Solid Lubricants

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ABSTRACT

The state of knowledge of solid lubricants is reviewed. The subject is presented from a historical perspective, and presents the results of research on solid lubricants from the 1940's to the present. Emphasis is placed largely, but not exclusively, on work performed at NASA Lewis Research Center with a natural focus on aerospace applications. However, because of the generic nature of the research the information presented in this review is applicable to most areas where solid lubricant technology is useful.

FORWARD

The objective of this paper is to provide an overview of solid lubricants. No attempt has been made to cite every significant reference on the subject. References were selected largely, but not exclusively, from literature describing the results of research programs at NASA Lewis Research Center from the NACA era (pre-1958) to the present. The focus of this research has naturally been toward aerospace applications, but the generic nature of the research makes the results applicable to most areas of solid lubricant technology.

INTRODUCTION

Graphite and molybdenum disulfide (MoS2) are the most frequently used inorganic solid lubricants. Graphite and molybdenite (the naturally-occurring form of MoS2) were used for lubrication purposes prior to the Industrial Revolution. In the early applications, molybdenite was probably used because it looks like graphite and was mistaken for it - a good choice for the wrong reason. A significant technical literature on the subject of solid lubricants is of relatively recent origin. Some sporadic technical references to solid lubricants appeared prior to 1940. For example, (Paxton, 1979), cited an account by (Salto, 1906) of carbon as a brush material for electric motors, with an observation concerning the "unique self-lubricating properties of carbon." Winer (1967) in his excellent literature review of MoS2 as a
lubricant, cites some early patent literature that suggests the use of molybdenite as a lubricant, for example: (Cooper and Damerell, 1939). The first technical journal article cited by Winer describes MoS2 as a lubricant for vacuum, (Bell and Findlay, 1941). The earliest really substantial body of technical literature on solid lubricants appeared in the mid and late 1940's. The solid lubricants research of that era to the present is well-documented. An excellent review of the subject is given in the Chapter on "Nonconventional Lubricants" in the book Advanced Bearing Technology by Bisson and Anderson (1964). More recent examples of reviews of solid lubrication were authored by Sliney, (1974) and (1982) and Lancaster, (1984). This paper encompasses the period from about 1948 to the present (1991). The solid lubricants discussed include dichalcogenides (such as MoS2), graphite, graphite fluoride, and polyimides. Less conventional solid lubricants used under extreme temperature conditions include stable fluorides and lubricious oxides. Preparation techniques include air spraying, physical vapor deposition, plasma spraying, and powder metallurgy processes such as sintering and hot isostatic pressing.

CHARACTERISTICS OF SOLID LUBRICANT MATERIALS - There are some material properties that are characteristic of solid lubricants. Direct microscopic observations of the dynamics of solid lubrication show that sliding is accompanied by severe ductile shear of the solid lubricant film, (Sliney, 1978). This implies that to provide a low friction coefficient the solid lubricant must have low shear strength. If the lubricant is crystalline, shear occurs by slip along preferred crystallographic planes. This slip is observed as a severe plastic flow in which the individual solid lubricant particles coalesce into a continuous, crystallographically oriented thin film which adheres to the lubricated surfaces and shears within the film. Low shear strength alone does not insures lubrication if the material does not adhere to the lubricated surface. The importance of adherence of the solid
lubricant film was previously emphasized by Peterson and Johnson (1954) in a paper on the effect of crystal structure on the friction of possible solid lubricants.

Another property of importance is low abrasivity. This is a relative property that is a function of the hardness ratio of the lubricant and the bearing material. Obviously, the lubricant particles should be softer than the bearing material to avoid abrasive wear.

Finally, the solid lubricant must be thermochemically stable in the environment of the application. A consideration of this property is important when selecting solid lubricants for high temperature applications, but is equally important for moderate temperature applications to insure adequate storage stability and to avoid corrosion by atmospheric components such as oxygen and salt spray.

LAYER LATTICE SOLID LUBRICANTS - Layer lattice is a term used to describe crystal structures that consist of basal planes that are parallel to each other and consist of hexagonally oriented atoms (Fig. 1). The spacing between the planes is the c-spacing. The spacing between atoms within the basal planes is the a-spacing. Compounds with a high c/a ratio have very anisotropic shear properties with preferred shear parallel to the basal planes or perpendicular to the c-axis of the crystal structure. The dichalcogenides (disulfides, diselenides, and ditellurides) of molybdenum and tungsten have this structure. Brainard (1969) showed that with the possible exception of tungsten diselenide, all of these compounds have lubricating properties, especially in vacuum. Table 1 lists this data giving the maximum temperatures for lubrication with burnished dichalcogenide films in vacuum.

