-chromium (Ni-Cr) alloys, by means of physical direct-current sputtering. The friction characteristics and endurance life of the sputtered MoS_2 films on Ni-Cr and Nb substrates were examined in ultra-high vacuum (10^{-11} torr or 1.33×10^{-9} N/m^2). The friction experiments were conducted with a hemispherical rider of Nb sliding on the thin film of MoS_2 which was deposited on the disk surface.

APPARATUS

Triode Direct-Current Sputtering Apparatus

A sputtering system was constructed utilizing a three electrode (triode) geometry consisting of a thermionic cathode, an anode, and the target. This system is shown schematically in figure 1(a) and photographically in figure 1(b). The components of the sputtering system are enclosed in the vacuum chamber (45-cm bell jar). The components are as follows:

(1) Thermionic cathode, a spiraled filament of 0.1-centimeter-thick tungsten wire which, when heated, acts as a thermionic electron source
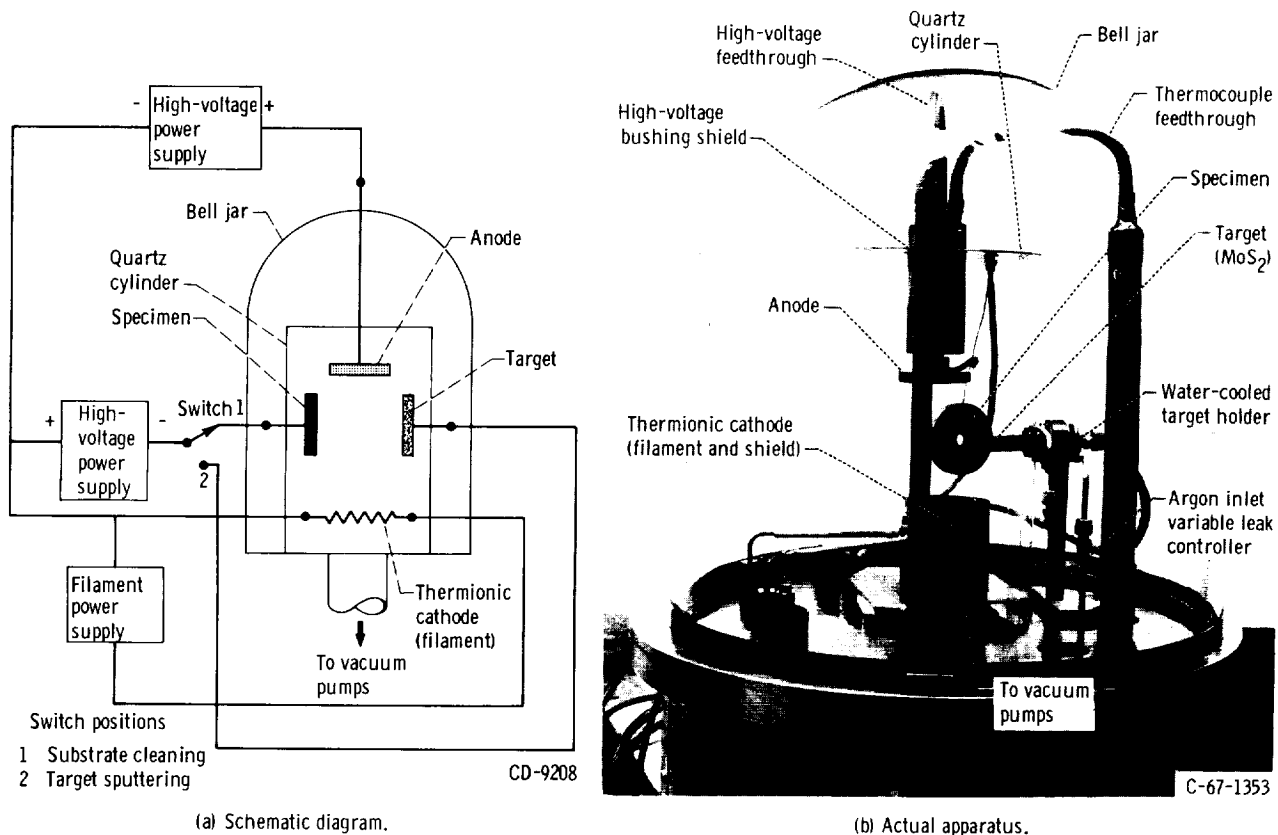
(a) Schematic diagram.

