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MICROSTRUCTURAL AND WEAR PROPERTIES OF SPUTTERED CARBIDES AND SILICIDES

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ABSTRACT

Sputtered Cr_3C_2, Cr_3Si_2, and $MoSi_2$ wear-resistant films (0.05 to 3.5 μm thick) were deposited on metal and glass surfaces. Electron transmission, electron diffraction, and scanning electron microscopy were used to determine the microstructural appearance. Strong adherence was obtained with these sputtered films. Internal stresses and defect crystallographic growth structures of various configurations within the film have progressively more undesirable effects for film thicknesses greater than 1.5 μm. Sliding contact and rolling-element bearing tests were performed with these sputtered films. Bearings sputtered with a duplex coating (0.1-μm-thick undercoating of Cr_3Si_2 and subsequently 0.6-μm coating of MoS_2) produced marked improvement (>10.5×10^7 cycles) over straight MoS_2 films.

INTRODUCTION

To optimize wear resistance for functional mechanical components, various chemical processes and coating techniques have been used to obtain a hard, adherent, dense surface layer or coating. One of the most recent methods that demonstrates great promise for deposition of high-temperature compounds is sputtering. It also has a high degree of operational flexibility. Sputtering is essentially the only reliable direct method (without using binders) whereby hard coatings such as carbides, nitrides, and silicides can be deposited on friction and wear surfaces. Sputtering does not depend on the material melting point or vapor pressure and can be directly applied to surfaces without changes in composition. For mechanical systems that require close tolerances, sputtering offers the extraordinary ability to control film thickness to a millionth of a centimeter.

The sputter deposition technique selected will determine the mode of wear and the life of the coating. The factors involved are adherence, coherence, chemistry, and the nature of the coating growth morphology. As with all surface coatings a possible form of coating failure is early loss of adherence to the substrate. Under this condition the coating may not wear by normal, relatively slow attrition but rather by a more accelerated wear mechanism wherein coating spallation and delamination occur. The wear debris formed under these accelerated wear conditions could act in an abrasive manner and thereby accelerate the wear process. This type of coating failure can be avoided by sputter deposition, proper pretreatment of the surface, and control of the coating conditions.

The various wear mechanisms (adhesive, abrasive, corrosive, surface fatigue, etc.) have been described and evaluated in the literature (1,2). The objective of this paper is twofold: first, to illustrate and evaluate sputtered carbide (Cr_3C_2) and silicide (Cr_3Si_2, $MoSi_2$) coatings by electron transmission, electron diffraction, and scanning electron microscopy and to determine how such coating characteristics as adherence, coherence, density, thickness, internal stresses, and growth morphology affect the wear-resistant coating; and second, to evaluate these sputtered coatings under sliding conditions with a disk and pin configuration and under rolling conditions with sputtered ball bearings.

APPARATUS AND PROCEDURE

The sputtering apparatus used in this study was a radiofrequency-diode system with a superimposed direct-current bias, as shown in Fig. 1. This apparatus is described in reference (3). The sputtering targets were 12.7-cm-diameter Cr_3C_2, Cr_3Si_2, and $MoSi_2$ disks. The sputtering conditions were kept constant with a radiofrequency power density of 3.5 W/cm^2 at 7 MHz and an argon pressure of 20 millitorr.

For the investigation of the microstructural properties of the above carbides and silicides, substrates of 304 stainless steel, copper, and glass were used. Prior to sputter deposition, the metal surfaces were direct-current sputter cleaned for 10 minutes. The distance between the target and the specimen was 2.5 cm. A Chromel-Alumel thermocouple was imbedded in the specimen, and the temperature was maintained at 145° C. The coating thickness ranged from 0.05 to 2 μm. These coatings were examined by electron transmission and electron scanning microscopy. Friction, wear, and endurance of these sputtered carbides and silicides were evaluated under sliding and rolling conditions in vacuum. The sliding tests were conducted in a high-vacuum friction apparatus with a pin and disk configuration as previously described (3).

The basic components of the apparatus are the disk, a 6.35-cm-diameter flat, and a 4.75-mm-radius rider. The friction tests were conducted at speeds from 40 to 80 rpm, using loads of 50 to 250 grams in a vacuum of 10^{-5} torr.