Compounds of this type have an $AX_2$ stoichiometry. Their crystal structures consist of hexagonal arrays of cations each bonded to a pair of pendant anions (one on each side of the basal plane). Therefore a double
layer of anions is present between each plane of cations. Strong, ionic bonding exists within each basal plane, but there are primarily weak Van der Waals forces within the double anion layers. Therefore, these compounds easily preferentially orient during sliding to allow slip of the basal planes nearly parallel to the sliding surfaces. This orientation behavior during sliding was demonstrated by electron and x-ray diffraction techniques early in the scientific investigation of MoS2; e.g., Godfrey and Bisson (1952), I. Ming Feng, (1952). Recent fundamental studies of sputtered MoS2 films have shown that, although reorientation occurs during sliding, the as-deposited crystal orientation has an influence on the wear life and chemical durability of the films (e.g., Fleischauer and Bauer, (1988) and Lince (1990). Graphite also has a layered, hexagonal crystal structure, but does not appear to be an intrinsic solid lubricant. As will be discussed later, graphite requires adsorbed moisture or additions to develop lubricating ability.

It is also relevant that metals with a hexagonal crystal structure and a c/a ratio greater than about 1.6 exhibit predominantly basal plane slip while those with a lower c/a ratio exhibit predominantly prismatic and pyramidal slip. Buckley (1971) showed that those hexagonal metals that exhibit basal slip have lower friction coefficients in vacuum than the others.

MoS2 and other Dichalcogenides - The most used solid lubricant of this chemical class is MoS2, the second is WS2, and the other dichalcogenides are found in scattered specialty application. MoS2 and WS2 are intrinsic solid lubricants in that, unlike graphite, they do not require adsorbed materials or additives to develop lubricating capability. In fact, they lubricate best in the absence of such materials and are therefore lubricants of choice for vacuum applications. MoS2 is commonly used to lubricate moving mechanical components in space vehicles.
MoS2 is applied to surfaces by a number of methods including: simple rubbing or burnishing, air spraying of resin bonded or inorganically bonded coatings, and more recently, by physical vapor deposition techniques (PVD) such as sputtering.

Burnished films are the easiest and least expensive to apply, but have very limited wear life. Resin bonded, spray coatings, especially the heat cured variety have superior wear life and are frequently used in ordinary air environments. They are typically 5 to 15 μm thick with friction coefficients of about 0.06 to 0.15 depending upon humidity and sliding conditions.

Early research with sputtered MoS2 was reported by Spalvins and Przybyszewski (1967). Their MoS2 films, which they deposited in a DC sputtering apparatus, were about 0.2 μm thick and were nearly stoichiometric. Figure 2 shows that the coatings had good frictional characteristics and good endurance in pin on disk tests in vacuum. However the endurance life and friction coefficients of sputtered MoS2 are not as good in air as they are in vacuum. The effect of atmospheric pressure on the friction of MoS2-lubricated nickel is shown in Fig. 3, Spalvin’s (1978); the friction coefficient increases from about 0.04 to 0.15 as the vacuum chamber pressure is increased above 100 torr.

Friction coefficients for sputtered MoS2 as low as 0.01 in vacuum have been reported by Roberts, (1986). In the same reference, he also reported on the adverse effects of atmospheric contaminants. Oxygen and especially water vapor in room air causes a slow oxidative degradation of MoS2, leading to early failure. This behavior is illustrated in Fig. 4. On the other hand, resin bonded coatings of high quality have good shelf life and superior wear life in air, probably because of the oxidation protection afforded by the resin binder.
Oxidation kinetic data for the MoS2 and WS2, as determined by high-temperature x-ray diffraction, were reported by Sliney (1963). Some oxidation kinetics data from this study for loosely-compacted MoS2 powders of 1 \( \mu \text{m} \) particle size are given in Fig. 5(a). The data show that oxidation rate is strongly influenced by air flow rate through the reaction chamber. Increasing the air flow rate by a factor of about 6 increased the oxidation rate by a factor of 10 or more. At the lower flow of \( 5.5 \times 10^{-6} \ \text{m}^3/\text{s} \), MoS2 was oxidized to molybdic oxide (MoO3) in 1 hr at 400 °C. At the higher air flow rate, the temperature for an oxidation half-life of 1 hr was reduced to 300 °C.

Figure 5(b) compares the oxidation kinetics of MoS2 and WS2 at the lower air flow rate. The curves intersect with MoS2 oxidizing more rapidly than WS2 above 340 °C. Comparison of these data with the results of friction experiments, Fig. 6(b), shows that the loss of lubricating ability of these compounds in air coincides with the temperatures at which rapid oxidation occurs.

**Graphite** — The largest volume tribological uses of carbon are as electrically conducting brushes for motors and generators and as the rubbing element in mechanical seals. The graphite form of carbon, which has a hexagonal, layered crystal structure (Fig. 1), also has application as a powder or bonded solid lubricant coating. In spite of its desirable crystal structure, graphite is not an intrinsic solid lubricant. It lubricates in a normal air atmosphere, but fails to lubricate at high altitudes or in vacuum. Savage (1948) reported convincing experimental evidence that graphite must adsorb moisture or some other condensable vapor such as hydrocarbons in order to be lubricative. This model appeared to be substantiated by the observation that, even in the presence of condensable vapors, graphite failed to lubricate above the desorption temperature.
However, Peterson and Johnson, (1954), observed that graphite again becomes lubricative at high temperatures when the lubricated metal becomes visibly-oxidized. Some of their results showing the effect of temperature on the friction coefficient of graphite-lubricated cast Inconel sliding on Inconel X-750 in air are shown in Fig. 7. The authors postulate that restoration of lubrication at about 425 °C was due to interaction of graphite with oxides of the metal. The surface oxides were thought to promote adhesion of the graphite to the lubricated surfaces. The maximum temperature for lubrication with graphite films is limited by oxidation to about 550 °C.