(b) Actual apparatus.

Figure 1. - Triode direct-current sputtering apparatus.

(2) Anode, a flat stainless-steel disk to which a positive potential of about 500 volts was applied to establish a glow discharge between it and the thermionic cathode

(3) Target, the material to be deposited, a cylindrically shaped compact of MoS_2 (1.3 cm in diam and about 5 cm in length).

This MoS_2 cylindrical compact was made without a binder by utilizing compacting pressures of 50 000 to 100 000 psi (34.47×10^7 to 68.94×10^7 N/m^2). The MoS_2 target was held in a water-cooled holder, in order to keep the target temperature from rising excessively. A negative potential was applied to this target.

(4) The substrate material (Nb and a Ni-Cr alloy disk) placed close to target material on which the atoms ejected from the target were deposited to form a continuous film

A thermocouple gage monitored the chamber pressure during sputtering, and pure argon was admitted to the vacuum chamber through a variable leak-control valve.

Ultra-High-Vacuum Friction Apparatus

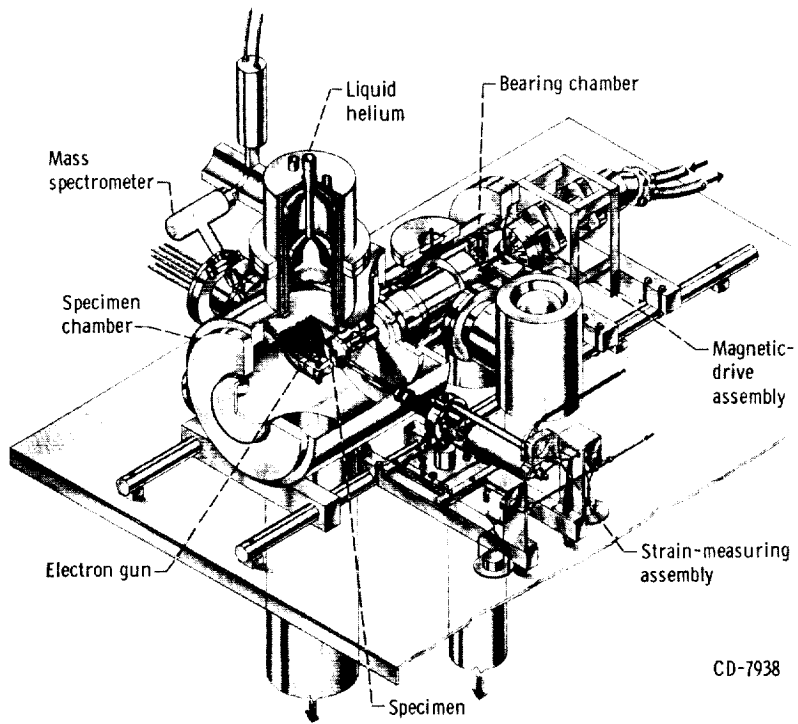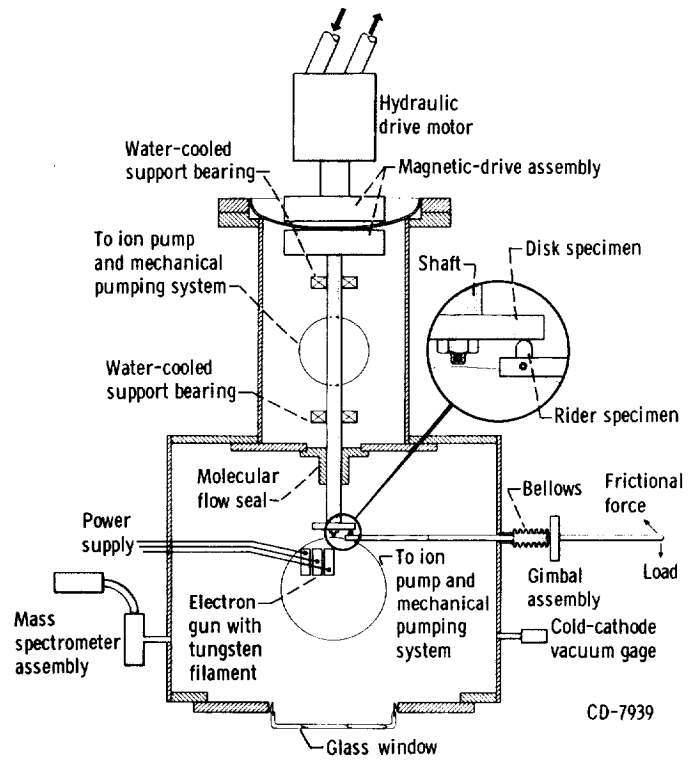The vacuum-friction apparatus (fig. 2) was used to determine the coefficient of

