SOLID LUBRICANT MATERIALS FOR HIGH TEMPERATURES - A REVIEW*

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Solid lubricants that can be used above 300 °C in air are discussed. The scope of the paper includes coatings and self-lubricating composite bearing materials. The lubricants considered are representative dichalcogenides, graphite, graphite fluoride, polyimides, soft oxides, oxidatively stable fluorides, and hard coating materials. A few general design considerations revelant to solid lubrication are interspersed throughout the paper.

INTRODUCTION

This paper is a review of selected research data which illustrate the tribological properties of materials that are likely to be or are now in use as high-temperature solid lubricants. The term "high temperature" is relative to one's frame of reference; therefore a definition is necessary. For this paper we will somewhat arbitrarily define "high temperature" solid lubricants as those that will not rapidly oxidize or otherwise thermally degrade in air at temperatures to at least 300 °C. Above this temperature most oils, greases, and all but a few organic polymers are not oxidatively stable for any appreciable time.

The scope of this paper includes coatings and self-lubricating composites. The materials considered are representative dichalcogenides, graphite, graphite fluoride, polyimides, soft oxides, oxidatively stable fluorides, and hard coating materials. A few general design considerations relevant to solid lubrication are interspersed throughout the paper.

LAYER LATTICE SOLID LUBRICANTS

Layer lattice solid lubricants have a hexagonal-layered crystal structure. Their shear properties are anisotropic with preferred planes for easy shear parallel to the basal planes of the crystallites. In some of the compounds such as molybdenum disulfide (MoS_2), a low shear strength is intrinsic to the pure material. In others, notably graphite, the presence of absorbed gases or intercalated "impurities" between the basal planes appears to be necessary to develop desirable friction characteristics (ref. 1).

The most common representatives of this class of lubricants are graphite and the dichalcogenides, notably MoS_2 and WS_2. Since a large volume of literature exists for these materials (e.g., ref. 2), they will not be discussed in detail here except to emphasize the importance of chemical reactivity in determining the suitability of a solid lubricant for a specific application. The maximum useful temperatures for solid lubricants depends strongly on the composition of the ambient atmosphere, the required life at temperature, and factors

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such as oxygen availability at the lubricated surface (is the coating openly exposed to the atmosphere or shielded within conforming bearing surfaces), airflow rates, lubricant particle size, and the influence of adjuvants and binders.

The Dichalcogenides

The maximum temperature for lubrication with MoS_2 in an air atmosphere is limited by oxidation to about 400 °C under favorable conditions. Some oxidation kinetics data for loosely compacted MoS_2 powders of 1-μm average particle size are given in figure 1(a) (from ref. 3). At a modest airflow rate over the compact, 50 percent of the MoS_2 was oxidized to molybdic oxide (MoO_3) in 1 hour at 400 °C. At a six times higher airflow rate, the temperature for an oxidation half-life of 1 hour was reduced to 300 °C. Figure 1(b) compares the oxidation kinetics of MoS_2 and WS_2 at the lower airflow rate. It is interesting that the curves for MoS_2 and WS_2 intersect, with MoS_2 oxidizing more rapidly above about 340 °C. Friction experiments were conducted with a pin-on-disk apparatus using a hemispherically tipped pin in sliding contact with the flat surface of a rotating disk. A comparison of the oxidation data of figure 1 and the friction data of figure 2(b) (from ref. 3) shows that the loss of lubricating ability of MoS_2 and WS_2 in air coincides with the temperatures at which rapid conversion to the oxides occurs.

Figure 2(a) also shows that both compounds lubricate to much higher temperatures in a nonreactive argon atmosphere. In an inert gas or vacuum the maximum useful temperature is a function of the thermal dissociation rates rather than the oxidation rates of the lubricants. Thermal dissociation rates and the friction coefficients of molybdenum and tungsten disulfides, diselenides, and ditellurides in vacuum have been systematically studied (ref. 4). The major results, summarized in table I, indicate that the disulfides are the most stable, the diselenides are intermediate, and the ditellurides are the least stable. However, thin burnished films of the diselenides with their higher densities evaporate more slowly than the disulfides. Apparently for the very thin, burnished films used in this study, the evaporation rates were the controlling factor in determining the maximum temperature for effective lubrication. A more recent paper described the thermal stability and lubricating characteristics of various bonded MoS_2 coatings in vacuum (ref. 5). The limiting temperatures for a significant wear life of these coatings ranged from 600 to 700 °C in agreement with the 650 °C limiting temperature for burnished MoS_2 reported in reference 4.

Graphite

Although MoS_2 and WS_2 are "intrinsic" solid lubricants that are most effective in a vacuum or a nonreactive gas atmosphere, it has been long known (ref. 6) that graphite, in contrast, is a poor intrinsic lubricant that requires the presence of absorbed vapors such as water or hydrocarbons to develop good lubricating properties. Certain solid adjuvants such as cadmium oxide (CdO) and other oxides or salts are also helpful in improving the lubricating ability of graphite. Figure 3 (from ref. 7) illustrates the remarkable effect of CdO addition on lubrication with graphite powder from room temperature to 540 °C. Without the CdO addition graphite lubricated at room temperature and above

425 °C but not at intermediate temperatures. Low friction at room temperature was attributed to the beneficial effect of absorbed moisture. High friction at intermediate temperatures was attributed to desorption of water and possibly other gases. Low friction above 425 °C was attributed to interaction of graphite with oxides of the lubricated metal. Graphite itself begins to oxidize at about 400 °C. Nevertheless it has been reported that graphite can be used as a wire-drawing lubricant for tungsten and molybdenum at temperatures as high as 1100 °C in ambient air conditions (ref. 8). Oxidation of graphite and of the metals occurs rapidly at the drawing temperatures. However, the time at high temperature is so short that effective lubrication is achieved. Therefore high-temperature lubrication must take into account the interaction of the lubricant, the atmosphere, and the surface being lubricated and must further balance reaction rates against the required residence time of the lubricant within the contact.

Graphite Fluoride

Graphite fluoride $(CF_x)_n$, also referred to as carbon monofluoride (when $x = 1$) is a relatively new solid lubricant that can be loosely described as a layer lattice intercalation compound of graphite. It is prepared by the direct reaction of graphite with fluorine gas at controlled temperature and pressure. It is gray to pure white depending on its stoichiometry. The subscript "x" in $(CF_x)_n$ can vary from about 0.3 to 1.1. For $x \geq 1$, the compound is pure white, electrically nonconductive, and nonwettable by water (hydrophobic). There is some debate about whether $(CF_x)_n$ is a true intercalation compound because the basal planes of the graphite crystallites are distorted to a puckered, non-planar configuration when the compound is formed. However, there is no doubt that the original graphite crystal lattice is the primordial lattice from which the crystal structure of $(CF_x)_n$ is formed. The fluorine-to-carbon bonds are covalent, with the fluorine atoms located between the distorted basal planes. The spacing between the basal planes is expanded from 3.4 Å in graphite to 7.5 ± 1.5 Å in $(CF_x)_n$ (ref. 9). The crystal lattice expansion and the distortion of the carbon basal planes are schematically represented and compared with the crystal structure of graphite in figure 4. Although $(CF_x)_n$ is not known to oxidize in air, it decomposes thermally above about 450 °C to form carbon tetrafluoromethane, other low-molecular-weight fluorocarbons, and carbon (ref. 10).

Some early research on the lubricating properties of $(CF_x)_n$ was reported in reference 11. In this study, thin lubricating films of $(CF_x)_n$ were burnished on 440C and 301 stainless steel disks and evaluated in pin-on-disk experiments. Wear life and friction coefficient data for burnished $(CF_x)_n$ and MoS_2 films on 440C are compared in figure 5. Film failure was considered to be the time at which the friction coefficient exceeded 0.3. The $(CF_x)_n$ films were the more durable over the entire temperature range shown. Friction coefficients were for the most part well below 0.1 up to the failure temperatures of the coatings, which are indicated by the arrows in figure 5. Failure temperature was 400 °C for MoS_2 and 480 °C for $(CF_x)_n$. These failure temperatures correlate well with expectations based on the oxidation kinetics data for MoS_2 (fig. 1) and the previously referenced thermal decomposition temperature of $(CF_x)_n$. Similar results were obtained for the lubrication of 301 stainless steel with $(CF_x)_n$, but burnished MoS_2 films failed immediately on this alloy. General agreement with these results was obtained with burnished $(CF_x)_n$ by using a flat rub block on a cylinder specimen configuration (ref. 12).