The rolling tests were conducted with 204-size, 440C stainless steel bearings (11 balls of 0.714-cm diameter with a radial clearance of 0.0058 cm, a ball pocket diameter clearance of 0.018 cm, and a retainer clearance of 0.028 cm). The bearing races and cage were sputter coated with a 0.1-μm-thick underlayer of Cr_3Si_2 and subsequently sputtered with a 0.6-μm-thick MoS_2 film.

These sputter-coated bearings were tested in a bearing endurance test apparatus with the bearing assembly shown schematically in Fig. 2 (4). The bearing assembly consists of two test bearings mounted on a rotatable shaft. A speed of 1750 rpm and a thrust load of 137.9 newtons (31 lbf) were applied to the bearings in a vacuum environment of 10^{-8} torr. The running conditions of the bearings were monitored by the motor current, and the endurance life was monitored by an automatic timer.

RESULTS AND DISCUSSION

Characteristics of Sputtered Cr_3C_2, Cr_3Si_2, and $MoSi_2$ Films as Deposited

Adherence. The primary requirement for a wear-resistant coating is strong adherence. The degree of adherence determines the life of the coating and the mode of the wear process. How the coating is attached to the surface is more important than the volume of coating present. Sputtered carbide, nitride, and silicide coatings have the advantage (over coatings applied by other methods) of strong adherence. This advantage is obtained as a result of such characteristically unique features in the sputtering technique as proper surface pretreatment (surface etching) and biasing of the surface during sputter deposition. During biasing, sputtered carbide coating formations have exhibited stronger adherence, probably because the mixing of the backsputtered substrate material and the sputtered carbide forms a graded interfacial region, which is a highly desirable able characteristic for strong adherence. Carbide and silicide films less than 1 μm thick have resisted large deformations without the layer flaking or chipping, despite the fact that the coating material is particularly brittle in the bulk form.

Density. Electron transmission microscopy (ETM) was used to determine the structure and grain size of sputtered Cr_3Si_2 and Cr_3C_2 coatings about 0.05 μm thick on copper. A typical micrograph and its corresponding diffractogram of sputtered Cr_3Si_2 are shown in Fig. 3. The micrograph illustrates that the film has a continuous, homogeneous structure and is characterized by broad, diffuse diffraction rings, which indicates an amorphous structure. The estimated average particle size was between 1.5 and 4.5 nm. Sputtered Cr_3C_2 was very similar in microstructural appearance to Cr_3Si_2. Electron diffraction indicates the extremely small size and amorphous nature of the particles. 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 stronger the film. The extremely small particle size and the resultant high density probably affect the wear particle generation in a favorable way during the wear process (5).

Film thickness and stresses. Coatings that are deposited on surfaces are usually in a state of mechanical stress, and this effect becomes even more pronounced with hard surface coatings such as carbides and silicides. The total internal stress in a coating can be expressed as follows:

$$\sigma_{tot} = \sigma_i + \sigma_{th}$$

where

σ_i intrinsic stress produced during film deposition

σ_{th} thermal stress due to thermal expansion mismatch

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^2, 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 (6). 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 Cr_3Si_2, $MoSi_2$, and Cr_3C_2 films adhere strongly to both metal and glass substrates. Because of this strong adherence, film delamination or separation occurs within the coating as it increases in thickness. Fig. 4 illustrates this effect where film delamination occurs in a sputtered Cr_3C_2 film about 3.5 μm thick.

Surface topography. Surface topography of the substrate and coating has a pronounced effect on the wear mechanism. It is impossible to prepare surfaces that are atomically smooth over an appreciable area. Macrodefects can be eliminated; however, microdefects such as dislocations and point and extended defects limit the best surface obtainable. Various unusual crystallographic defect growth features are formed in the matrices of the sputtered carbide and silicide films.

Typical SEM micrographs in Fig. 5 show the surface views and a fracture cross section of the coating. The exact configuration and dimensions of the nodules, whether they are individual, fused, overlapping, or extreme localized growth features forming unusual complicated configurations are shown in Fig. 5. The surface morphological composition as revealed by the higher SEM magnification is composed of individual crystallites as shown in Fig. 6. These crystallites have a spherical shape and are about 0.6 μm in diameter.

As the film thickness increases, so does the size of the crystallographic defects. Surface irregularities or imperfections are the preferential nucleation and growth sites of the sputtered films. At these nucleation sites, accelerated growth occurs relative to the matrix growth. As a consequence the crystallographic defects extend above the matrix surface. A distinct separation or mismatch boundary is formed between these crystallographic defects and the matrix. These distinct boundaries are the weakest areas in the coating, and it will have a tendency to break around the nodule edges.