Physical Vapor Deposition (PVD) of Tribological Coatings - Vapor deposited coatings for tribological applications are of two major types: soft, solid lubricant coatings and hard wear resistant coatings. The basic processes for applying PVD coatings are simple vapor deposition, sputtering, and ion plating. Schematic diagrams of the sputtering and ion plating processes are reproduced in Figs. 8 and 9 from Spalvins, (1987). In recent years various ion beam assisted deposition methods, which are modifications of the more basic process, have been used to deposit very adherent tribological coatings, e.g., Kuwano and Nagai, (1986); Erdimer et al. (1990). Sputtered MoS2 has already been discussed in the section on dichalcogenide solid lubricants. Two other categories of PVD tribologically significant coatings are sputtered hard coatings for wear control and ion plated soft metals for lubrication.

Sputtered hard coatings - The hardness and oxidation characteristics of some hard coating materials are given in Table 2. These very hard materials are brittle. Therefore, they must have very good adhesion to the substrate to avoid delamination and they must not be too thick if they are to withstand bearing surface stresses and substrate elastic deformations under dynamic
(sliding, rolling) contact conditions. Acceptable coating thicknesses are typically 0.2 to 1.0 μm. Hard coats alone can provide wear resistance. They also are used as an intermediate coating between the substrate and a solid lubricant film.

Figure 10 from Spalvins (1975) compares the endurance lives in vacuum of MoS2 lubricated ball bearings with and without an intermediate 0.1 μm hard coating of sputtered Cr3Si2 on the raceways. Sputtered 0.2 μm thick MoS2 coatings were applied to the raceways and the cages of the bearings. The bearings without the intermediate coating had reasonably good life of about 200 hr, but those with the hard coat did not fail in 1000 hr at which time the tests were stopped. Figure 11 from the same paper shows that 1000+ hr bearing life can also be achieved without the intermediate hard coat by sputter coating the bearing balls in addition to the cage and raceways with MoS2. Unfortunately these tests were stopped after 1000 hr. Also the combined effect of MoS2 on all surfaces and an intermediate hard coat on the raceways and/or the balls was not investigated.

**Graphite Fluoride** - Graphite fluoride (CF$_x$), is not as well known as MoS2 and graphite, but it has some unique properties that make it attractive as a solid lubricant. It is an electrical insulator in contrast to graphite and it is nonwettable by water. The frictional properties are less influenced by humidity than either MoS2 or graphite. Graphite fluoride is also known as carbon monofluoride because of its nominal 1:1 carbon to fluorine stoichiometry. However, the stoichiometry can be controlled from about $x = 0.25$ to 1.1. For $x = 1.0$ to 1.1, the compound is pure white and therefore is preferred for applications where discoloration by the lubricant must be avoided.

Wear life and friction coefficient data from pin on disk tests reported by Fusaro and Sliney (1970) for burnished films of CF$_x$ on sand blasted 440C
steel are shown in Fig. 12. The corresponding data for MoS2 is included as a baseline for comparison. Film failure was taken as the time at which the friction coefficient reached 0.3. A very dry air atmosphere was used because of the deleterious effect of moisture on lubrication with burnished MoS2. The CF\textsubscript{x} films were the more durable over the entire temperature range. Friction coefficients were well below 0.1 for both compounds up to their failure time or temperature. Failure temperatures of 400 °C for MoS2 and 480 °C for CF\textsubscript{x} correlate well with the oxidation kinetics results for MoS2 shown in Fig. 5 and the thermal decomposition temperature for CF\textsubscript{x} reported by Kuriakose and Margrave (1965). Therefore CF\textsubscript{x} was the better lubricant under the conditions of these tests. McConnell et al. (1977) reported that MoS2 had superior load bearing capacity in tests on a Falex test machine in which double V-blocks are loaded against a rotating cylinder coated with the test lubricant. However, the load carrying capacity of CF\textsubscript{x} is considered by this author to be adequate for most conforming sliding contacts, especially when combined with a suitable binder such as a polyimide varnish. Fusaro (1979) in his paper on the mechanism of graphite fluoride lubrication describes the lubricating process with this material as consisting of plastic flow of thin films of graphite fluoride between the sliding surfaces.

Polyimide and Polyimide-Bonded CF\textsubscript{x} Coatings - Data reported by Fusaro (1972) from pin on disk experiments with polyimide varnish coatings on 440C steel are given in Fig. 13, where the endurance lives and friction coefficients are shown as a function of temperature. Results are compared for three different controlled atmospheres: dry argon, dry air, and air containing 10E4 ppm water vapor. The data show that there is a sharp transition in the life and friction between 25 and 100 °C above which lower friction and much longer wear life were observed. This transition in the
friction and endurance of polyimide coatings has been attributed to a second order relaxation in the molecular bonds of the polymer, (Fusaro, 1977).