$(CF_x)_n$ exhibits an extreme degree of plasticity within a lubricated contact. It has been observed (ref. 13) that all this ability to readily undergo plastic flow within the contact is a characteristic that all good solid lubricants have in common; nonlubricated solid particles tend to fragment within the contact and, if of sufficient hardness, will embed in one surface and abrade the other. To illustrate the two extremes, compare the plastic behavior of $(CF_x)_n$ shown in figure 6 with the brittle behavior of SiC in figure 7. MoS_2 and graphite also readily flow within a moving concentrated contact. The order of plasticity subjectively observed is $(CF_x)_n$ > MoS_2 > graphite.

Various resin binders have been used with $(CF_x)_n$ to achieve longer wear lives and higher load capacities than can be achieved with burnished films. Good results were generally obtained in regard to low friction and wear, but there is some discrepancy in the reported load capacity of the coatings in Falex V-block tests. Reference 14 for example reported a high load capacity for epoxy - phenolic resin - bonder $(CF_x)_n$, but the authors of reference 15 reported, on the basis of their Falex evaluation, that $(CF_x)_n$ is not considered to be suitable for use in heavy load application. Therefore $(CF_x)_n$ coatings may not be the lubricant of choice for highly loaded, concentrated (Hertzian) sliding contacts. However, there are $(CF_x)_n$ coatings that have quite adequate load capacity for lubricating bearings with conformal contacts such as plain spherical bearings or cylindrical bushings. Polyimide-bonded $(CF_x)_n$ in particular has been extensively studied and will be discussed in the next section.

POLYIMIDES

Polyimide Coatings

A few organic polymers are oxidatively stable and also have glass transition temperatures above 300 °C. Examples are polyquinoxilines, polybenzimidazoles, and polyimides. Of these, the polyimides are by far the most readily available and have been the most studied by tribologists. Polyimide coatings have been studied as self-lubricating varnishes (ref. 16) and as resin binders for inorganic solid lubricants (refs. 16 and 17).

The results of pin-on-disk experiments with polyimide varnish coatings on 440C stainless steel are given in figure 8. Wear life and friction characteristics were determined in three different atmospheres: dry argon, dry air, and air containing 10^4 ppm of water vapor. In all these atmospheres there is a transition in the friction and wear life properties of the polyimide films between 25 and 100 °C. Above the transition temperature polyimide films performed well as solid lubricants. Low friction and long wear lives were obtained even with no solid lubricant additive in the film. At room temperature the polyimide films did not lubricate nearly as well as they did from 100 to 500 °C. This transition in the tribological properties of polyimide has been attributed to second-order relaxation in the molecular bonds of the polymer between 25 and 100 °C (ref. 18).

Polyimide-Bonded Graphite Fluoride Coatings

The effect of adding $(CF_x)_n$ or MoS_2 to the polyimide varnish is illustrated in figure 9. The solid lubricant additions clearly improve the wear life and friction at room temperature. In effect, the undesirable friction transition below 100 °C is totally masked by the addition of the solid lubricant pigments.

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A promising application for polyimide-bonded $(CF_x)_n$ coatings is as a backup lubricant for compliant (foil) gas bearings at temperatures to 350 °C. About 100 °C higher gas temperature capability can be achieved by substituting PI-bonded $(CF_x)_n$ for the more conventional PTFE coatings. Current research by this author shows that these coatings are remarkably durable in start-stop endurance testing of foil bearings.

Polyimide Composites, Background

Polyimides are also used in heat-cured composite bearing materials. It is shown in references 19 to 21 that polyimide and polyimide compositions containing various powder fillers had interesting possibilities as self-lubricating bearing materials. Polyimide bearing materials with powdered solid lubricant additives such as graphite and MoS_2 have found many applications. However, the powdered additives significantly reduce the mechanical strength of the molded polyimide. A polyimide with a compressive strength of 207 MPa (30 000 psi) without additives will typically have about one-half of that compressive strength when 10 to 20 wt % of solid lubricant powder is incorporated into the polymer. However, lubricating properties can be improved with no loss of strength by using graphite fiber, which provides both lubrication and reinforcement.

The potential of graphite-fiber-reinforced polyimide (GFRPI) as a self-lubricating composite material was first demonstrated in accelerated crossed-cylinder wear tests (ref. 22). The performance of GFRPI in oscillating plain spherical bearings was reported in reference 23; in that research chopped graphite fiber reinforcement was used. The fibers were incorporated into the B-staged polyimide and mixed to achieve a random fiber distribution; then the mixture was transfer molded into the bearing and cured under heat and pressure.

GFRPI composite bearing materials fabricated from layers of woven graphite fabric and polyimide have also been reported (e.g., ref. 24). The discussion in this paper is confined to chopped-fiber-reinforced bearing materials.

Chopped-Fiber-Reinforced Polyimides

Pin-on-disk studies. - The evaluation of chopped-GFRPI composites in a pin-on-disk tribometer is reported in reference 25. In these experiments hemispherically tipped 440C stainless steel pins were slid against the flat surface of rotating GFRPI disks. Two types of graphite fiber and two polyimides were evaluated. The fiber properties are given in table II. The fiber designated type L is a relatively low-strength, low-modulus fiber; the type H fiber has a medium tensile strength and an elastic modulus approximately 10 times higher than the type L fiber. The molecular structures of the two polyimides are given in figure 10. Type A is an addition polyimide and is highly crosslinked. Type C is a condensation polyimide and has a linear, essentially noncrosslinked polymeric structure. Type A polyimides do not produce water vapor as a product of the advanced stage of polymerization (as do type C) and therefore are sometimes considered easier to mold into void-free parts.

Figure 11(a) gives the friction characteristics of the various composites at 25 and 300 °C in air containing 10^4 ppm of water vapor. At 25 °C the friction coefficient is about 0.2 for all of the composites, but at 300 °C the

type AL composite has the lowest friction coefficient (~ 0.05). Profilometer traces (fig. 11(b)) of the wear tracks on the GFRPI disks after 300 000 sliding passes (disk revolutions) showed that the AL composites were also the most wear resistant at both temperatures.

Bearing tests. - Three self-aligning plain spherical bearing designs and cylindrical bushings were tested. The spherical bearing designs shown in figure 12 consisted of (1) a GFRPI spherical element in a steel outer ring; and (2) a steel spherical element and outer ring with a 1.5-mm-thick self-lubricating GFRPI liner transfer molded into the bearing and bonded to the outer ring.

In the first design tested, the spherical element was a molded composite ball of type AL GFRPI (ref. 23). Friction coefficients for various fiber loadings are shown in figure 13 for temperatures from 25 to 350 °C. Data for a conventional spherical bearing with a glass-fiber-reinforced PTFE liner are shown for comparison. Friction decreased in a regular manner with increasing graphite content. The composite ball with the highest fiber content of 60 wt % gave the lowest friction but failed by brittle fracture at 315 °C and a 35-MPa (5000-psi) radial load. It was concluded that a fiber loading between 45 and 60 percent is about the optimum tradeoff between minimum torque and maximum dynamic load capacity. The standard PTFE-lined bearing had very low friction to 200 °C, but the liner extruded out of the bearing at 250 °C.

When several modifications of the bearing designs shown in figure 12 were compared (refs. 26 and 27), it was found that the design variations had little influence on bearing friction (fig. 14) but had a significant effect on bearing load capacity (fig. 15). It is clear that much higher dynamic load capacity is achieved with a thin (1.5 mm) GFRPI liner between the ball and the outer ring than with a bearing consisting of a GFRPI ball and a metal outer ring. Dynamic load capacities for cylindrical bushings with GFRPI liners are reported in reference 28, and they were about the same as for the lined sphericals. In general, GFRPI-lined oscillating plain bearings for high-load, low-speed applications have dynamic load capacities of about 140 MPa (20 000 psi) from room temperature to 260 °C and about 70 MPa (10 000 psi) at 320 °C. Bearing design changes such as the addition of edge-retention features to prevent the liner from being squeezed out of the bearing at high loads are expected to further improve load capacity.

UNCONVENTIONAL SOLID LUBRICANTS

Soft Oxides and Fluorides, Fusion-Bonded Coatings

In a search for even higher temperature solid lubricants much research has been performed on various soft oxides and with fluorides of alkali metals and alkaline earth metals. Oxides are of course obvious candidates for consideration when oxidation-resistant compounds are required. The hard oxides, typical of ceramic materials, such as alumina, silica, and the silicates have good wear resistance but generally high friction coefficients. Furthermore unpolished surfaces or wear debris from hard oxides are abrasive to softer, metallic counterface materials.