The defect structures act as stress raisers in the film. When these sputter-coated surfaces come in contact during sliding or rotation, the crystallographic defects can initiate cracks in the film or may simply be ejected, leaving a cavity. The size of these defects can have a pronounced effect on the mechanical properties and the friction and wear characteristics of the film. They are potential sources for producing damaging abrasive wear particles. This is particularly true in fretting, where two surfaces have oscillatory relative motions of small amplitude, as for example in shrink fits, spline couplings, and bolted joints. It is also important to recognize that the diameter of these nodules increases as the film thickness increases. A high concentration of these cavities creates porosity and eventually weakens the film structure.

Friction and Endurance Tests with Sputtered Cr_3C_2 and Cr_3Si_2

Sliding friction tests. Fig. 7 compares the coefficients of friction for a 440C stainless steel rider sliding on a 440C disk with 0.2-μm-thick sputtered Cr_3Si_2 and Cr_3C_2 films, respectively, as a function of applied loads from 50 to 250 g. The tests were conducted in a vacuum of 10^{-4} torr with a sliding speed of 80 rpm. Under identical experimental conditions, the Cr_3C_2 film had a coefficient of friction from two to three times higher than that of the Cr_3Si_2 film. A typical wear track for sputtered Cr_3C_2 on a 440C disk run at 250-g load and speeds of 80 rpm for 5 minutes is shown in Fig. 8. Wear damage can be observed on the right side of the wear track. When the wear debris of the film was examined by SEM, besides the film fragments that appear planar, sparsely scattered spherical balls were also seen (Fig. 9). At this time it is difficult to explain the exact source or reasons for their formation; however, two reasons can be offered: (1) the reduction in surface energy of the deformed wear particles to a lower energy state favors the spherical shape, and (2) spherical crystallites may be dislodged from the surface (Fig. 6) as can be seen by observing the surface structure of the film.

Bearing tests with sputtered underlayer of Cr_3Si_2 covered with sputtered MoS_2 film. A series of bearing endurance tests were conducted where the races and cages were sputter coated with a 0.1-μm-thick underlayer of Cr_3Si_2 film and subsequently covered with a sputtered MoS_2 film about 0.6 μm thick. This combination showed a significant improvement in endurance over bearings that were sputter coated directly only with a 0.6-μm-thick film of MoS_2. A comparison of these endurance lives is shown in Fig. 10. The endurance life with the Cr_3Si_2 underlayer was over 1000 hours, as compared with 187 hours for the directly sputtered MoS_2 films. Since 1000 hours (10.5×10^7 cycles) was selected as the maximum endurance limit, the tests were discontinued once that limit was reached. The Cr_3Si_2 underlayer was applied so as to coat the bearing surfaces with a very hard, thin, glassy, surface finish. The primary objective was to contour the surface asperities with a uniform adherent film that would act as a barrier to the movement of dislocations during asperity deformation. This was anticipated to have a tendency to hinder direct metal-to-metal contact, which otherwise could occur and lead to metallic seizure.

SUMMARY OF RESULTS

The microstructural appearance of sputtered Cr_3C_2, Cr_3Si_2, and $MoSi_2$ films as evaluated by electron transmission, scanning electron microscopy, actual sliding contact, and rolling-element bearing tests revealed the following results:

1. The sputtered silicide and carbide films adhered strongly to the substrate.

2. The particle size of the sputtered film contributes to its high density and strength.

3. Internal stresses become more apparent with film thicknesses in excess of 1.5 μm.

4. Depending on the substrate topography, crystallographic defect structures can be formed in the matrix. These defect structures are detrimental to friction and wear surfaces.

5. During sliding friction, Cr_3Si_2 films exhibited a coefficient of friction two to three times lower than that of Cr_3C_2.

6. Bearings coated with 0.1 μm of Cr_3Si_2 and subsequently with 0.6 μm of MoS_2 had considerably longer (fivefold) endurance lives than bearings sputtered with only MoS_2.

