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Solid lubricants for applications at elevated temperatures

A review

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Relative motion between mating surfaces at elevated temperatures often causes substantial material degradation due to friction and wear. Conventionally, solid lubricants have been used to reduce wear damage and friction drag under extreme conditions where liquid lubricants do not function properly. The recent trend towards higher operating temperatures in advanced power generating systems, i.e. turbomachinery, gas turbines, and hot adiabatic diesel engines, has imposed severe limitations on the currently available solid lubricants. The unusually aggressive conditions in these systems phased out most conventional solid lubricants and gave impetus to the search for more efficient materials. This paper discusses the lubricating characteristics of four different groups of materials known to provide lubricity under elevated temperature conditions. These groups are polymers, laminar solids, metal fluorides and metal oxides. Polymer lubricants are efficient lubricants within the range from room temperature to about 300 °C. Laminar solids extend that range to about 450 °C. Graphite, also a laminar solid, is an exception since it can offer excellent lubricity beyond 450 °C in the form of gaseous oxidation products. Stable fluorides and metal oxides are useful lubricants between 500 and 1000 °C, though their performance is rather poor at lower temperatures.

1. Introduction

In its most general sense, a solid lubricant is a material applied between two mating surfaces to provide protection from damage during relative movement and to reduce friction and wear. Solid lubricants have been known for centuries, but their use in the modern sense only dates back about 50 years. The major advantages of solid lubricants over liquid lubricants include: better lubricity and higher chemical stability at elevated temperatures; good dimensional stability that allow precision finishing to high accuracy; ability to function without cooling thus eliminating cooling systems; and no seals are required to isolate them from process fluid. On the other hand, solid lubricants trial behind liquid lubricants in that they generally have higher coefficients of friction, they are nonrenewable, they cannot carry heat away as oils do, they have no damping effects, and they require close control during application to moving parts.

Graphite and molybdenum disulphide are the oldest known solid lubricants and are perhaps the most widely used in industry. Both materials have planar (laminar) structures that facilitate shear in certain directions. Other materials that have gained wide acceptance as solid lubricants, such as polytetrafluoroethylene (PTFE), possess different structures and properties and may thus belong to a different class of lubricants. At present, there is no specific scheme for categorization of solid lubricants, although one based on composition, and temperature capability appears to be satisfactory and is used in this review. This article reviews the friction, wear and lubrication behaviour of various solid lubricants which are potentially useful for applications involving temperatures ranging between ambient and about 1000 °C.

2. Polymers

Polymers have been successfully used in many applications involving friction and wear. Most polymers have low friction coefficients, low densities, good corrosion resistance, good machinability, and they can be used under vacuum and at cryogenic temperatures. Polyimides and polytetrafluoroethylene (PTFE) are the most important solid lubricants in the polymer group because of their excellent thermal stabilities and good friction characteristics. In some applications, however, the use of these materials is limited by excessive cold flow under load (particularly at high temperature), poor thermal conductivity, high thermal expansion, low radiation stability, inability to dissipate heat efficiently, and lack of strength and dimensional stability.

2.1. Polyimides

By definition, polyimide refers to a class of long-chained polymers with repeating imide groups as an integral part of the main chain. The chains consist of aromatic rings alternated with heterocyclic groups,

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with multiple bonds providing the high thermal stability. Polyimides are resistant to most common chemicals and solvents but are attacked by alkalies [1]. Several types of polyimides are being used in bearings, gears, seals, prosthetic human joints [2, 3], and mechanical parts operating below 300 °C. Certain additives such graphite fibres can improve the mechanical strength, load carrying capacity and the lubrication performance of polyimides [4, 7].

The tribological properties of polyimide films, polyimide solid bodies, polyimide-bonded solid lubricant films, and polyimide composites have been compared by Fusaro [1, 8, 9]. It was concluded that the upper limit for self lubrication of polyimide in air is 350 °C, depending on the type of polyimide and the nature of the application. Polyimides tend to be brittle and to wear by the brittle fracture of surface layers. Graphite fluoride $(CF_x)_n$ can improve their friction behaviour by allowing easy shear in a very thin surface layer under light contact stresses. Addition of MoS_2 and $(CF_x)_n$ solid lubricants to polyimide varnishes was found to improve the wear life and friction at room temperature [10]. Figure 1 shows that the undesirable friction behaviour of the polyamide film below 100 °C is totally masked by the addition of another solid lubricant, such as graphite fluoride or molybdenum disulphide. Both additives provide a coefficient of friction below 0.1, indicating good lubricity, up to about 400 °C where the polyamide begins to decompose appreciably.