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On the other hand, soft oxides such as lead monoxide (PbO) are relatively nonabrasive and have relatively low friction coefficients, especially at high temperatures, where their shear strengths are reduced to the degree that deformation occurs by plastic flow rather than brittle fracture. Binary and ternary eutectic oxide systems are of interest because the melting-point suppression, which is the primary characteristic of eutectic systems, tends to lower the shear strength relative to the individual oxides. If the second oxide is a vitrifying agent such as SiO_2, glaze (glass) formation is promoted at the sliding surface, and this also tends to modify friction by introducing a viscous component of shear. This increases or decreases friction depending on the viscosity of the glaze within the sliding contact. Therefore the friction characteristics of an oxide coating are controlled by a mechanism involving either or both crystalline shear and viscous drag.

Increasing the surface temperature reduces both crystalline shear strength and glass viscosity within the sliding contact and therefore tends to reduce the friction coefficient of oxide surfaces. This is illustrated in figure 16 (ref. 29), which gives the effect of ambient temperature and sliding velocity on the friction coefficients of a stainless steel alloy lubricated with a coating of $PbO-4PbO \cdot SiO_2$. At low sliding velocities the PbO coating lubricated effectively over only a very small temperature range of about 500 to 650 °C. With increasing sliding velocity frictional heating rates increased and low friction was achieved at ever lower ambient temperatures until at 6 m/sec friction coefficients of 0.2 or lower were observed from room temperature to 650 °C. Because of the narrow range of temperatures at which PbO lubricates effectively at low velocities, its use has been limited to high-speed, high-temperature applications such as the lubrication of dies for high-speed wire drawing.

Other studies showed that chemically stable fluorides of some Group I and II metals, such as LiF, CaF_2, and BaF_2, also lubricate at high temperature but over a broader range of temperatures than PbO. For example, coatings with compositions from the CaF_2/BaF_2 binary eutectic system lubricate from about 500 to 950 °C. The tribological properties in air of fused fluoride coating with the composition $62BaF_2-38CaF_2$ are given in figure 17 (ref. 30). Data for uncoated specimens are given for comparison.

The fluorides of the rare earth metals are another group of metal halides that are chemically stable and have shown promise as high-temperature solid lubricants. In an exploratory study of their lubricating properties cerium trifluoride (CeF_3) and lanthanum trifluoride (LaF_3) were the best solid lubricants among the rare earth fluorides (ref. 31). The individual CeF_3 or LaF_3 powders lubricated nickel-base super alloys in air to at least 1000 °C. Friction coefficients were 0.3 to 0.4 from room temperature to 500 °C but averaged about 0.2 at higher temperature. These compounds received little further attention in the lubrication literature but definately should be considered where friction coefficients of 0.2 to 0.4 combined with good antiwear characteristics at high temperature are required.

Coatings of oxide and fluoride compositions that melt at a lower temperatures than the substrate metal can be applied by well-known procedures for applying glass or porcelain enamel glazes. In brief, an aqueous slurry of the oxide or fluoride powders is sprayed onto the metal, cured to dryness, then furnace-fired above the melting point of the coating composition. Upon cooling, a fusion-bonded, dense coating is obtained. Good adhesion depends on reasonably matched thermal expansion coefficients and other factors such as the

nature of the high-temperature interactions that take place between the melt, the metal, and the atmosphere during firing. Fusion-bonded fluoride coatings can be applied by a similar procedure. However, while oxide coatings are generally fired in air, inert or reducing atmospheres are generally used for fluorides to avoid contamination of the coatings with oxides of the substrate metal.

Fluoride-Metal Composites

Composite bearing materials in which the solid lubricant is dispersed throughout the structure are advantageous when long lubricant life is required. In some cases a thin, bonded solid lubricant coating is used as an overlay on the self-lubricating composite material. This assures the minimum friction coefficient obtainable by enrichment of the composite surface with lubricant while providing long life because of the underlying, self-lubricating composite material. The friction and wear of a composite consisting of a porous, sintered metal matrix infiltrated with barium fluoride - calcium fluoride eutectic are shown in figure 18 (from ref. 32). Wear life comparisons for composite coatings in air and hydrogen are given in table III. Wear life is herein defined as the number of sliding cycles before the friction coefficient rises above 0.3. It is clear that the composites have longer endurance than the coatings. However, these composites are difficult and time consuming to prepare. The process involves preparing a sintered, porous metal matrix that is then infiltrated with molten fluorides at about 1000 °C, cooled, and finish machined. If an overlay is used, the coating material is next sprayed on from an aqueous slurry and then cured in an argon atmosphere at about 950 °C. Similar compositions can be prepared more conveniently by plasma spraying.

Fluoride-Metal Composite Coating

Mixed powders of, for example, CaF_2 and metal can be deposited by plasma arc spraying to form a composite coating on a wrought metal substrate. Excess coating material is applied, and the coating is then surface ground to the desired thickness (usually 0.010 to 0.020 cm) and a smooth surface finish. Two coatings of this type that have been successfully applied in extreme environments, for example, the space shuttle and the hot section of small jet engines, are designated PS100 and PS101. Their compositions by weight are

PS100:   67 nichrome, 16 1/2 calcium fluoride, 16 1/2 glass
PS101:   30 nichrome, 30 silver, 25 calcium fluoride, 15 glass

The glass in these compositions is a special sodium-free glass that protects the nichrome from oxidation. Its composition is 58 SiO_2, 21 BaO, 8 CaO, 13 K_2O.

Figure 19 (ref. 33) gives friction coefficients in air for oscillating journal bearings. The cylindrical bores of the bearings were coated with 0.025 cm of PS100 or PS101. A preoxidized, but otherwise uncoated, unlubricated bearing is included for comparison. The oxide film on the preoxidized bearing provided some protection against galling for a time, but the bearing seized at 870 °C. Friction coefficients for the bearing lubricated with PS100 were lower at all temperatures, and effective lubrication was achieved from about 500 to 900 °C. The beneficial effect of silver in reducing low-temperature friction while only

moderately reducing the maximum-temperature capability of the coating system is illustrated by the data for PS101. Friction coefficients of the order of 0.2 were obtained at all temperatures from room temperature to 870 °C.

The friction and wear data for bearings with PS101 lubrication, which were tested in moderate vacuum, cold nitrogen gas, and air, are summarized in table IV. The lowest bearing friction was observed in the 5×10^{-2}-torr vacuum, where the friction coefficient was 0.15. Wear rates tended to decrease with test duration. Total diametral bearing wear was 4.5×10^{-3} cm after 5000 oscil-lating cycles. In cold nitrogen (-107 °C) friction coefficients were typically 0.22 and diametral wear after 5000 journal oscillations was 3.8×10^{-3} cm. As previously discussed, the friction coefficient in air from room temperature to 870 °C was approximately 0.2 over the entire temperature range. Wear rates also were uniformly low over the entire temperature spectrum. These results clearly demonstrate the versatility of PS101 for lubricating plain journal bearings over an exceptionally wide range of temperatures and atmospheric conditions.

In general, the maximum useful temperature in air for a fluoride coating with a superalloy matrix is limited by oxidation of the alloy. Even with a protective glass within the composite structure, the superalloy oxidizes more rapidly in the composite than in the wrought metal state. The oxidation tem-perature limit is about 900 °C for composites with a nickel superalloy matrix and about 650 °C for cobalt matrix coatings.

Fluoride-Oxide Composite Coatings

Because of the limitations imposed by oxidation of the metal matrix coat-ings, completely nonmetallic coatings are of interest. It has been reported that plasma-sprayed coatings of NiO containing about 15 percent CaF_2 have good high-temperature wear resistance (ref. 34). This coating is plasma sprayed onto seal bars for regenerators that are used in automotive gas turbine engines to improve thermal efficiency. The coatings must be wear resistant at high temperature while in sliding contact with a porous ceramic regenerator core. The core material is generally lithium-aluminum silicate (LAS), magnesium-aluminum silicate (MAS), or aluminum silicate (AS).