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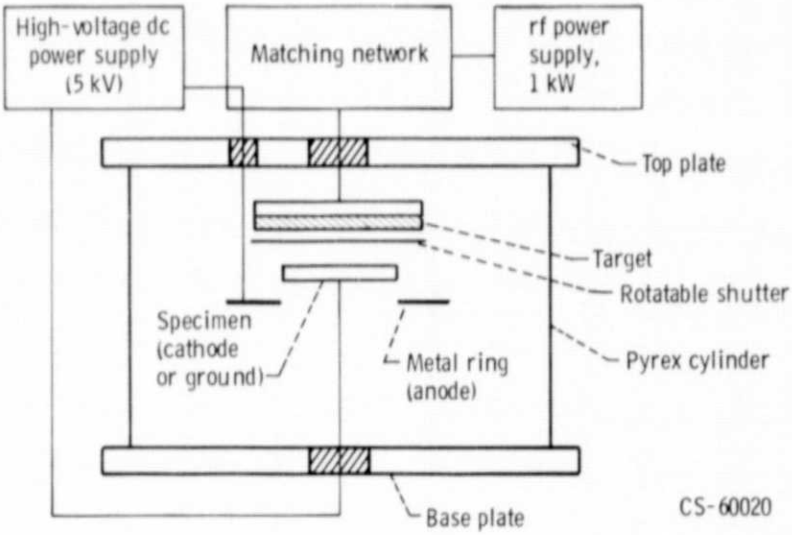
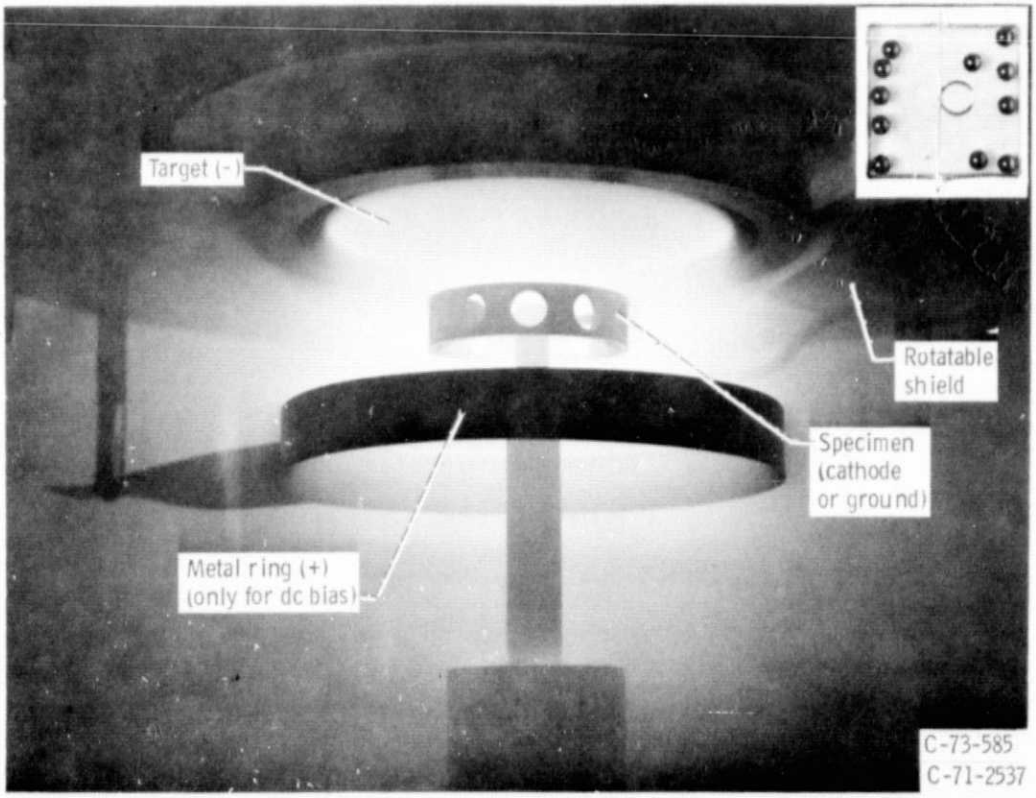


(a) Schematic diagram.



(b) View of apparatus during sputter coating.