3

Figure 2. - Ultra-high-vacuum friction apparatus.

4

friction for the coated and uncoated surfaces. The apparatus has two distinct chambers, the specimen chamber and the bearing chamber, both of which are connected to the fore-pumping system.

The forepumping system of the apparatus includes a cold trap made up of molecular sieves backed by liquid-nitrogen-cooled containers. This system is connected to two mechanical pumps through a 5-centimeter stainless-steel vacuum valve.

The specimen chamber is connected to the mechanical pumping system by a bakable high-vacuum valve and is provided with a 400-liter-per-second ion pump, as well as cryopumping surfaces (liquid nitrogen and liquid helium). The specimen chamber contains a cold-cathode discharge vacuum gage for measuring pressures. The pressure in the specimen chamber was approximately 10^{-11} torr (1.33×10^{-9} N/m^2). The specimen and bearing chambers were baked at 644° and 477° K, respectively.

The bearing chamber, which is connected to the forepumping system by a 5-centimeter valve, is equipped with a 125-liter-per-second ion pump. The bearing chamber also contains a liquid-nitrogen-cooled titanium sublimation pump. Pressure in the bearing chamber was about 10^{-10} torr (1.33×10^{-8} N/m^2).

The shaft projects through the rear wall of the test chamber by means of a molecular flow seal (fig. 2). On the bearing-chamber end of the shaft a 20-pole magnet is mounted and is separated from the drive magnet, which is outside the vacuum chamber, by a 0.08-centimeter diaphragm (0.40-cm air gap). The drive magnet is powered by a hydraulic motor with a variable speed capability. Because of instabilities in the drive motor at low speeds (10, 20, and 100 rpm), these speeds were obtained by utilizing a speed reducer with a ratio of 10.

The shaft is supported on bearings in the bearing chamber. The shaft-support bearings have a large clearance and are mounted in a cartridge so that the shaft expansion takes place into the test chamber. Thus, the possibility of the magnet striking the diaphragm is eliminated. Because loading was applied by deadweights, the expansion did not change the load on the specimens. The bearing cartridge was water cooled to prevent any damage to the bearings during the bake-out cycle.

The 6.35-centimeter-diameter disk specimen was mounted on the end of the horizontal shaft in the test chamber. Against the disk, a 0.47-centimeter-radius hemispherical rider specimen was loaded. The rider was held in place by a rigid arm, which projects through a port in the side of the vacuum chamber. The seal was made at the wall by utilizing a bellows connection between the chamber wall and the rigid arm. A removable gimbal assembly, which is used to load the rider against the disk surface and to monitor the frictional force through a strain-gage assembly, was fastened to the rigid arm outside the vacuum chamber. A sliding velocity of 2.54×10^{-2} meter per second was used for these experiments.