The effect of adding graphite fluoride or MoS2 to the polyimide varnish is shown in Fig. 14, (Fusaro and Sliney, 1973). The coating formulations contained 3 parts by weight MoS2 to one part polyimide solids dissolved in a solvent or 3 parts of CFx to two parts of polyimide solids. The density of CFx is about one-half that of MoS2; therefore the two formulations contained equal volume percentages of solid lubricant. The solid lubricant additions clearly reduce the friction and greatly increase the wear life of the coatings at room temperature. The effect of the molecular relaxation transition on the tribological properties is completely eliminated by the solid lubricant additions. The CFx addition also resulted in improved coating endurance at all temperatures to 500 °C, while MoS2 addition deteriorated the endurance of the coating relative to the base polyimide films.

Wagner and Sliney (1984) have reported on polyimide bonded CFx films that are excellent back-up lubricants for compliant (foil) gas bearings at temperatures up to about 350 °C. This is about 100 °C higher than the limit for PTFE films that are commonly used in foil bearing applications.


**Polymer Composites** - Many polymers, including nylon, acetal, polyethylene, PTFE, and others are used in the unfilled or filled forms as bearing materials. Solid lubricant fillers are typically powdered graphite, MoS2, or CFx. The powdered additives can improve the friction and wear properties, but usually weaken the material and as a consequence, reduce their load carrying capability. Where maximum load capacity is needed, fiber
reinforcement is used. The fibers are in the form of woven fabric, chopped fibers or filament windings. Glass fabric is often used to reduce creep of bonded PTFE liners in air frame bearings and other heavily loaded bearings. Polyester fibers have been found to be an effective nonabrasive reinforcement for PTFE bearing liners.

Sliney and Williams, (1983), reported on tests of nonmetallic plain cylindrical bearings consisting of an aramid (Kevlar) fiber-reinforced shell with a bonded, self-lubricating woven liner of polyester fiber-reinforced PTFE. The results are summarized in Fig. 15 and show that low friction and wear and load capacities in excess of 207 MPa (30 ksi) are achieved from -23 to 121 °C. The bearings are limited by creep deformation at higher temperatures.

Considerable research has been done on graphite fiber reinforced polymers as self-lubricating bearing materials. Giltrow and Lancaster reported on the friction and wear properties of composites incorporating chopped graphite fibers in thermoplastic and thermosetting resins including high temperature polyimide (1968, 1970). In addition to high strength, graphite fibers have the additional advantages of high thermal conductivity and lubricating ability. Graphite fiber reinforced polyimide (GFRPI) is of particular interest for aeronautics applications, and has been extensively researched at NASA Lewis for air frame and gas turbine engine applications. The NASA composites contained chopped graphite fibers and were prepared by transfer molding and curing under heat and pressure.

The results of pin on disk bench tests for 440C steel pins sliding against GFRPI were reported by Fusaro and Sliney (1978). Favorable tribological properties were observed with several combinations of addition (A) and condensation (C)-type polyimides and low (L) and high modulus (H-type)
fibers. Figure 16 gives the friction coefficients and wear track profiles of the various composites at room temperature and at 300 °C. In those tests, the best results were obtained with an addition type polyimide reinforced with low modulus graphite fibers, (AL) composite.

**Bearing Tests of GFRPI** - Plain cylindrical and plain spherical bearing designs with self-lubricating GFRPI surfaces were tested to 350 °C in several test programs at NASA Lewis. The spherical bearing designs evaluated are shown in Figs. 17(a) and (b). The first bearings tested had molded spherical elements of AL-type GFRPI with various graphite contents in steel outer rings. Friction coefficients for various fiber loadings are shown in Fig. 18 for bearing temperatures from 25 to 350 °C, (Sliney and Johnson, 1972). The results for a conventional glass fiber reinforced bearing are included for comparison. The composite with the highest graphite fiber content provided the lowest bearing torque but failed by brittle fracture at 315 °C. The next lowest torque was provided by the composite with 45 wt % of graphite fibers and no failures occurred with a 35MPa (5000 psi) radial load. A 1:1 fiber to polymer ratio was used in all subsequent tests. The standard PTFE-lined bearing had very low torque to 200 °C, but failed when the liner extruded out of the bearing at 250 °C.

Several modifications of the bearing designs shown in Fig. 17 were compared, (Sliney and Jacobson, 1975) Fig. 19 shows that no significant difference was noted in bearing friction for the two bearing designs. However, a much higher load capacity is achieved with design (b), which consists of a steel ball and a thin (1.5)mm gfrpi liner bonded to a steel outer ring (Sliney, 1979). The dynamic load capacities of cylindrical bushings with GFRPI liners had about the same dynamic load capacities as the
GFRPI lined sphericals if a liner retention step was provided at each end of the bushing, (Sliney, 1985).

Gardos and McConnell (1982) have published an extensive, 4-part report on the preparation and performance of self-lubricating, polyimide composites reinforced with three-dimensional woven graphite fibers. The purpose of the three-dimensional weave is to afford maximum strength and load capacity. Load capacities up to 200 MPa were obtained during low speed, oscillating tests.