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

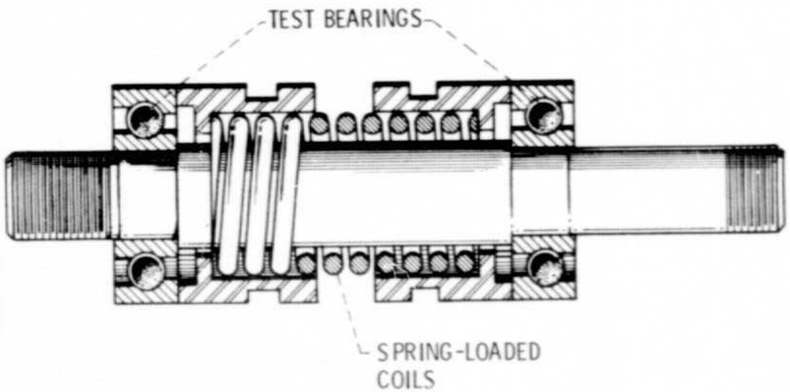


Fig. 2. - Schematic of vacuum bearing endurance assembly.

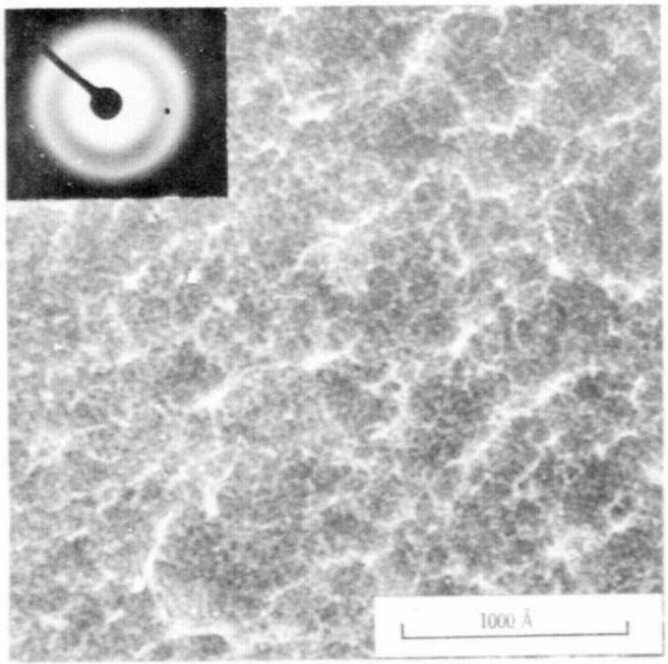


Figure 3. - Electron transmission micrograph and diffractogram of sputtered Cr_3Si_2 on copper.

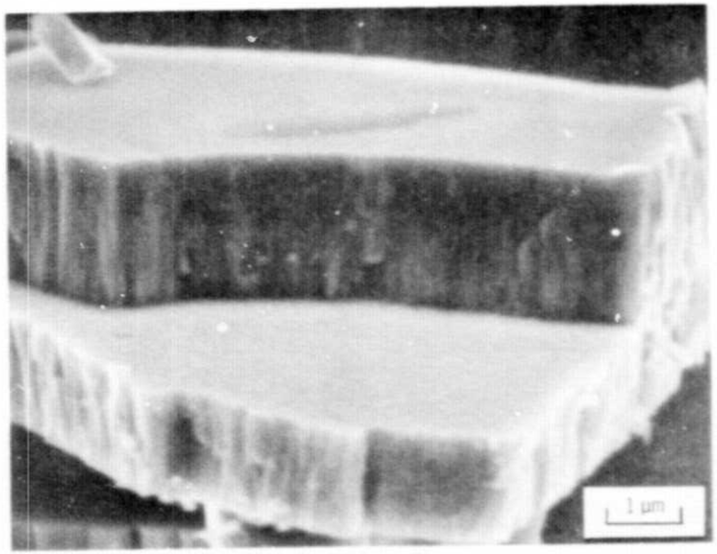


Figure 4. - Separation within a 3.5 μm film of sputtered Cr_3C_2.