SPUTTERING MECHANISM AND PROCEDURE

Sputtering is generally performed in an argon atmosphere of several microns pressure. A potential is applied across the electrodes to ionize the gas. The material to be sputtered is made the cathode (target). The material sputtered from the target is ejected through the plasma and deposited as a film on the specimen. The basic mechanism of sputtering is thus a process where the positive argon ions, which form a gaseous plasma, are accelerated through an electron-free region (Langmuir sheath) with sufficient energy (40 to 60 eV or 6.4×10^{-18} J) to knock off or sputter the negatively charged target material. In explaining the actual sputtering phenomena, current theories (refs. 2 to 4) favor a momentum exchange energy transfer. The sputtered material is deposited on the specimen, which is placed close to the target source. For compounds, such as MoS_2, which have a wide disparity in vapor pressure of the constituents, the material can be deposited nearly stoichiometrically without thermal dissociation. In this method, the basic mechanism is essentially independent of the target temperature, provided the target temperature is below the vaporization or dissociation temperature of the target material.

In this experiment, the bell jar was evacuated to a pressure of approximately 10^{-7} torr (1.33×10^{-5} N/m^2) and subsequently purged several times with pure argon through a variable leak valve. Finally, the system was again evacuated, and argon was introduced at a controlled rate. A constant pressure was maintained in the bell jar at about 10^{-3}torr (1.33×10^{-1} N/m^2). A positive potential (fig. 1(a)) of about 500 volts (relative to the filament) was applied to the anode. The thermionic cathode emitter (tungsten filament) was heated to emission temperature, and a glow discharge occurred. A negative potential (fig. 1(a)) of 2000 to 4000 volts was then applied to the specimen. This application resulted in the attraction of positive argon ions from the gas discharge. The impingement of the argon ions on the surface of the specimen resulted in a cleaning action by sputtering. After the cleaning process had continued for about 20 minutes, the negative potential on the specimen was quickly switched to the target material (MoS_2). This procedure resulted in bombardment of the target by the argon ions, which were attracted by its negative potential. Molybdenum disulfide was therefore sputtered from the surface of the target and subsequently deposited on the previously cleaned specimen. The spacing between the target and the specimen was about 4 centimeters.

RESULTS AND DISCUSSION

Molybdenum Disulfide Film Deposition by Sputtering

Molybdenum disulfide was sputtered on Nb and Ni-Cr alloy surfaces. These speci-

mens were selected because they were used in previous studies (ref. 5). The original MoS_2 cylindrical target material and the sputtered MoS_2 films were analyzed chemically and spectrographically. The weight percentages of the constituent elements are listed in table I. The increased weight percentage of iron in the sputtered film probably came from the stainless-steel filament holders, which were also sputtered to some extent.

TABLE I. - CHEMICAL AND SPECTROGRAPHIC

ANALYSIS OF MOLYBDENUM DISULFIDE

Element	Original MoS_2 powder (target material)	Sputtered film
	Concentration, wt. %	
Mo	58. 60	48. 75
S	39. 44	38. 90
Fe	. 12	9. 75

The sputtered MoS_2 film was scraped off a reference glass slide and was analyzed by X-ray diffraction (Debye-Scherrer powder method). The diffraction maximums obtained in this method had broad lines, and, therefore, it was not possible to make accurate readings. Line broadening is generally caused by particle sizes in the range 2×10^{-5} to 10^{-6} centimeter or by strain effects (ref. 6). When the particles are much smaller than 100 angstroms (10^{-8} m) the diffraction lines are so broad that it is not possible to distinguish them from the general background. Consequently, it was not possible to make any measurements. In this investigation, the line broadening was probably caused by the small size of the sputtered particles. It was concluded that the MoS_2 film, which was deposited, consisted of very small particles, since sharp X-ray diffraction lines could not be obtained. These X-ray diffraction results for sputtered MoS_2 are in agreement with the general concept that sputtered films normally are not crystalline, unless the specimen is heated to recrystallization temperature. In this investigation, the specimen temperature was approximately 477° K. In sputtering a continuous film forms immediately, without nucleation. In all vapor-deposition methods, however, the film is formed in two steps: nucleation (at selected surface sites) followed by growth.

The thicknesses of the sputtered films were measured with an interference microscope on a reference glass slide located at the same distance from the target as the specimen. The films were in the range of 2000 to 3000 angstroms thick.