Current preliminary research at Lewis indicates that plasma-sprayed coat-ings based on zirconium oxide (ZrO_2) have attractive tribological properties. Figure 20 gives the friction and wear coefficients of plasma-sprayed ZrO_2-CaF_2 coatings with and without silver additions. In these experiments the coating was on the cylindrical surface of a rotating disk and placed in sliding contact with two flat nickel-base superalloy rub blocks. Both coating combinations had fairly high wear rates at room temperature, but wear rates were much lower for the ZrO_2-CaF_2 coating at 650 °C. Silver additions were detrimental and did not have the beneficial effect of improving room-temperature friction and wear that they had on the metal matrix composites. Wear of the uncoated metal shoes that slid against the coatings was low in all cases, indicating that the coatings were not particularly abrasive to the metal rub shoes. Friction coefficients were 0.4 at room temperature and 0.22+0.04 at 650 °C for the ZrO_2-CaF_2 coating. Higher temperature experiments will demonstrate whether these coatings have a maximum-temperature advantage over the metal matrix plasma-sprayed coatings.

VACUUM-DEPOSITED COATINGS

Vacuum-deposited coatings used in tribological applications fall into two main composition categories: soft lubricating coatings and very hard, wear-resistant coatings. The methods of application also are in two principal categories: sputtering and ion plating. These techniques have been rapidly adopted by industry especially for aerospace applications (refs. 35 and 36). A very large variety of vacuum-deposited coatings are becoming available; therefore only a few representative examples are discussed here.

Soft Solid-Lubricant Films (Sputtered)

The most common vacuum-deposited tribological coatings are sputtered dichalcogenides, especially MoS_2, and ion-plated soft metals such as gold, silver, and lead. These coatings are often very thin, of the order of 2000 to 5000 Å in thickness. Compounds such as MoS_2 are usually applied by sputtering because with proper procedures pure, essentially stoichiometric compounds can be deposited. In contrast, ion plating tends to dissociate chemical compounds. However, ion plating is an appropriate technique for depositing elemental metals because (1) dissociation is obviously not a problem; (2) high ion impact energies can be used to enhance adhesion; (3) excellent throwing power is achieved when coating parts with complex shapes; and (4) rapid deposition rates can be achieved.

The use of sputtering to deposit MoS_2 lubricating films was first reported in reference 37. The films were nearly stoichiometric, indicating minimal dissociation of MoS_2 by the sputtering procedure used. Figure 21 shows that the coatings, which were only about 2000 Å thick, had good durability in the sliding contact and low friction coefficients of 0.05 to 0.10 in vacuum. Unfortunately durability was much lower in air. For example, 204 size ball bearings with sputtered MoS_2 on the cage, balls, and races easily survived 1000 hours of operation in vacuum at 1750 rpm and a 138-N (31-lb) radial load, but when air was admitted into the vacuum chamber, the bearings failed in less than 1 hour (ref. 38). Figure 22 from the same reference shows an abrupt rise in the friction coefficient obtained with sputtered MoS_2 as the ambient air pressure was increased above about 300 torr. For air applications the thicker, more conventional bonded MoS_2 coatings are usually preferred; the sputter coatings are favored for vacuum applications.

Soft Metal Lubricant Films (Ion Plated)

The wear lives of ion-plated gold and vapor-deposited gold were compared in reference 39 with the following results. Figure 23 shows that ion-plated gold had nearly twice the wear life of the vapor-deposited film. Furthermore the friction coefficient of ion-plated gold increased gradually, giving adequate indication of impending failure, while the vapor-deposited film failed abruptly without warning. The longer wear life of the ion-plated film was attributed to its superior adherence to the substrate metal.

The use of ion-plated lead films for lubrication of ball bearings in vacuum has been reported (ref. 40). The ion-plated film generated less debris and torque variation than vapor-deposited lead. This was again attributed by the authors to the superior adherence of ion-plated films.

Sputtered Hard Coatings

Sputtered hard coating are used primarily for wear control. The oxidation temperatures and hardness of some important carbides and nitrides are compared in table V. Coatings of all of the compounds listed are hard enough to be expected to have good wear resistance if adequate bonding to the substrate can be achieved. However, a considerable variation in oxidation resistance exists. Chromium carbide, boron carbide, silicon nitride, and silicon carbide are oxidatively stable to at least 1000 °C; but tungsten and titanium carbides oxidize during long-duration exposure to air at temperatures above about 540 °C. Tungsten carbide tends to oxidize more rapidly than titanium carbide because its oxides are volatile at high temperature and their sublimation tends to accelerate the oxidation. Titanium nitride is another promising hard coating material, but it too will convert to the oxide above 550 °C. However, some TiC and TiN sputtered coatings have shown surprisingly good resistance to oxide conversion at higher temperatures than those listed in table V. Oxidation occurs, but the rate is very low, probably because of high coating density and the passivating nature of the initially formed oxide film, which protects the coating against catastrophic oxidation.

Sputtered chromium oxide (Cr_2O_3) is an interesting antiwear coating. In start/stop tests, an optimized, sputtered coating of Cr_2O_3 on nickel-chromium foil bearings has shown outstanding endurance over a wide temperature range (ref. 41). For example, the coating did not wear out after 9000 start/stop rubs against a journal coated with chromium carbide at temperatures from room ambient to 650 °C (ref. 42).

Great care is required in the sputtering process because reactive gases in the sputtering chamber can react with the sputtered material to alter its composition. This effect can be an annoyance, or it can be used to advantage in a process known as reactive sputtering in which controlled contaminants are intentionally introduced into the vacuum chamber to obtain the desired coating composition. It has been shown in reference 41, for example, that a controlled mixture of TiC and TiN can be codeposited by using a TiC target in combination with a partial pressure of nitrogen in the sputtering chamber.

CONCLUDING REMARKS

Solid lubricants for use above 300 °C were discussed. The more conventional layer lattice solid lubricants such as MoS_2 and graphite in the form of powders or bonded coatings are serviceable in air to 350 to 400 °C under proper conditions and can be used to much higher temperatures for short durations as, for example, in some metalworking processes. The high-temperature polyimides have about the same upper temperature limitations as MoS_2 and graphite and are conveniently used in the form of graphite-fiber-reinforced, self-lubricating composites. For higher temperatures some soft oxides and fluorides provide lubrication to as high as 900 °C. They are currently used as fused coatings (0.001 to 0.002 cm thick) on metal substrates or as the lubricating component of metal matrix composites. The composites are prepared by powder metallurgy methods or by plasma arc spraying. For wear control sputtered hard coatings of some selected carbides, nitrides, and oxides are serviceable to 1000 °C if adequate adhesion to the substrate is maintained at all temperatures required by the application. Thin, sputtered MoS_2 films, typically of 2000 to 5000 Å

thickness, are very effective in vacuum but of limited durability in reactive atmospheres such as air. Ion-plated films of soft metals such as gold and lead are effective lubricants particularly for solid-lubricated rolling contact bearings.

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TABLE II. - TYPICAL GRAPHITE FIBER PROPERTIES

Property or Characteristic	Type "L"		Type "H"	
	English Units	SI Units	English Units	SI Units
Tensile strength	9.0×10^4 lb/in^2	6.2×10^8 N/m^2	2.8×10^3 lb/in^2	2.0×10^9 N/m^2
Elastic Modulus	5.0×10^6 lb/in^2	3×10^{10} N/m^2	5.7×10^7 lb/in^2	3.9×10^{11} N/m^2
Length	0.25 in.	6.4×10^{-3} m	0.25 in.	6.4×10^{-3} m
Diameter	3.3×10^{-4} in.	8.4×10^{-6} m	2.6×10^{-4} in.	6.6×10^{-6} m
Specific gravity	1.4	1.4	1.4	1.4

TABLE I. - RESULTS OF THERMAL STABILITY AND FRICTIONAL EXPERIMENTS IN VACUUM OF 10^{-9} to 10^{-6} TORR

Compound	Probable onset of thermal dissociation as detected by TGA, °C	Dissociation products first detected by mass spectrometry, °C	Maximum temperature at which burnished films provided effective lubrication, °C
MoS_2	930	1090	650
WS_2	870	1040	730
$MoSe_2$	760	980	760
WSe_2	700	930	760
$MoTe_2$	700	700	540
WTe_2	700	700	(a)

[a]Friction coefficient greater than 0.2 at all temperatures.