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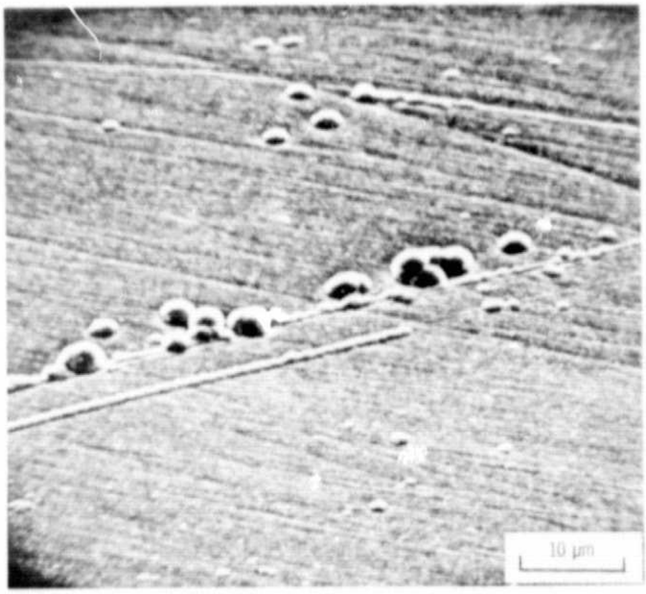
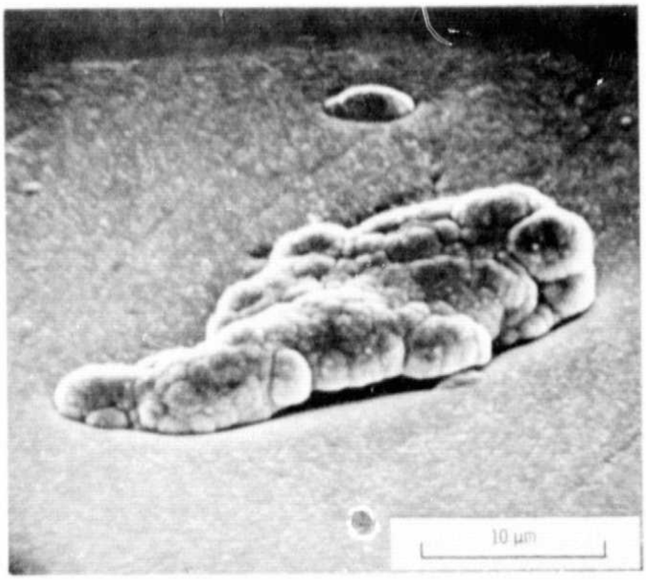
(a) Overlapping nodule.



(b) Isolated and fused nodules.



(c) Extreme localized outgrowth.

Figure 5. - Fracture cross section and surface view of sputtered $MoSi_2$ and Cr_3C_2 film.