**EXTREME TEMPERATURE SOLID LUBRICANTS** - All of the solid lubricants so far discussed suffer thermal decomposition or oxidative degradation at 550 °C or in most cases lower temperatures. For higher temperatures, classes of materials that have shown some promise are lubricious oxides and some fluorides of alkali metals, alkaline earth metals, and rare earth metals.

It is well-known that the tenacious oxides formed on nickel and cobalt base super alloys at high temperatures have a profound effect on reducing friction and wear, e.g., (Johnson and Sliney, 1962). Lankford et al. (1987) showed that certain metals, when ion beam mixed into the surface of zirconia and silicon nitride ceramics, reduce their friction against some counterface materials at 800 °C. The beneficial effect is attributed to oxidized films of the implanted metals.

Oxidatively stable fluorides such as CaF2 and BaF2, are lubricious from about 400 to 900 °C (Sliney, Strom, and Allen, 1965). Other fluorides that have shown some lubricating capability at high temperatures are LiF, MgF2, and fluorides of some rare earth metals, particularly, LaF3 and CeF3, (Sliney, 1969, 1970). At NASA Lewis, fluorides have been applied as: (1) ceramic bonded coatings using a porcelain enameling process, as (2) fusion bonded all-fluoride coatings, and as (3) constituents of plasma sprayed composite coatings. Most recently, they have been incorporated as components of free-
standing powder metallurgy composites. This results of this research are summarized in the following section.

Ceramic Bonded Fluorides - Early research on ceramic coatings and ceramic bonded CaF2 coatings at NASA Lewis was summarized by Johnson and Sliney (1962) and Sliney (1972). Detailed references are given in the bibliographies of those papers. The coatings are prepared by spraying and firing procedures similar to those used in porcelain enameling, but the compositions are very different compared to conventional porcelain enamels and are specially formulated with the objective of achieving good tribological properties. Since at least some of the components of these coatings melt during the firing process, they are referred to as "fusion-bonded" coatings. In most cases the coating thickness is 0.002±0.001 cm.

In a formulation study of ceramic compositions, a CoO-based coating and a BaO-based coating for nickel-chromium super alloys, which provided tribological benefit to at least 800 °C (1500 °F), were developed. High surface temperatures due to frictional heating at high sliding velocities or high bulk specimen temperatures were beneficial to lubrication with these coatings. The friction and wear for cast Inconel sliding on uncoated and on coated Inconel X-750 at a sliding velocity of 2.2 m/s are shown in Fig. 19. Both coatings provided a considerable reduction in pin wear compared to the un lubricated case. Friction was reduced over the entire temperature range with the CoO-based coating and up to about 600 °C with the BaO-based coating. Lower friction was obtained when the CoO-based composition was used as a binder for CaF2. Friction and wear for coatings prepared from blended powders with a 3:1 CaF2 to binder ratio are shown in Fig. 21. Friction coefficients were about 0.25 at room temperature and gradually decreased to about 0.15 at
800 °C. Very careful coating procedures are necessary to achieve a uniform distribution of CaF2 throughout the ceramic binder.

Another approach was to prepare coatings from composite powders to avoid segregation during spraying and firing (fusion bonding) of the coatings. A composition near the ternary melting point for the CaF2, Ca2SiO4, CaO ternary system was chosen, and the CaF2/BaF2 binary eutectic was substituted for CaF2 to lower the melting point. The coating was fusion bonded by firing in air at 980 °C. The friction coefficient as a function of temperature at two sliding velocities is shown in Fig. 22. Friction was quite high at the lower sliding velocity of 2.5 m/s, (0.5 at room temperature and gradually decreasing to about 0.3 at 600 to 800 °C). However, at 10 m/s, friction coefficients were less than 0.2 at all temperatures. Even at the lower speed, the pin wear factors were 1/1000 those of the uncoated metal, or about 10E-6mm3/Nm.

Fused Fluoride Coatings - Sliney, Strom, and Allen (1965) reported on the performance of coatings consisting entirely of stable fluorides with emphasis on compositions from the BaF2-CaF2 binary system. Results of friction and wear tests are shown in Fig. 23. Over the entire temperature range of 25 to 816 °C and at two sliding velocities of 2.3 and 10 m/s the coatings were responsible for very substantial reductions in friction and wear relative to the uncoated metals. At 2.2 m/s the friction coefficient at room temperature was rather high at 0.4 and decreased with temperature to 0.2 at 260 °C and 0.11 at 800 °C. At 10 m/s, friction coefficients were 0.2 at room temperature, gradually decreasing to about 0.15 at 800 °C. No coating failures occurred in one hour tests (52 200 cycles at 2.3 m/s and 227 000 cycles at 10 m/s).

The relatively high friction at low temperature and sliding velocities led to an investigation in which it was found that the addition of silver to the BaF2-CaF2 coatings could result in a uniformly low friction from room
temperature to 800 °C. This is illustrated in Fig. 24 from Olson and Sliney (1967) which compares the friction-temperature characteristics of fluoride coatings with and without a 35 wt % silver addition.