2.2. Polytetrafluoroethylene (PTFE)

The other major and more widespread polymeric solid lubricant is the fluorocarbon resin PTFE $(CF_2)_n$. This compound has been used in industry since 1941 under the original trademark of the Du Pont Company, "Teflon". PTFE retains good thermal stability, useful mechanical properties, and good lubricity up to 260 °C [11], and compared with nylon or other plastics is somewhat soft with a relatively low tensile strength. In addition, its coefficient of friction is one of the lowest of any known solids, including graphite or MoS_2 [12, 13]. A value of 0.04 is usually quoted for the coefficient of friction of PTFE against steel, but a value as low as 0.016 has been observed at very high loads [14, 15]. The low friction of PTFE has been attributed [16] to its low adhesion to the mating surface, the low shear stress needed to overcome adhesion at the interface, and to its ability to transfer on the bare surfaces resulting in PTFE versus PTFE contact.

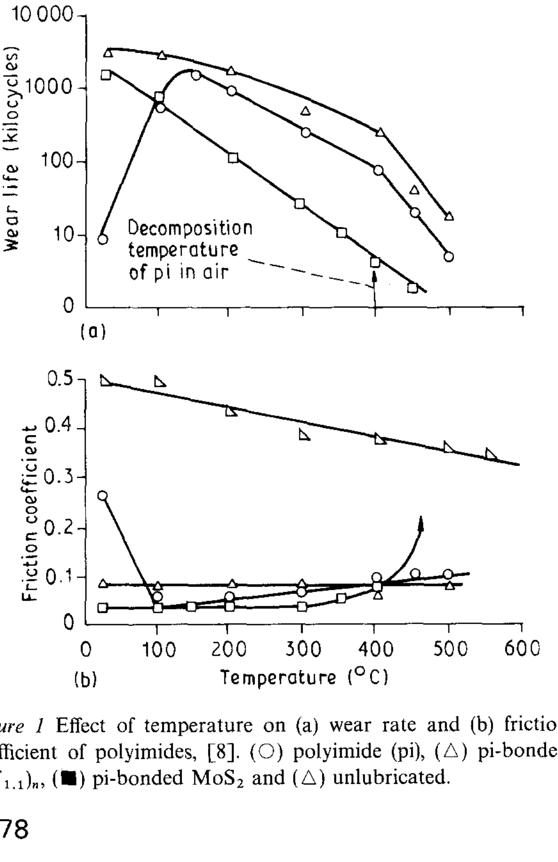

Figure 1 Effect of temperature on (a) wear rate and (b) friction coefficient of polyimides, [8]. (○) polyimide (pi), (△) pi-bonded $(CF_{1.1})_n$, (■) pi-bonded MoS_2 and (△) unlubricated.

PTFE is usually reinforced with additives or filler reinforcements in order to reduce cold flow and withstand severe load and speed conditions as well as to reduce its wear rate. The most common filler materials may include MoS_2, graphite, and glass fibres. Other important filler materials are bronze or bronze/graphite which are particularly useful at cryogenic temperatures; lead or lead oxide which improve wear resistance at elevated temperatures, and ceramics such as ZrO_2 or aluminium silicate which improve the cold flow and high temperature deformation under load. PTFE is commonly used in the form of filled or unfilled solid parts, sheets or tapes. It can be applied as thin sintered or resin-bonded films on surfaces of metal and ceramic substrates. It has been widely used in the form of powders which may substitute graphite powders in some applications. PTFE fibres and woven fabrics containing cotton or glass fibres are commercially used in bearings, gaskets and other applications. It has been used as a basic ingredient in speciality greases for aggressive environment; and in the manufacture of PTFE impregnated porous metallic substrates such as bronze, silver or copper.

3. Laminar solids

These materials, sometimes called layer lattice compounds, have a planar (i.e., hexagonal-layered) crystal structure in which the atoms within a plane are held together by a chemical bond stronger than the bond between the planes. This provides an isotropic shear property with preferred easy shear parallel to the basal planes of the crystallites. This result in the ability of basal planes to slide easily over one another. This class of materials comprises the most widely used solid lubricants which normally provide low friction coefficients. The most common of these materials are graphite and dichalcogenides, notably MoS_2 and WS_2.