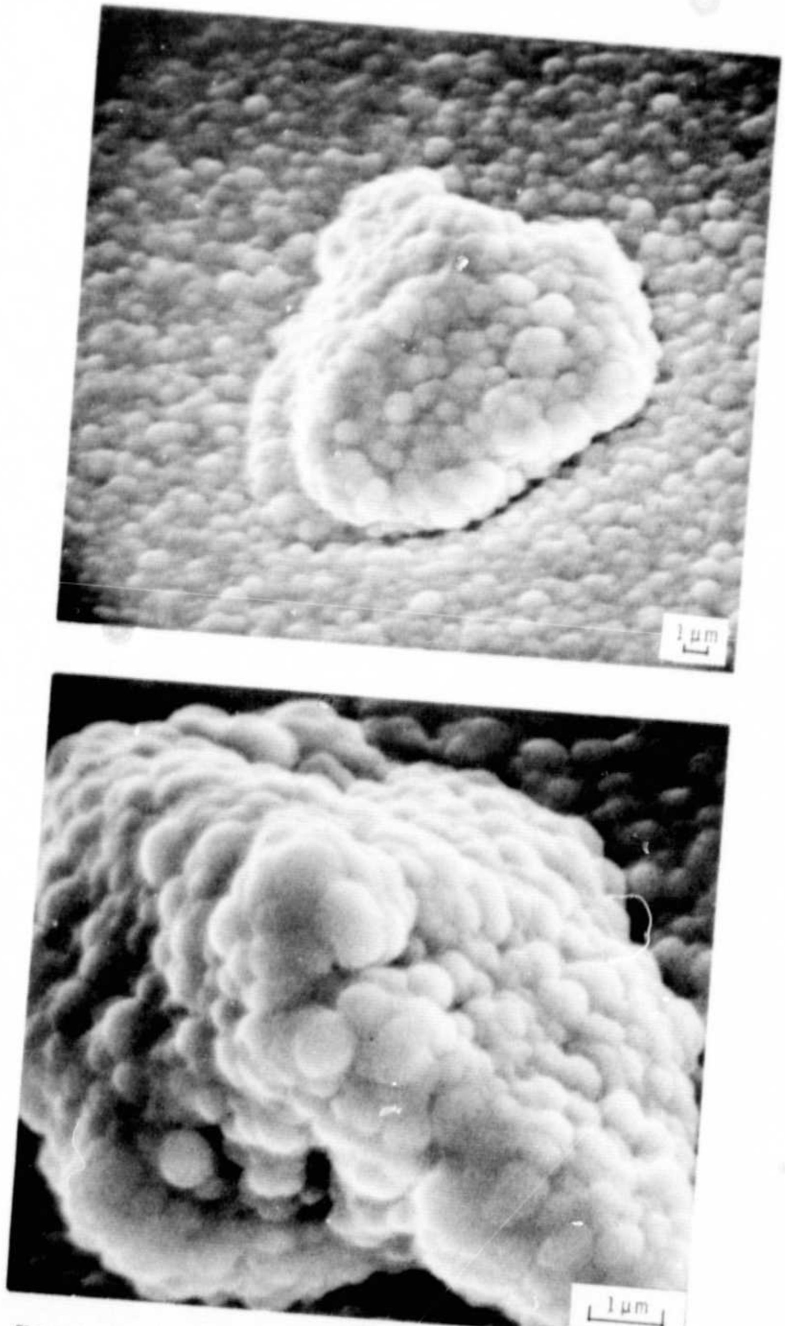


Figure 6. - Surface structure of the nodule and the matrix of sputtered Cr_3C_2.

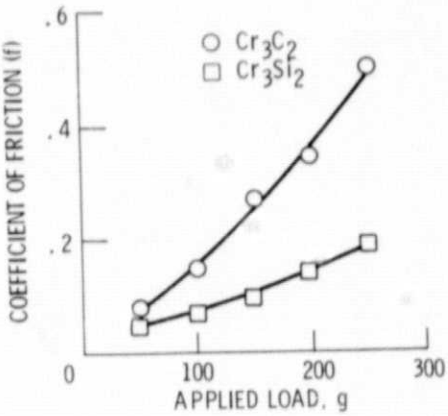


Fig. 7. - Coefficient of friction as function of load for 440C rider sliding on 440C disk with sputtered Cr_3C_2 and Cr_3Si_2. Film 2000 Å thick.

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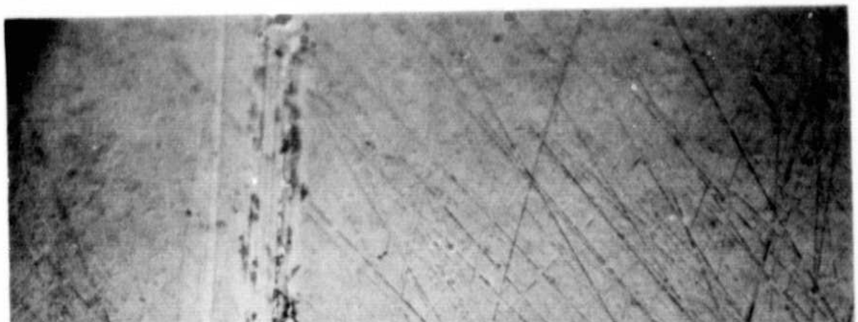

Figure 8. - Wear track of sputtered Cr_3C_2 on 440C disk.