TABLE III. - COMPARATIVE WEAR LIFE OF FLUORIDE COMPOSITES AND COATINGS IN AIR AND HYDROGEN

Specimen temperature	Cycles at which friction coefficient increased to 0.30[a]			
	Air		Hydrogen	
	Composites	Coatings	Composites	Coatings
25·	(b)	(c)	[d]1 560 000	(c)
260	2 750 000	115 000	[d]1 499 000	(c)
540	1 105 000	389 000	[d]1 610 000	275 000
650	1 370 000	(c)	[d]1 370 000	(c)
816	850 000	(c)	570 000	(c)

[a]Based on single runs.
[b]Low wear rate but friction coefficient of 0.30 to 0.35.
[c]No test.
[d]Experiments terminated before failure. (Friction coefficient did not increase to 0.3 during number of cycles indicated.)

TABLE IV. - PERFORMANCE SUMMARY FOR OSCILLATING PLAIN

SLIDING BEARINGS SELF-LUBRICATED WITH A PLASMA-

SPRAYED COATING IN VARIOUS ATMOSPHERES

[PS101 Coating: 30 Ag, 30 NiCr, 25 CaF_2, 15 glass; 0.025 cm
(0.010 in.) thick; 3.5×10^7 N/m^2 (5000 psi) unit load, ±15°
oscillation at 1 hertz.]

Bearing temperature		Ambient atmosphere	Typical friction coefficient	Increase in radial clearance	
				cm ×10^3 (milliinches)	
°C	°F			After 100 cycles	After 5000 cycles
Room	Room	Vacuum 5×10^{-2} torr	0.15	1.3 (0.5)	4.5 (1.8)
-107	-160	Nitrogen	.22	0.3 (0.1)	3.8 (1.5)
Room	Room	Air 760 torr	.24	.5 (0.2)	7.0 (2.8)
540	1000		.19	.5 (0.2)	6.0 (2.4)
650	1200		.21	.3 (0.1)	2.5 (1.0)
870	1600	↓	.23	.3 (0.1)	2.5 (1.0)

TABLE V. - BULK PROPERTIES OF SOME HARD COAT MATERIALS[a]

Material	Microhardness, kg/mm^2	Oxidation temperature[b], °C
B_4C	4200	1090
TiC	3200	540
SiC	2900	1650
Cr_3C4	2650	1370
WC	2050	540
Si_3N4	2000	1400
TiN	1950	540
Cr_2O3	[c]1800	----

[a]Data from: Engineering Properties of Ceramic Materials,
Battelle Memorial Institute, Published by American
Ceramic Society, Columbus, Ohio, 1966.
[b]Temperature for appreciable detrimental oxidation (passi-
vating oxide films form at lower temperatures).
[c]Estimated conversion from published Moh hardness of 9.
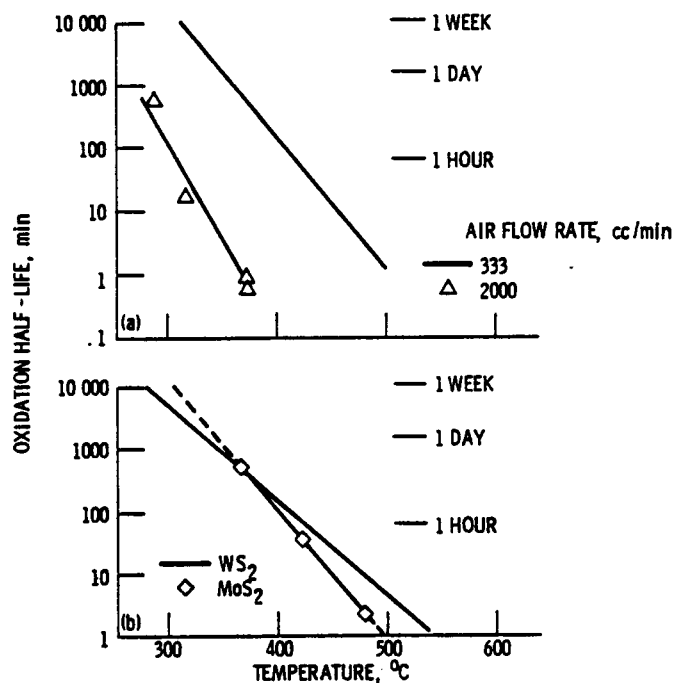
(a) Oxidation characteristics of MoS_2 at two air flow rates.

(b) Comparative oxidation of WS_2 and MoS_2 air flow rate, 1/3 L/min.

Figure 1. - Oxidation kinetics of MoS_2 and WS_2 average particle size: 1 μ, compact density; 50 %.
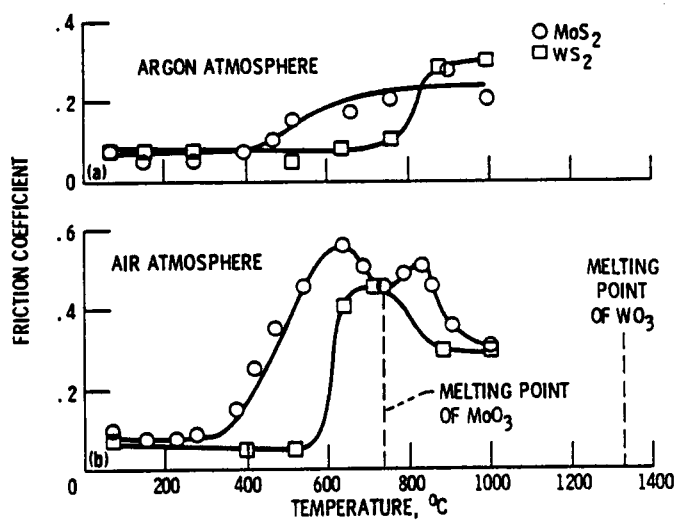
Figure 2. - Friction characteristics of MoS_2 and WS_2 in argon and in air.

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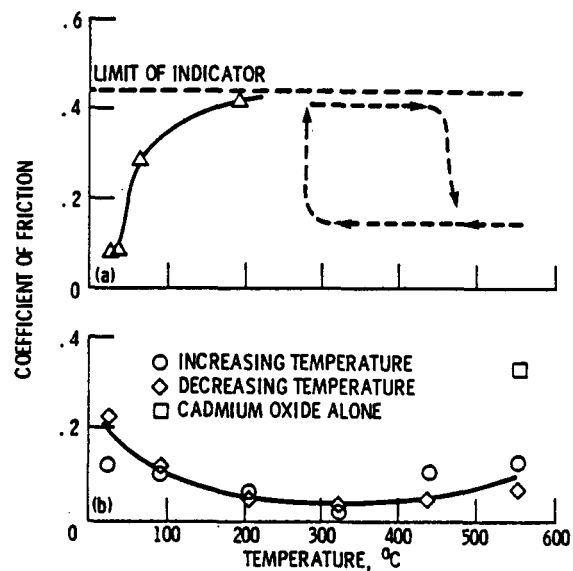
(a) Graphite alone.

(b) Cadmium oxide - graphite mixture.

Figure 3. - Effect of oxide adjuvant on lubrication with graphite.
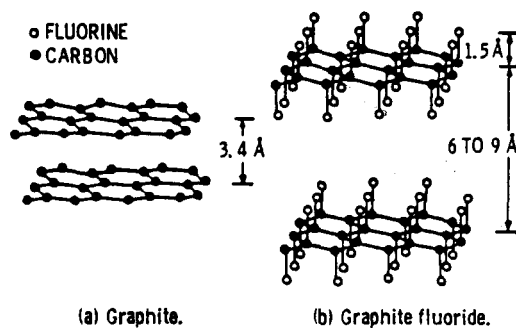
(a) Graphite.

(b) Graphite fluoride.

Figure 4. - Structure of graphite and proposed structure of graphite fluoride illustrating the expansion of the carbon layer planes due to the intercalation of fluorine atoms.
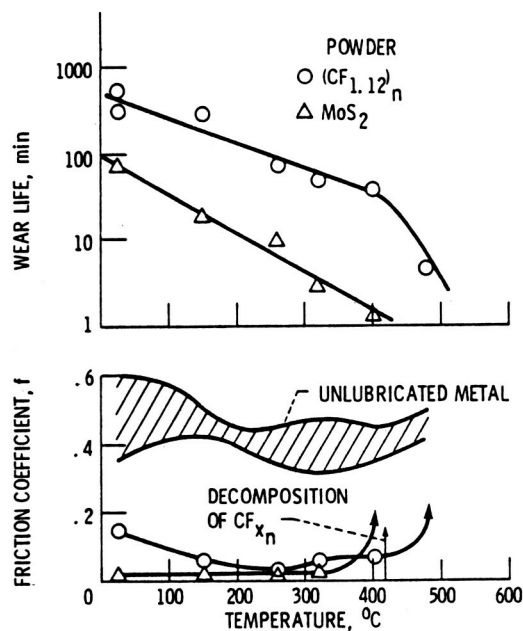
Figure 5. – Effect of temperature on wear life and friction coefficient of graphite fluoride ($(CF_{1.12})_n$) and molybdenum disulfide powders burnished on sandblasted 440-C stainless-steel disks. Riders, 440-C stainless steel; linear sliding speed, 1.6 m/s; load, 500 g; atmosphere, dry air (moisture content, 20 ppm).