Comparison of Ceramic Bonded and Fused Fluoride Coatings - The ceramic bonded coatings studied have good friction and wear properties at high surface temperatures that encourage the formation of a smooth, in some cases vitreous, glaze on the sliding surfaces. They are not generally effective at low ambient temperatures except at high sliding velocities where frictional heating generates high surface temperature. Unfortunately, some vitreous glazes, which provide lubrication by viscous shear at high temperature, develop very high viscosity below their softening temperature. Below this temperature, the high viscosity of the glaze can result in very high bearing torque or even "lockup" of the bearing. A restart cannot occur until the bearing is heated above the softening point of the glaze. This phenomena is not generally observed in pin on disk tests where the contact area is very small and the adhesive bond is easily broken but has been observed in conforming contact, plane spherical bearings. This problem has not been observed with the nonvitreous glazes formed on the sliding surfaces of fused fluoride coatings that have no vitreous oxides in their composition.

Plasma Sprayed Coatings - When coatings are fusion bonded in a furnace, the entire part is heated above the melting point of at least one of the coating components. The high temperatures involved are not acceptable for some substrates, titanium, for example. An alternative method is plasma-spraying which only minimally heats the substrate. Plasma spraying is also more convenient (after the optimum plasma spray equipment parameters are determined), and can be used to deposit combinations of materials that are not amenable to furnace heat treatment. The first reported plasma spray...
tribological coatings developed at NASA Lewis are called PSI00 and PSI01, (Sliney, 1979). The former is a three component composite coating of CaF2, sodium-free glass, and a nickel-chromium alloy binder. The other, in addition, contains silver to improve low temperature friction. Figure 25 shows the wear and friction-temperature characteristics of these coatings in low speed, oscillating, plain spherical bearings. It is clear that the silver addition reduces friction at low temperatures without an adverse effect on lubrication at high temperatures. Both coatings are somewhat conformable or ductile, and have moderately good wear characteristics. Coating and counterface wear factors are typically on the order of 10^{-5} \text{mm}^3/\text{Nm}. PSI00 and PSI01 are indicated for high temperature applications involving moderately loaded, (up to at least 34 MPa) sliding contact bearings, and for shaft seals requiring a high degree of coformability.

The PS200 series of plasma spray coatings were later developed (Sliney, 1986; Sliney and DellaCorte, 1987). In this coating, the lubricating solids are distributed throughout a wear-resistant matrix of Ni-Co alloy-bonded chromium carbide (Cr3C2). The two most-studied compositions are PS200 which contains 10 wt \% each of Ag and CaF2/BaF2 eutectic and PS212 which contains 15 wt \% each of the two lubricants in the bonded carbide matrix. The friction coefficients for these coatings are typically 0.30 to 0.35 from room temperature to 900 \degree C at a sliding velocity of 2.7 m/s, and tend to decrease at very high sliding velocities. Wear factors are about 1/10 of those for the PS100 series of coatings. In a composition optimization study, PS212 had somewhat lower friction and wear in pin on disk tests, than PS200, however, PS200 may be of interest where a harder coating is preferred.

Promising results have been obtained in a number of prototype tests of high temperature mechanical components coated with PS200 or PS212. These
include: start/stop tests of hydrodynamic gas bearings at temperatures up to 650 °C by Wagner and Sliney, (1986) and DellaCorte, (1988) and a test of a 4-cylinder Stirling engine with PS200-lined cylinders reported by (Sliney, 1986) and (Allen and Tomazic, 1987).

**Self-Lubricating Powder Metallurgy Composites** - Plasma spray coatings are appropriate for flat surfaces and outside diameter surfaces that are readily accessible for spraying with a plasma spray gun. However, it is difficult or impossible to spray the inside surfaces of components such as small cylindrical bearings, valve guides, and bushings. These are the type of components that lend themselves to being made by powder metallurgy processes. The PS212 composition was used to make free-standing powder metallurgy (PM212) parts by sintering and by hot isostatic pressing, (HIPing). The HIPed version is fully dense while the sintered version is about 75 percent of theoretical density. The compressive strength to 900 °C and coefficient of thermal expansion of sintered and of HIPed PM212 are given in Fig. 26 (Edwards, et al. 1990). The HIPed version is about three times stronger than the sintered version, but both materials retain compressive strength to at least 700 °C that equals or exceeds the room temperature strength of many grades of bearing bronze and carbon sliding contact bearing materials.

Thermal expansion coefficients are bracketed by those of such common alloys as cast iron and nickel base super alloys.