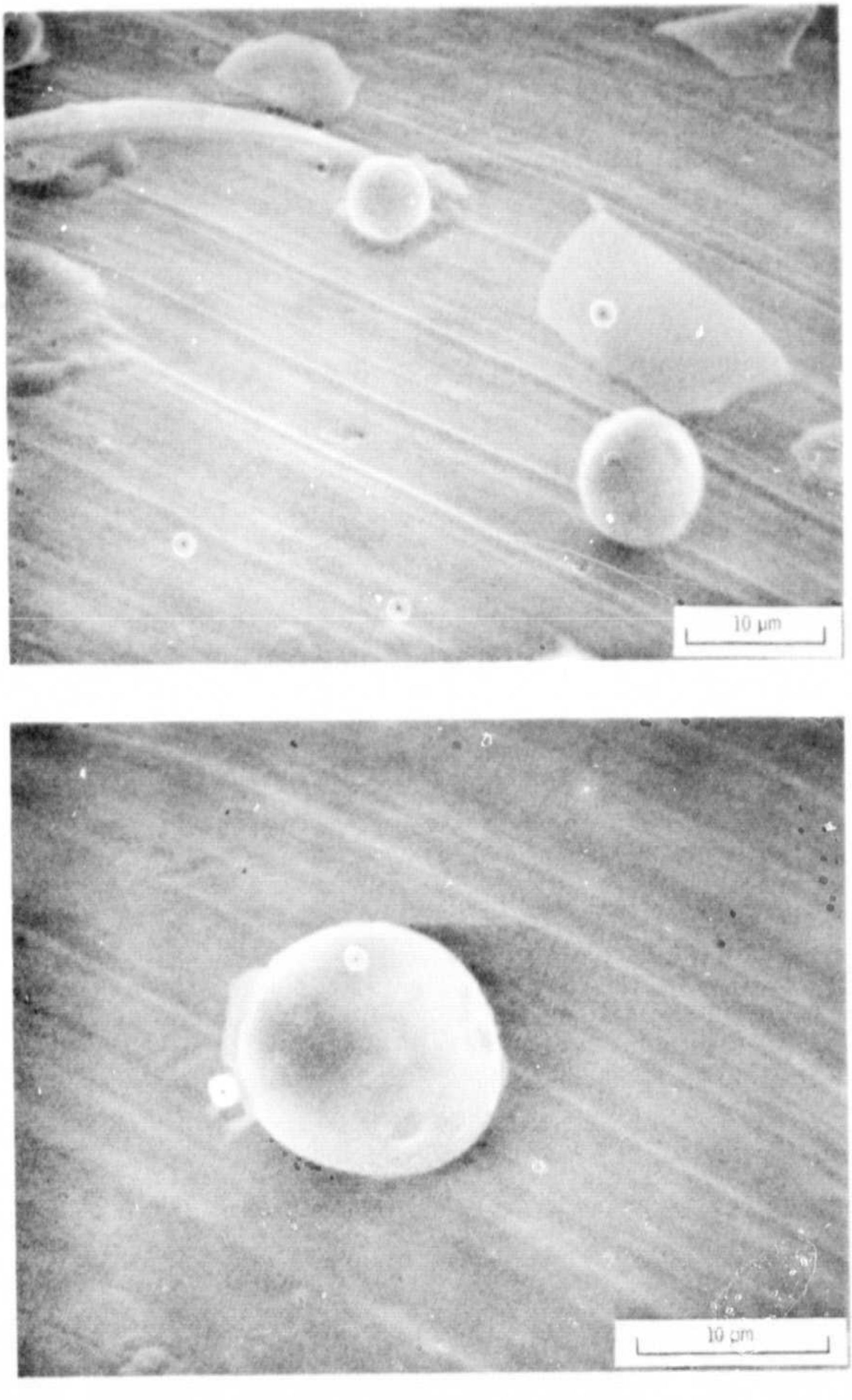

Figure 9. - Wear debris of sputtered Cr_3C_2 film.

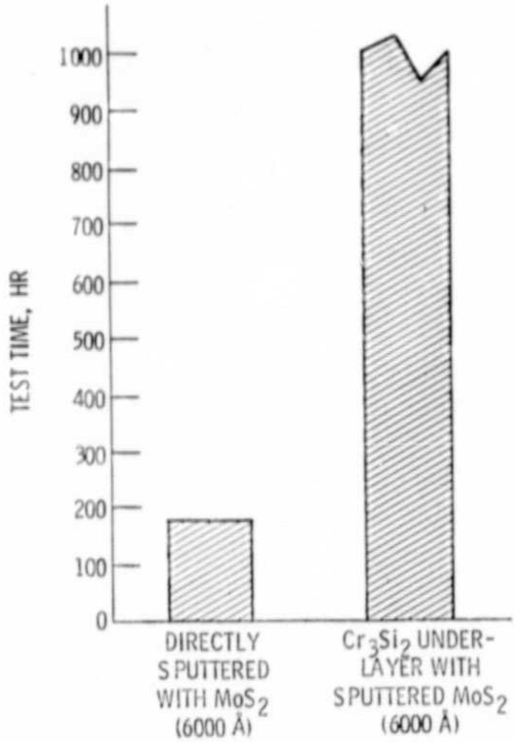

Fig. 10. - Endurance lives of 440C stainless-steel ball bearings with sputtered MoS_2 films on races and cage - with and without a Cr_3Si_2 underlayer.

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