(a) FIRST PARTICLES ENTERING CONTACT.

(b) PROGRESSIVE FILM FORMATION.

(c) PROGRESSIVE FILM FORMATION.
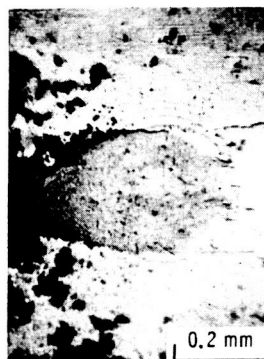
(d) COMPLETE FILM FORMATION AFTER ONLY 10 mm OF SLIDING.

Figure 6. – Behavior of graphite fluoride in initially unlubricated contact. Load, 13.2 N (3 lb); original magnification, X150.

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(a) SiC PARTICLE ENTERING CONTACT.

(b) PARTICLE PART WAY THROUGH CONTACT.

(c) PARTICLE AT CONTACT EXIT.

(d) CONTACT AFTER 10 DISK REVOLUTIONS.
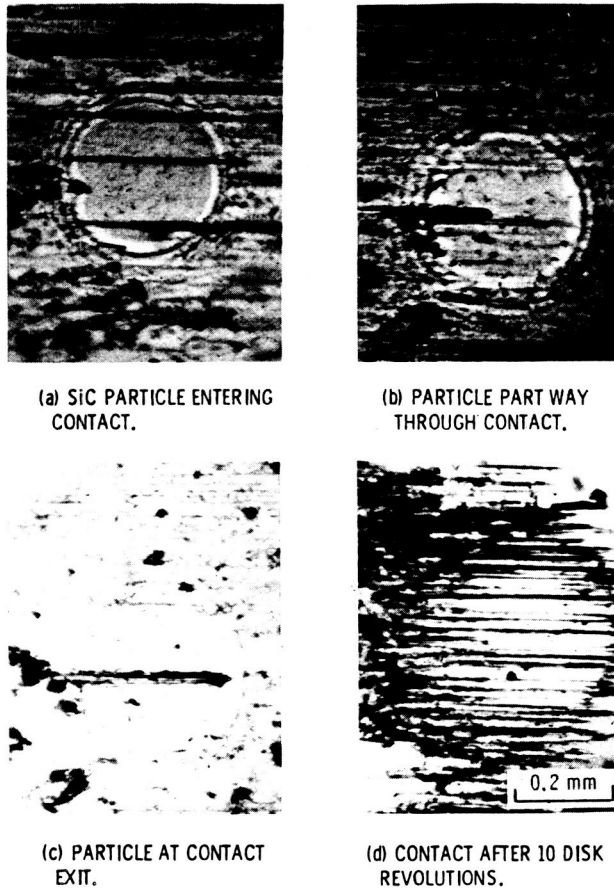
Figure 7. - Abrasive action of silicon carbide particles. Load, 13.2 N (3 lb); original magnification, X150.
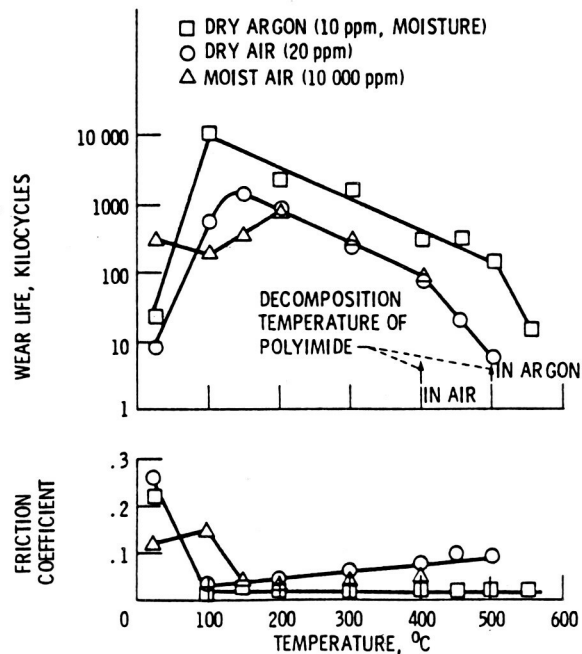
Figure 8. - Friction coefficient and wear life as a function of temperature for thin films of polyimide run in atmospheres of dry argon, dry air, and moist air. Load, 1 kg; velocity, 3 m/sec.

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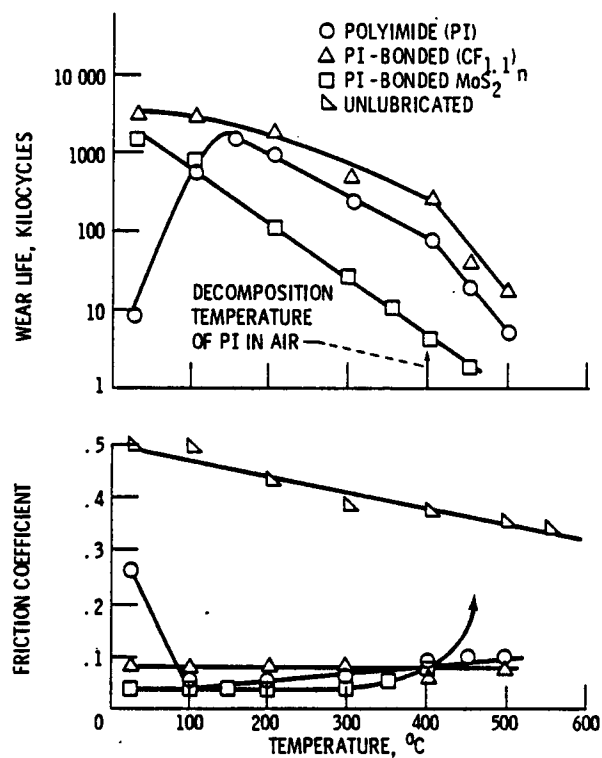
Figure 9. - Friction coefficient and wear life as a function
of temperature for three solid lubricant films run in dry
air (moisture content, 20 ppm). Load, 1 kg; velocity,
3 m/sec.
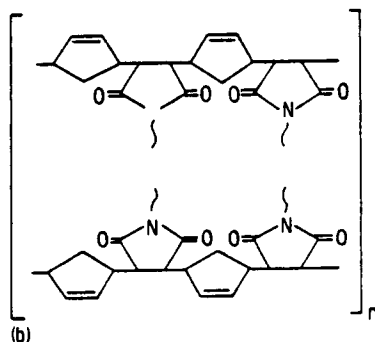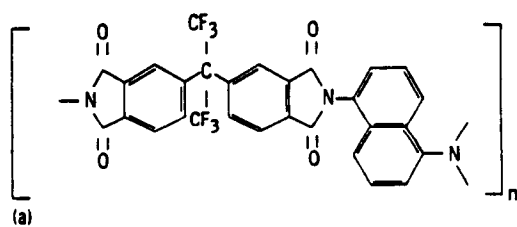
(a) Condensation-type of polyimide polymer (type "C").

(b) Addition-type of polyimide polymer (type "A").

Figure 10. - Two major types of polyimide structures.