3.1. Graphite

Graphite is an allotropic form of carbon. It is a transition element, having properties of both metals and non-metals. It is insoluble in all common solvents. The carbon atoms in graphite are covalently bonded and situated at the corners of regular hexagons. The basal planes of the hexagons are parallel but slightly offset laterally, (Fig. 2). Although graphite is widely

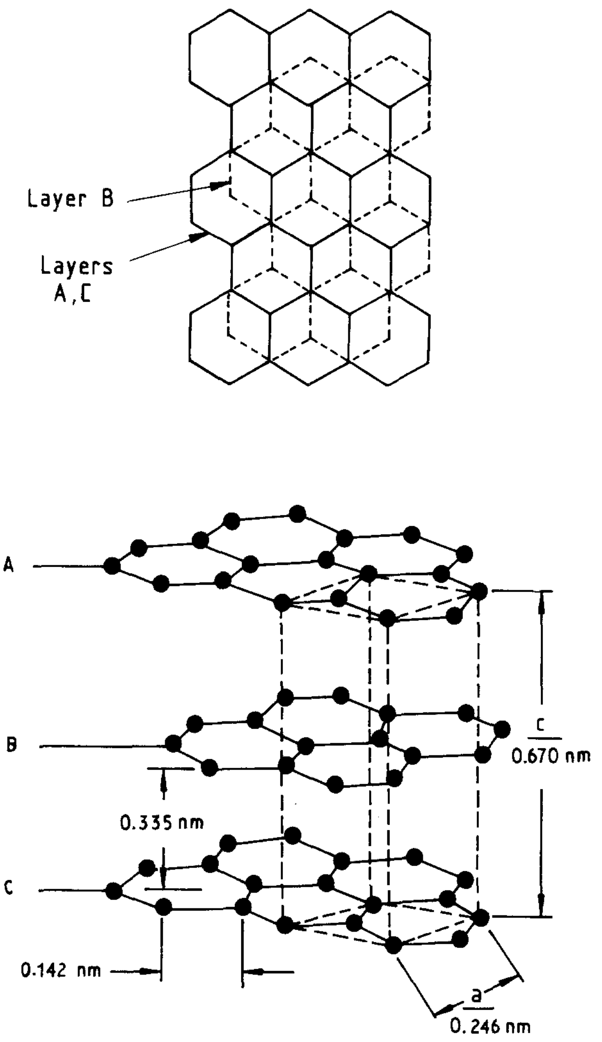

Figure 2 Crystal structure of graphite.

used as an efficient solid lubricant, its efficiency is curtailed by its high shear strength when dry [17, 18]. Graphite must absorb air, oxygen, moisture, or hydrocarbon vapours to develop the low shear strength required in a solid lubricant. This major deficiency makes graphite unsuitable for use in vacuum or at high altitude [11, 19]. Many attempts have been made to explain the mechanism by which graphite lubricates [20], nevertheless, despite its proven efficiency as a lubricant, no agreement has been reached so far. In air, graphite's limiting factor is its high oxidation rate. Small particles begin to oxidize at an appreciable rate at about 450 °C [21, 22], which is its maximum use temperature. Sliney showed that the friction coefficient of graphite is low ($\mu \approx 0.1$) below 100 °C, but it increases to about 0.4 between 100 °C and 425 °C. Above 425 °C, the friction coefficient falls again below 0.2, indicating good lubricity. Peace [20], indicated that under oxidizing conditions, graphite may maintain good lubricity up to 600 °C; and may be used in metal forming processes at temperatures as high as 1100 to 1200 °C to provide lubrication for limited periods. Because the oxidation products of graphite are gases, good lubricity can be provided at extreme temperatures if the graphite can be continuously replenished.

Graphite may be used as a dry powder, and more often in the form of suspended dispersion in oils and greases, [15, 20]. Composites of graphite with MoS_2, metals and metal-oxides have also found many useful industrial applications. Graphite fluoride $(CF_x)_n$, prepared by reacting graphite with fluorine gas without combustion at 420–550 °C [23] shows excellent lubrication and oxidation resistance and does not require adsorption of vapours to provide good lubricity up to ~ 560 °C. The spacing between basal planes is expanded from 0.335 nm for graphite to 0.817 nm for $(CF_x)_n$ which result in a decrease in shear and cleavage strength parallel to the basal planes. The stoichiometry of $(CF_x)_n$ ranges from $x = 0.7$ to $x = 1.1$, the best lubrication and thermal stability being at high values of x. Above 450 °C, it decomposes to form tetrafluoromethane, other low molecular weight fluorocarbons, and carbon [24]. Comparison of the wear and friction behaviour of burnished $(CF_x)_n$ and MoS_2 films on 440 stainless steel indicate that $(CF_x)_n$ films are more durable, with friction coefficient well below 0.1 up to failure temperature [10, 25]. The failure temperature is 480 °C for $(CF_x)_n$ compared with 300 °C for MoS_2.