The tribological properties of sintered PM212 pins sliding on uncoated Rene 41 disks were reported by DellaCorte and Sliney (1990). Figure 27 shows that friction coefficients at a sliding velocity of 2.7 m/s are about the same for sintered PM212 pins sliding on Rene 41 disks as they are for Rene 41 pins sliding on PS212-coated disks. The effect of sliding velocity on the friction
The coefficient of sintered PM212 is given in Fig. 28. At 760 and 900 °C, the friction coefficient decreases with increasing sliding velocity and is 0.2 at the highest sliding velocity of 8.1 m/s. Friction behavior is less straightforward at the lower temperatures, but friction coefficients are typically 0.30 to 0.35 except at the lowest velocity at room temperature. The trend of decreasing friction with increasing velocity suggests that friction coefficients considerably lower than 0.2 may be expected at the very high sliding velocities characteristic of shaft seals in turbomachinery. This effect may be due to the increased localized heating at high sliding velocities which soften the silver and fluoride surface films, thus reducing their shear strength without appreciably reducing the hardness and flow pressure of the material below the near surface region.

Wear factors for sintered PM212 are in the 10⁻⁶ to 10⁻⁵ mm³/nm range. Wear factors for HIPed PM212 pins are about one-half those of sintered pins from 25 to 760 °C, and René 41 disk wear appears to be independent of whether the composite is sintered or HIPed.

CONCLUDING REMARKS

The first reported solid lubricants research was conducted in the 1940's. The primary focus was initially on aeronautics applications, but the results of this research led to a much more general use of solid lubricants. Early research was concentrated on studies of MoS2 and graphite. Later, many other materials were investigated, e.g., graphite fluoride, polyimide films, and graphite fiber-reinforced polyimide self-lubricating composites. Sputtering and ion plating have become important processes for the deposition of solid lubricant films, and wear-resistant hard coatings, and this area of research continues to the present. Self-lubricating coatings and composites of thermochemically stable fluorides and of lubricious oxides have been developed.
for lubrication to 1000 °C, and most recently high temperature sliding contact bearing and seal materials for applications to 900 °C have been prepared by powder metallurgy processes.

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### TABLE 1. - RESULTS OF THERMAL STABILITY AND FRICTIONAL EXPERIMENTS IN VACUUM OF $10^{-7}$ to $10^{-4}$ N m$^{-2}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Probable onset of thermal dissociation as detected by tga, °C</th>
<th>Dissociation products first detected by mass spectrometry, °C</th>
<th>Maximum temperature at which burnished films provided effective lubrication, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>930</td>
<td>1090</td>
<td>650</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>870</td>
<td>1040</td>
<td>730</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>760</td>
<td>980</td>
<td>760</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>700</td>
<td>930</td>
<td>760</td>
</tr>
<tr>
<td>MoTe$_2$</td>
<td>700</td>
<td>700</td>
<td>540</td>
</tr>
<tr>
<td>WTe$_2$</td>
<td>700</td>
<td>700</td>
<td>a</td>
</tr>
</tbody>
</table>

*Friction coefficient greater than 0.2 at all temperatures.

### TABLE 2. - BULK PROPERTIES OF SOME HARD COAT MATERIALS

<table>
<thead>
<tr>
<th>Material</th>
<th>Microhardness, kg mm$^{-2}$</th>
<th>Oxidation temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$_4$C</td>
<td>4200</td>
<td>1090</td>
</tr>
<tr>
<td>TiC</td>
<td>3200</td>
<td>540</td>
</tr>
<tr>
<td>SiC</td>
<td>2900</td>
<td>1650</td>
</tr>
<tr>
<td>Cr$_3$C$_4$</td>
<td>2650</td>
<td>1370</td>
</tr>
<tr>
<td>WC</td>
<td>2050</td>
<td>540</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>2000</td>
<td>1400</td>
</tr>
<tr>
<td>TiN</td>
<td>1950</td>
<td>540</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>1800</td>
<td>--</td>
</tr>
</tbody>
</table>

*Data from: Engineering Properties of Ceramic Materials, Battelle Memorial Institute, Published by American Ceramic Society, Columbus, OH, 1966.

*Temperature for appreciable detrimental oxidation (passivating oxide films form at lower temperatures).

*Estimated conversion from published Moh hardness of 9.
Figure 1.—Structure of graphite. The individual sheets consist of closely packed atoms, separated by a relatively large distance from neighboring sheets.

Figure 2.—Average friction coefficients of niobium sliding on two different specimens coated with sputtered molybdenum disulfide in vacuum (10 \textsuperscript{-11} torr or 1.33x10\textsuperscript{-9} N/m\textsuperscript{2}). Load, 2.5N; speed, 5 feet per minute (2.54x10\textsuperscript{2} m/sec); ambient temperature.

Figure 3.—Effect of pressure on coefficient of sliding friction for sputtered MoS\textsubscript{2}. Load, 250 grams; speed, 40 rpm; substrate/rider, Ni/Ni; room temperature.

Figure 4.—Failure modes of sputtered MoS\textsubscript{2} under sliding motion. From Roberts (1986).
Airflow rate, m$^3$s$^{-1}$ $\times 10^{-6}$
5.5
33.3

(a) Oxidation characteristics of MoS$_2$ at two air flow rates.

(b) Comparative oxidation of WS$_2$ and MoS$_2$ with an air flow rate of $5.5 \times 10^{-6}$ m$^3$s$^{-1}$.

Figure 5.—Oxidation kinetics of MoS$_2$ and WS$_2$ with average particle size 1 $\mu$m and compact density 50%.