The significant feature of this method of applying MoS_2 to a substrate material is the avoidance of nonstoichiometry arising from dissociation. These studies indicate that nearly stoichiometric films can be obtained by sputtering MoS_2.

Friction and Endurance Characteristics of Sputtered Molybdenum Disulfide

The friction characteristics and endurance life of the sputtered MoS_2 films on Nb and Ni-Cr alloy substrates were examined in ultra-high vacuum (10^{-11} torr or 1.33×10^{-9} N/m^2). Actual traces of a friction experiment are shown in figure 3. The trace in figure 3(a) is typical for Nb sliding on Nb (without lubricant). The amplitude of the friction curve is relatively large, and the average coefficient of friction is 1.12. The friction
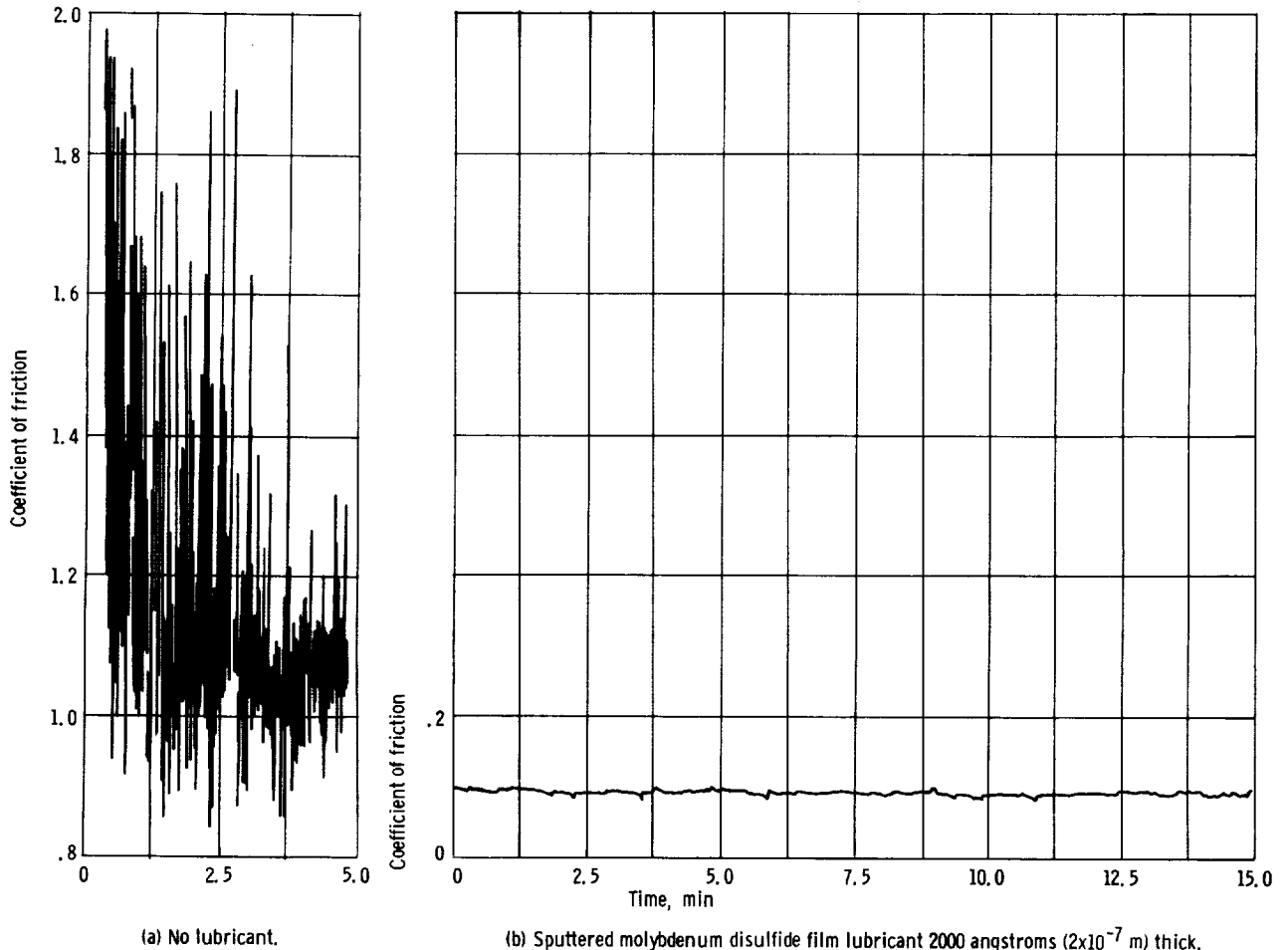

(a) No lubricant.