3.2. Molybdenum disulphide (MoS_2)

Molybdenum disulphide (MoS_2) is perhaps the most widely used and best documented solid lubricant. It resembles graphite in appearance, but has superior properties in many applications. MoS_2 has a hexagonal layered structure with a six-fold symmetry and two molecules per unit cell [26]. Each sulphur atom is equidistant from three molybdenum atoms, and each molybdenum atom is surrounded by six equidistant sulphur atoms at the corners of a triangular prism. Each layer in MoS_2 consist of a central molybdenum plane sandwiched between two planes of sulphur atoms (Fig. 3). The distance between the molybdenum atoms within the layer is 0.316 nm. The distance between adjacent sulphur layers is 0.308 nm. While the distance between adjacent molybdenum layers is 0.616 nm. These layers contain strong covalent bonding (in the same plane) but have a weak van der Waals type bond between the layers. As a result, shear can

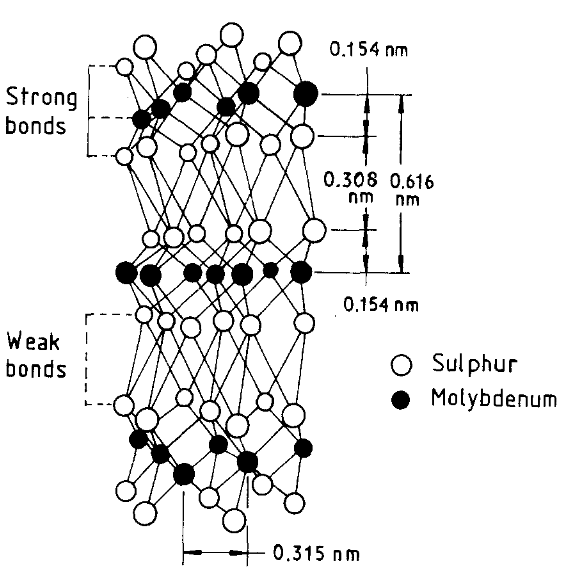

Figure 3 Crystal structure of MoS_2[15].

occur along these planes of weak bonding, causing them to slide over one another quite easily, thus enabling MoS_2 to function as a lubricant. The coefficient of friction of uncontaminated MoS_2 averages about 0.08 under ambient conditions, and up to 300 °C. This value may vary depending on the purity, method of application, load, and operating conditions above 300 °C.

The efficiency of MoS_2 as a lubricant degrade significantly due to oxidation. The oxidation product of MoS_2 is molybdenum oxide (MoO_3) which is considered abrasive to most alloys [27] and has been reported to increase friction and reduce wear life [28]. However, Centers [29] and Gardos [30] indicated that MoO_3 additions to MoS_2 considerably improve its tribological performance. Lavik *et al.* [31] reported that 50% oxidation of MoS_2 powder at 465 °C will occur in under 5 min. This is in agreement with the oxidation data reported by Sliney [32] who also showed that the oxidation rate is a function of particle size and the availability of air. The oxidation behaviour of bonded MoS_2 coatings is dependent on the type and composition of the additive. Inorganic resins (for example, sodium silicate) are more thermally stable than organic resin binders under oxidizing conditions. Sliney [18] suggested that this binder provides some form of oxidation protection to the MoS_2 by excluding air from the particles.

Unlike graphite, MoS_2 is considered a good lubricant in vacuum and requires no adsorption of vapours for improved lubricity [26, 33–35]. Sliney [18] showed that the coefficient of friction of resin-bonded MoS_2 in air is below 0.1, indicating good lubricity from room temperature to about 350 °C, above which, both friction coefficient and wear increase due to oxidation [26, 28] to MoO_3. In vacuum, MoS_2 provides satisfactory lubrication up to 1000 °C [19]. The results of Barry and Binkelman's [33] experiments on natural MoS_2 rubbed onto several metals indicated that the friction decreases with decreasing humidity. It was also found that; the load and speed have no effect on the friction coefficient in dry air.