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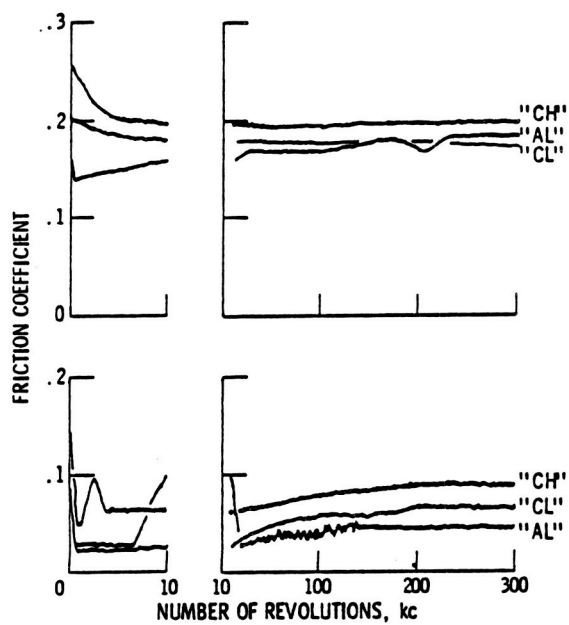
(a) Friction coefficients.
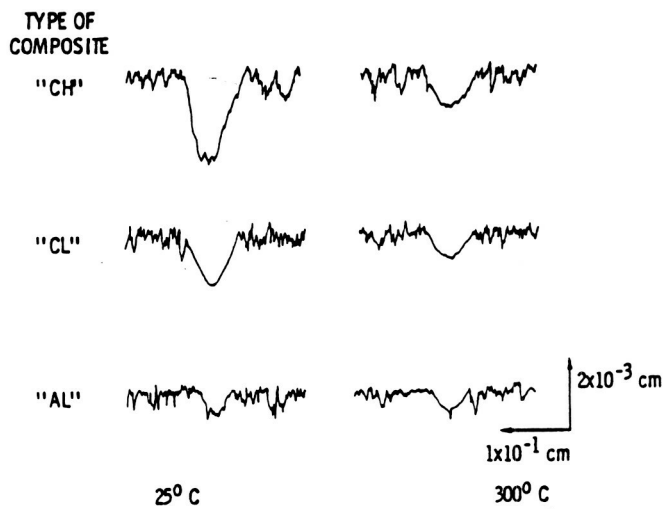
(b) Surface profiles of wear tracks after 300 000 cycles of sliding.

Figure 11. - Friction and wear of graphite fiber reinforced polymide composites in moist air atmospheres (10 000 ppm H₂0).
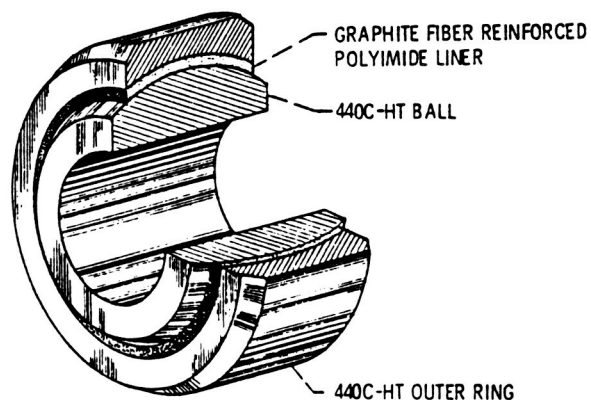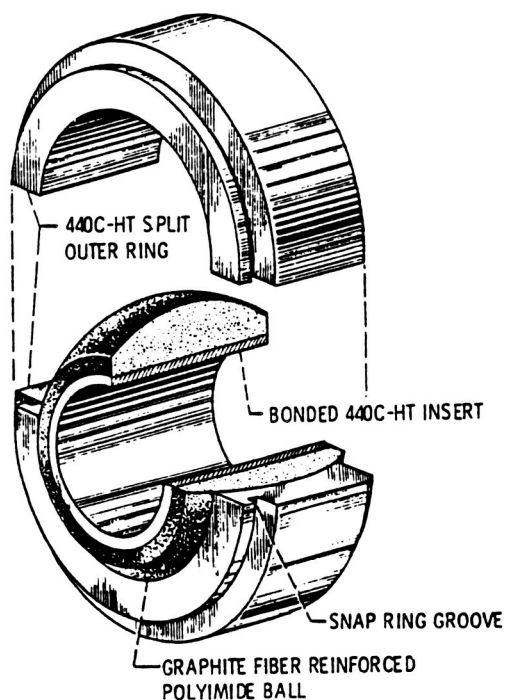
Figure 12. - Test bearings employing graphite fiber reinforced polyimide.

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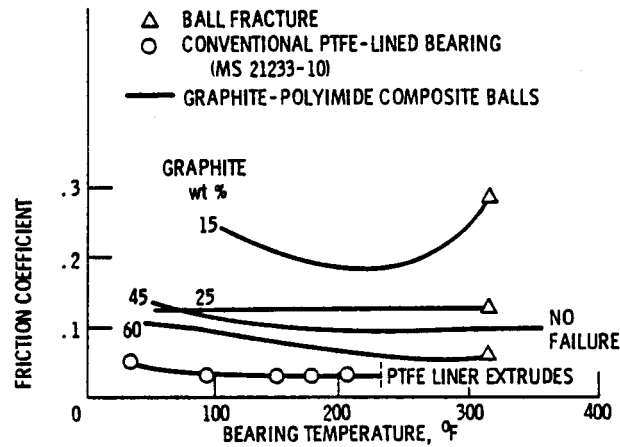
Figure 13. – Summary of friction of spherical bearings with polyimide – graphite-fiber composites of various fiber contents. Stellite 6B journal; radial unit load, 3.5×10^7 N/m² (5000 psi); journal oscillation in cylindrical bore at 1 Hz, ±15°.
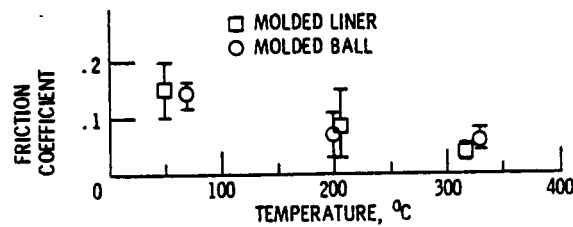
Figure 14. – Friction-temperature characteristics of two bearing designs lubricated with GFRPI composite.
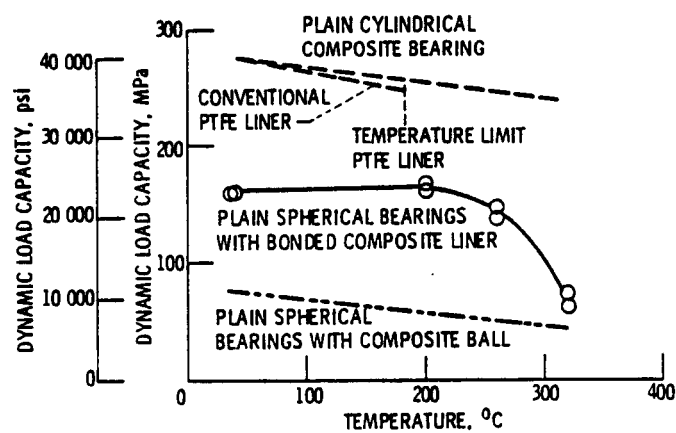
Figure 15. – Dynamic unit load capacities of three bearing designs self lubricated with GFRPI composite.
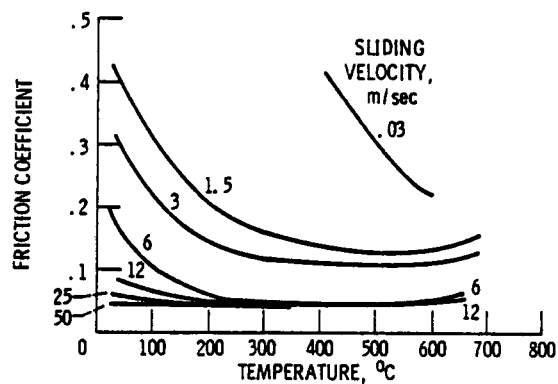
Figure 16. - Effect of sliding velocity and temperature on friction properties of bonded PbO-SiO$_2$. 0.003 cm thick; load, 1000 g.
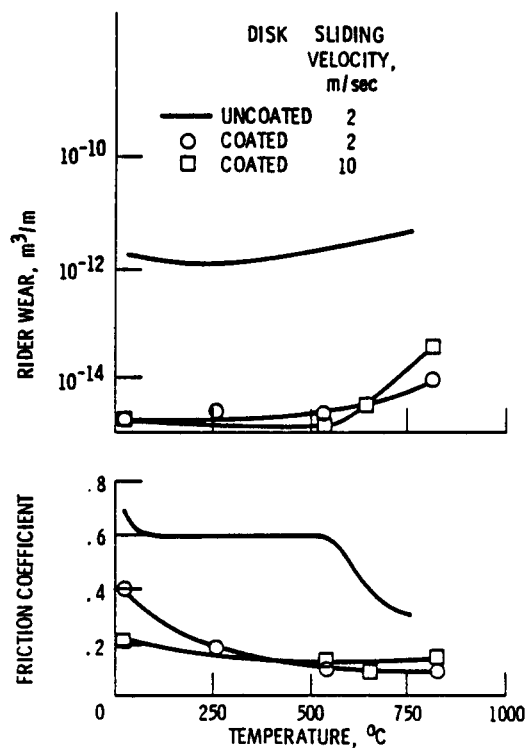
Figure 17. - Lubricating properties of 0.003 cm thick fused fluoride coating composition in air. Load, 500 g.
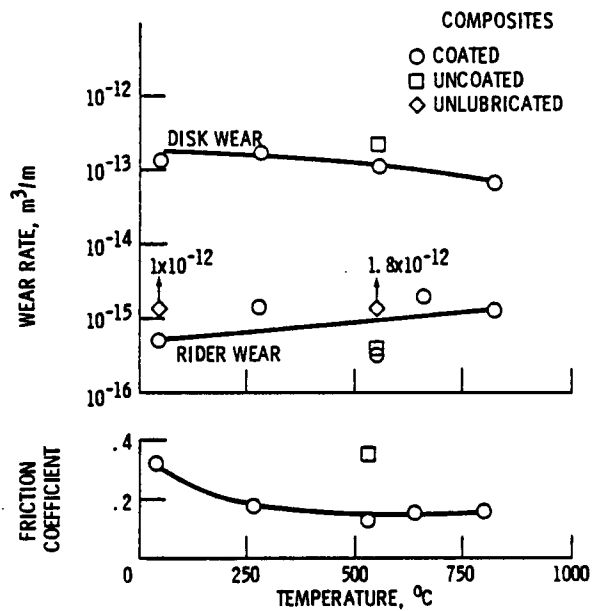
Figure 18. - Friction and wear of fluoride-Inconel composite disks and cast Inconel riders in air. (35 vol % BaF$_2$-CaF$_2$ eutectic, 65 vol % sintered Inconel; 500-g load, 10 m/sec.)
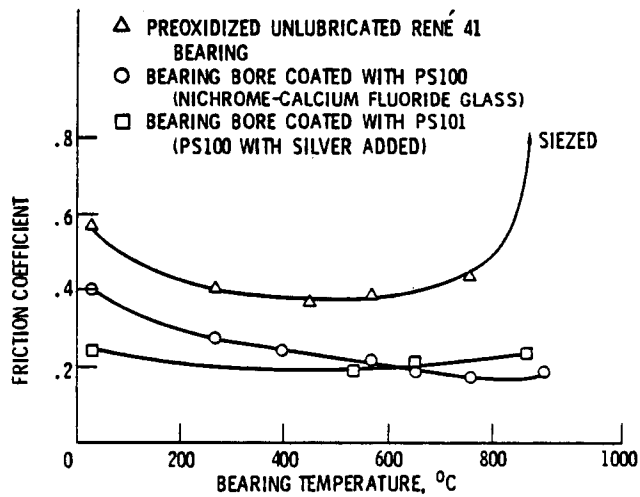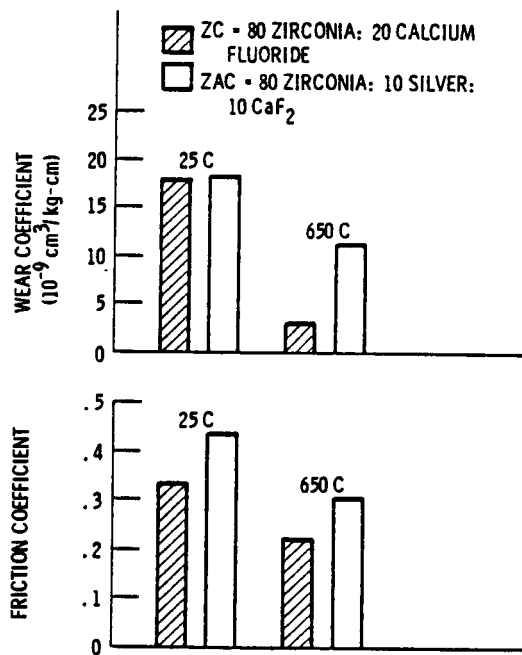