(b) Sputtered molybdenum disulfide film lubricant 2000 angstroms (2×10^{-7} m) thick.

Figure 3. - Actual friction traces of niobium sliding on coated and uncoated niobium. Pressure, 10^{-11} torr (1.33×10^{-9} N/m^2); load, 250 grams; speed, 5 feet per minute (2.54×10^{-2} m/sec).

trace in figure 3(b) is for Nb sliding on a Nb surface coated with sputtered MoS_2 film. The coefficient of friction is about 0.09, and the friction curve is smooth with practically no amplitude.

The actual friction traces in figure 3 were used to determine the average coefficients of friction in order to determine the friction curves in figure 4(a). The friction curve for sputtered MoS_2 on an Nb substrate with a film thickness of about 2000 angstroms (fig. 4(a)) maintained a constant coefficient of friction of 0.09 for more than 5 hours.
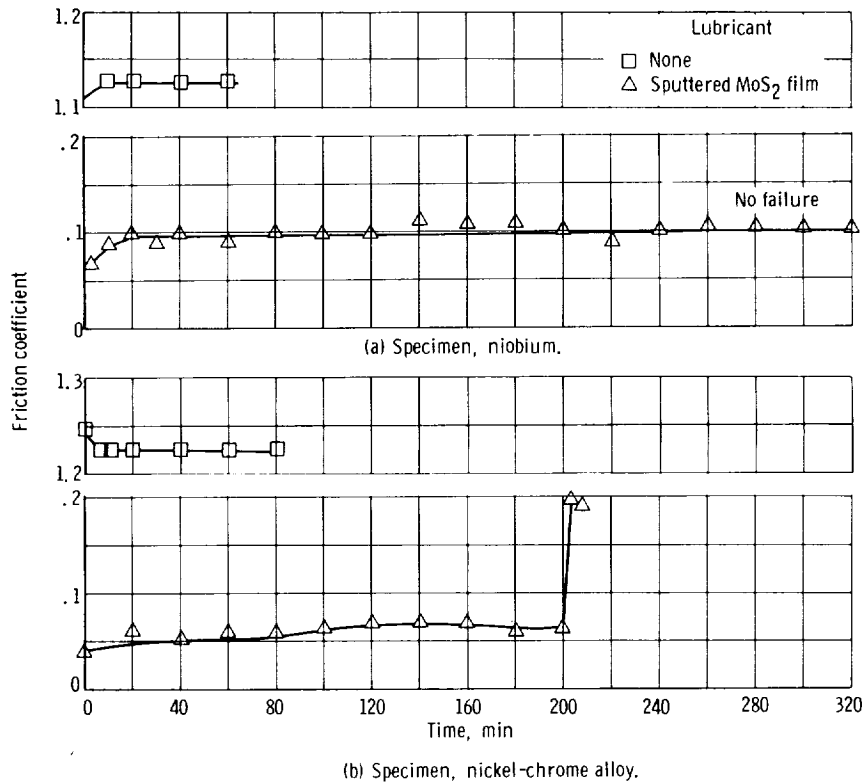
8

Figure 4. - Average friction coefficients of niobium sliding on two different specimens coated with sputtered molybdenum disulfide in vacuum (10^{-11} torr or 1.33×10^{-9} N/m^2). Load, 250 grams; speed, 5 feet per minute (2.54×10^{-2} m/sec); ambient temperature.

The sputtered MoS_2 lubricant film had not failed after 5 hours. The nominal range for the coefficient of friction for MoS_2 films is considered to be 0.03 to 0.08, as derived from many sources. The coefficient of friction for sputtered MoS_2 films is in agreement with the reported values.