MoS_2 can be applied in the form of rubbed-on (dry) powders or powders dispersed into oils. Unbonded coatings are the simplest form of application, and although not physically or chemically attached to the substrate material, they adhere to many substrates by mechanical [36] or molecular actions. In general, this type of coating has lower adhesion, wear life, and load-carrying capacity than bonded coatings. Most bonded coatings use organic (thermoplastic and thermo-setting) resins to adhere the lubricant strongly to the substrate. Cellulose or acrylic lacquers can be used up to about 65 °C [18]. Phenolics can withstand service temperatures up to 200 °C, whereas epoxy resins are thermally stable up to about 300 °C. Inorganic binders such as sodium silicates are more thermally stable than organic binders under oxidizing conditions and are recommended to bond MoS_2 for higher temperatures (400 °C) and improved wear life. MoS_2 has also been used to impregnate metal powder compacts or plastics to produce composites that continue to feed MoS_2 to the sliding surfaces. Application of very thin MoS_2 layer [38–40] or MoS_2–Ni [41] by sputtering showed excellent promise in providing effective lubrication.

3.3. Other laminar solids

In addition to MoS_2 and graphite, laminar solids include several sulphide, selenide, telluride compounds [42] as well as lead oxide and boron nitride. Among these compounds, WS_2, PbO, and BN appear to have certain advantages over MoS_2 or graphite for lubrication at high temperatures. Sliney [18] compared the coefficients of friction of MoS_2 and WS_2 and concluded that WS_2 is a better lubricant at high temperature in both air and nonoxidizing atmospheres. However, the usefulness of WS_2 is limited to about 650 °C in air, where it oxidizes appreciably. Bergmann *et al.* [43] studied the friction properties of several dichalcogenides, including MoS_2, WS_2, $MoSe_2$, $MoTe_2$, NbS_2, $NbSe_2$ and TaS_2 deposited on various metallic substrates. The results indicated better performances by MoS_2, $MoSe_2$, and $NbSe_2$. The oxidation behaviour of some of these materials was studied by Lavik *et al.* [31] who showed that TaS_2 and $TaSe_2$ are the most stable dichalcogenides in dry air where most of the oxidation occurs above 600 °C. Next in order of oxidation resistance were WSe_2, WS_2, and $MoSe_2$. It was also demonstrated that MoS_2, $MoSe_2$, and $TaSe_2$ when bonded with monoaluminium phosphate have oxidation resistances similar to those of the pure compounds.

Boron nitride (BN) is another important solid lubricant. Although it has a better thermal stability than MoS_2 or graphite, its use is rather limited because it is difficult to bond it to substrates. Its friction coefficient at room temperature is rather high (about 0.3), however it drops to about 0.15 at 600 °C [44].

4. Fluorides

Chemically stable fluorides from group I and II metals, i.e., LiF, CaF_2, BaF_2, and NaF; and from rare earth elements (LaF_3, CeF_3) are recognized as good lubricants over the temperature range from 500 to 1000 °C [10]. Many of these can be used at very high loads [45] or in chemically reactive environments [46]. Most of these compounds are brittle and nonlubricating at low temperatures but they become good lubricants above 500 °C when undergoing a transition to the plastic state. These materials have coefficients of thermal expansion that match many alloys to which they can be bonded. Most fluorides can be applied as fused fluoride coatings or as fluoride/metal or fluoride/ceramic self-lubricating composites or composite coatings.

4.1. Fused fluorides

Sliney *et al.* [10, 47, 48] investigated the lubricating properties of BaF_2–CaF_2 eutectics and rare earth metal fluorides at elevated temperatures. The results indicated that of the rare earth fluorides, cerium fluoride (CeF_3) and lanthanum fluoride (LaF_3) were the best solid lubricants. Friction coefficients of 0.3 to 0.4 were obtained in air from room temperature to about 500 °C when both compounds were applied to nickel-base superalloys. An average value of 0.2 for the coefficient of friction was obtained at temperatures above 500 °C and up to 1000 °C, indicating that these compounds have good potential as high temperature lubricants in oxidizing environments.