Figure 19. - Bearing friction.

Figure 20. - Wear and friction of plasma - sprayed coatings of zirconia and calcium fluoride, with and without silver. Double rub shoe tests with 22.7 kg per Inconel shoe against coated disk at 0.3 m/sec (150 rpm).
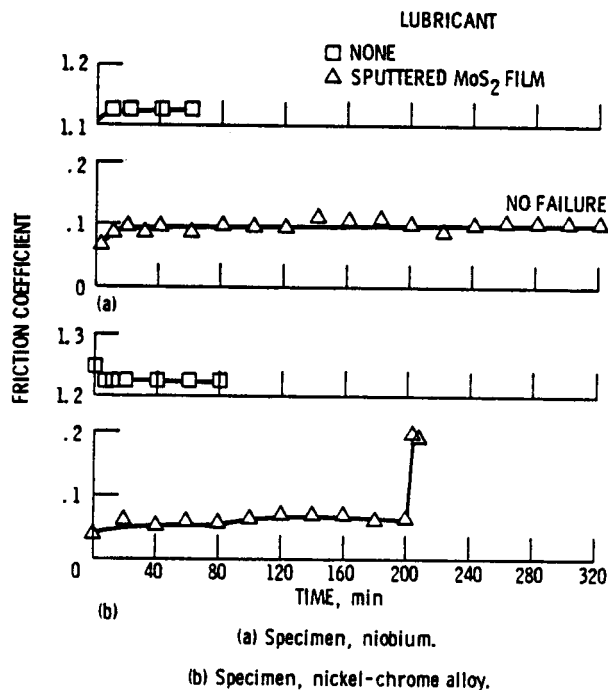

(a) Specimen, niobium.

(b) Specimen, nickel-chrome alloy.

Figure 21. - 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 g; speed, 2.54×10^{-2} m/sec; ambient temperature.
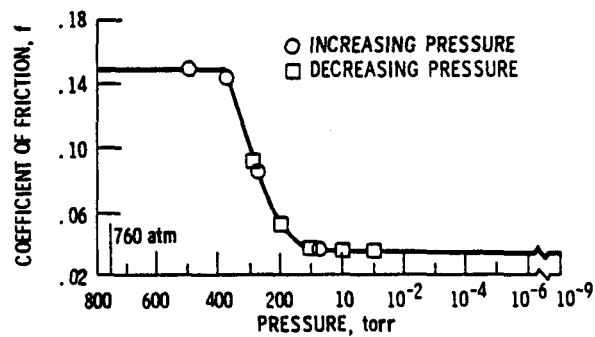
Figure 22. - Effect of pressure on coefficient of sliding friction for sputtered MoS_2. Load, 250 g; speed, 0.11 m/sec; substrate/rider, Ni/Ni; room temperature.
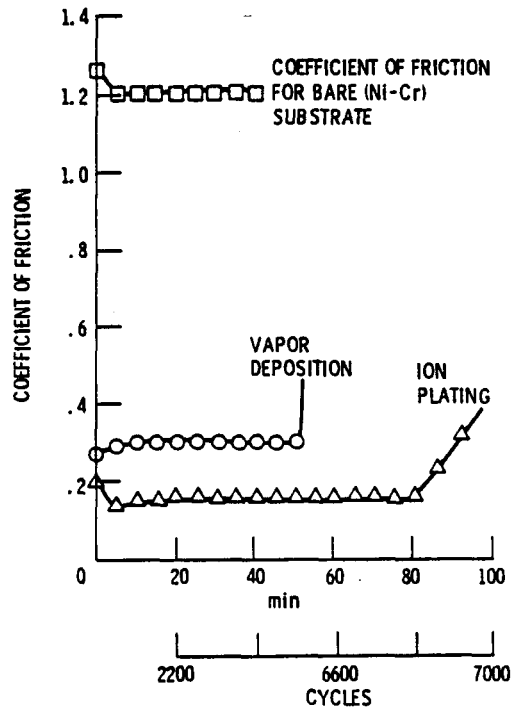

Figure 23. - Coefficient of friction of niobium sliding on (Ni-Cr) alloy with gold deposited by vapor deposition, and ion plating about 2000 Å thick (load, 250 g; speed, 1.52 m/min; ambient temperature 10^{-11} torr).

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