Figure 6.—Variation of friction coefficient with temperature of MoS$_2$ and WS$_2$ in (a) argon and (b) air in pin on disk tests. Steel pins with 4.76 mm hemispherical tip radius, 9.6 N, 0.025 m/s.

Figure 7.—Effect of oxide adjuvant on lubrication with graphite in pin on disk tests, steel pins with 4.76 mm hemispherical tip radius, 9.6 N, 0.025 m/s.

Figure 8.—Schematic of sputtering process.
Figure 9.—Schematic of ion plating process.

Figure 10.—Endurance lives of 440C stainless-steel ball bearings with sputtered MoS₂ films on races and cage - with and without a Cr₃Si₂ underlayer.

Figure 11.—Endurance lives of 440C stainless-steel ball bearings with and without sputtered MoS₂ film.

Figure 12.—Effect of temperature on wear life and friction coefficient of graphite fluoride ((CF₁₁₂)ₙ) and MoS₂ powders burnished on sandblasted 440C stainless-steel disc. Riders: 440C stainless steel with 4.76 mm hemispherical tip radius, linear sliding speed: 1.6 m s⁻¹; load: 5 N; atmosphere: dry air (20 ppm H₂O).

Figure 13.—Friction coefficient and wear life as a function of temperature for thin films of polyimide run in atmospheres of dry argon, dry argon, dry air, and moist air (10 000 ppm H₂O), against 440-C pins with 4.76 mm hemispherical tip radius, 9.6 N load, 2.7 m/s sliding velocity.
Figure 14.—Friction coefficient and wear life as a function of temperature for three solid lubricant films run in dry air, and moist air (10 000 ppm H₂O), against 440-C pins with 4.76 mm hemispherical tip radius, 9.6 N load, 2.7 m/s sliding.

Figure 15.—Effect of temperature on wear and friction of TFE-lined composite bushings. Bore diameter: 0.025 m, journal oscillation at ±25° and 10 CPM.

Figure 16.—Tribological performance of polyimide composites disks sliding against 440-C pins with 4.76 mm hemispherical tip radius, 9.6 N load, 2.5m/s sliding velocity.
Figure 17.—Test bearings employing graphite fibre reinforced polyimide.

Figure 18.—Summary of friction of spherical bearings with polyimide-graphite-fiber composites of various fiber contents. Stellite 6B journal, radial unit load, 35 MPa (5000 psi), journal oscillation in cylindrical bore at 1 hertz, ±15°.

Figure 19.—Bearings lubricated with GFRPI composite.
Figure 20.—Effect of temperature on lubricating properties of CoO-base and BaO-base coatings on Inconel X-750 sliding against Inco x-750 pins with 4.76 mm hemispherical tip radius, 9.6 N load, 2.2 m/s.

Figure 21.—Effect of temperature on lubricating properties of ceramic-bonded calcium fluoride coatings on Inconel X-750 sliding against Inconel X-750 pins with 4.76 mm hemispherical tip radius, 9.6 N load, 2.2 m/s.

Figure 22.—Friction-temperature characteristics of fluoride coatings modified with silicate and oxide additions, air atmosphere, 9.6 N load, 2.5 m/s sliding velocity.

Figure 23.—Lubricating properties of fused fluoride coating composition in air at two sliding velocities. Coating, 38 percent calcium fluoride-62 percent barium fluoride; coating thickness, 0.025 to 0.050 mm; duration of run, 1 hour; load, 500 grams; specimens, pins with 4.76 mm hemispherical tip radius sliding against coated disks; separate experiments with different specimen for each data point.
Figure 24.—Effect of temperature on friction coefficients of fused fluoride coatings, 0.04 mm thick sliding against cast Inconel pins of 4.76 mm hemispherical tip radius, 5 N load, 2.3 m/s sliding velocity.

Figure 25.—Plasma-sprayed coatings for self-aligning oscillating bearings, 34-MPa (5000 psi) radial load, ±15°, 1 hertz.
Superior maximum service temperature
Oil-lubricated bronze
Carbon-graphite
PM212

Linear thermal expansion in range of many engineering alloys

Mechanical strength compares favorably with conventional sliding bearing materials.

Figure 26.-Properties of PM-212: self lubricating powder metallurgy composite.

Figure 27.-Friction coefficient comparison of PM212 and PS212 (plasma sprayed coating) in air, 35 percent R. H. at 25 °C, 0.5 kg load, 2.7 m/s sliding velocity against Inconel 718 pins with 4.76 mm hemispherical tip radius.

Figure 28.-Friction coefficient versus sliding velocity, 0.5 kg load, in air, 35 percent R. H., sliding against Inconel 718 pins with 4.76 mm hemispherical tip radius.
The state of knowledge of solid lubricants is reviewed. The subject is presented from a historical perspective, and presents the results of research on solid lubricants from the 1940's to the present. Emphasis is placed largely, but not exclusively, on work performed at NASA Lewis Research Center with a natural focus on aerospace applications. However, because of the generic nature of the research the information presented in this review is applicable to most areas where solid lubricant technology is useful.