The friction curve for the sputtered MoS_2 on the Ni-Cr alloy substrate (fig. 4(b)) maintains a constant coefficient of friction (0.06) for more than 3 hours. Beyond this time, the coefficient of friction gradually increases. As the film (about 2000 Å thick) was broken, the coefficient of friction did not rise abruptly. As wear took place, the coefficient of friction rose gradually until it approached the coefficient of friction of the substrate material (1.22). These two friction curves (fig. 4) clearly indicate that sputtered MoS_2 films maintain the characteristic low coefficient of friction of MoS_2 and give relatively long-endurance lives during the friction experiment.

The durability of this thin (2000 to 3000 Å) MoS_2 film indicates that there was strong bonding adherence between the sputtered film and the substrate material, which subsequently minimized breakage or chipping during the friction test. These friction tests give good qualitative measure of film adherence. Generally, the film adherence to the substrate depends on such parameters as energy of ion bombardment, substrate cleanli-

ness, substrate temperature, compatibility of preferred crystal lattices, and relative atomic bonding energies. The thicknesses measured by interference microscope showed a good uniformity of thickness over the 6.35-centimeter-diameter disk. When the sputtering conditions during the deposition are kept constant, an exceptional repeatability of film thickness can be maintained.

These superior adherence characteristics of the sputtered MoS_2 film are caused by several factors: (1) cleaning of the substrate by sputtering prior to deposition, (2) the relatively high energies of the sputtered material, and (3) the continuous cleaning of the surface by the glow discharge itself. The cleaning of a surface by ion bombardment results in an etching of that surface (ref. 7). The surface is free of the skin effects of cold working that may be produced during mechanical polishing.

SUMMARY OF RESULTS

This investigation introduces a vacuum-deposition method (sputtering) for applying molybdenum disulfide (MoS_2) films to substrate materials. The method uses neither organic or inorganic binders nor the process of burnishing. The friction experiments showed that the coefficients of friction of the sputtered MoS_2 film (0.06 to 0.09) are in agreement with the values (0.03 to 0.08) reported in the literature for resin-bonded films. This agreement in friction coefficients results from the preserved stoichiometry of the sputtered film. The durability of the lubricating film gives a qualitative test of the strong bonding adherence between film and substrate. The film thickness was uniform, and repeatability of film thickness was maintained.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, August 24, 1967,
            129-03-13-02-22.

REFERENCES

1. Johnson, Robert L.; Buckley, Donald H.; and Swikert, Max A.: Studies of Lubricating Materials in Vacuum. Paper presented at the USAF-Southwest Research Inst. Aerospace Bearing Conference, San Antonio, Texas, Mar. 25-27, 1964.

2. Wehner, G. K.: Sputtering by Ion Bombardment. Advances in Electronics and Electron Physics. Vol. 7. L. Marton, ed., Academic Press, 1955, pp. 239-298.

3. Kay, Eric: Impact Evaporation and Thin Film Growth in a Glow Discharge. Advances in Electronics and Electron Physics. Vol. 17. L. Marton, ed., Academic Press, 1962, pp. 245-322.

4. Anon.: Ionic Bombardment Theory and Applications; International Symposium of the National Scientific Research Center, Dec. 4-8, 1962. Gordon and Breach Science Publishers, 1964.

5. Spalvins, T.; and Buckley, D. H.: Vapor Deposited Gold Thin Films as Lubricants in Vacuum (10^{-11} mm Hg). J. Vacuum Sci. Tech., vol. 3, no. 3, May-June 1966, pp. 107-113.

6. Azároff, Leonid V.; and Buerger, Martin J.: The Powder Method in X-Ray Crystallography. McGraw-Hill Book Co., Inc., 1958, pp. 246-266.

7. Bierlein, T. K.; Newkirk, H. W., Jr.; and Mastel, B.: Etching of Refractories and Cermets by Ion Bombardment. J. Am. Ceramic Soc., vol. 41, no. 6, June 1958, pp. 196-200.