Fused fluoride coatings can be applied by spraying, painting, or by suspension of water/fluoride onto metal surfaces then evaporating the water by heating it to 80 °C. The bonding is developed by heating in argon or hydrogen to the sintering or melting temperature of the coatings.

4.2. Fluoride-Metal Composites and Coatings

Fluoride-metal composites consist of a porous metallic matrix impregnated with fluoride-based solid lubricants. In some cases, the impregnated composite substrate is coated with a thin sintered film of fluoride for additional lubrication. The metal matrix provide desirable mechanical strength, suitable thermal expansion coefficient, and thermal conductivity. The non-metallic filler provides lubrication and, possibly, oxidation resistance. The composites can be used as self-lubricating materials or in the form of mixed powder coatings applied on metal substrate by commercial coating processes such as plasma spraying.

The friction behaviour of several fluoride-metal composites have been extensively studied by Sliney *et al.* [10, 49–54]. Nickel-containing composites (with BaF_2–CaF_2 eutectic) showed good lubrication characteristics between 260 °C and 537 °C [51]. Substituting Ni with Ni–Cr improved the wear and oxidation behaviour, but the coefficient of friction remained comparable to that of the nickel composites. In other work, Sliney and Fusaro [52] studied the lubrication behaviour of tungsten, molybdenum, and cobalt-molybdenum base composites (with CaF_2–BaF_2 eutectic) between room temperature and 900 °C. Sintered porous Co-25% Mo was better than W or Mo as a matrix for the CaF_2–BaF_2 eutectic lubricants. The friction coefficient of the Co–25% Mo/CaF_2–BaF_2 composite was 0.35 at room temperature and dropped off linearly with increasing temperature to 0.1 at 900 °C. The use of silver as a metal matrix with CaF_2–BaF_2 for lubricating steel surfaces was investigated by Amato and Martinengo [55]. The coefficient of friction obtained with this composite was 0.32 at room temperature, and decreased to 0.18 at 700 °C.

4.3. Fluoride-ceramic composite coatings

Ceramic bonded fluorides have excellent wear and oxidation resistance and are intended primarily for use at elevated temperatures. The coefficient of friction of coatings prepared from CoO–CaF_2 applied to Inconel-X ranges from 0.1 to 0.2 between 120 °C and 815 °C [56]. At all temperatures, the rider wear was significantly lower than that for unlubricated metals. Similar results were reported [55] for plasma-sprayed NiO containing about 15% CaF_2. The friction and wear behaviour of ceramic bonded calcium fluoride coatings was compared to those of MoS_2 and PbO–SiO_2 up to 815 °C [56]. The results are shown in Fig. 4. The binder used consists of a mixture of oxides of Ba, Co, and B. Below about 340 °C, friction and wear characteristics of the CaF_2 based coating is inferior to those of the other two coatings. The behaviour is reversed above 425 °C.

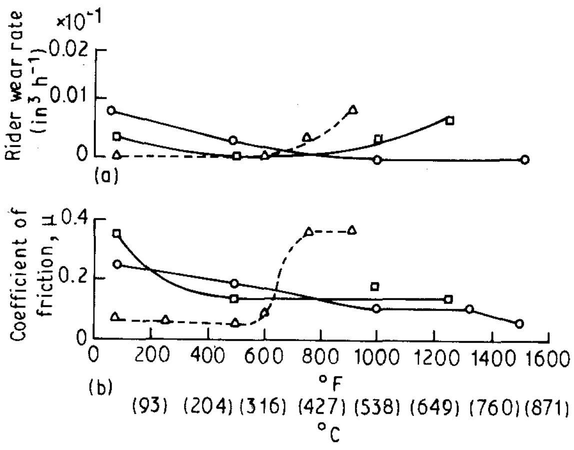

Figure 4 Effect of temperature on (a) wear and (b) friction of thin solid films [56]. (△) 0.0003-IN. MoS_2 ON 1020; (□) 0.001-IN. PbO–SiO_2 ON 440C; and (○) 0.001-IN. CaF_2-ceramic ON Inconel X.

The friction and wear behaviour of CaF_2–ZrO_2 plasma sprayed coatings was investigated by Sliney [10] between room temperature and 650 °C. The study showed a coefficient of friction of ~ 0.22 at 650 °C and very low wear rates. The coefficient of friction and wear rates of CaF_2-based composites containing various levels of Ca_2SiO_4 and CaO were also studied by Sliney [57] up to 815 °C. The friction coefficient (measured at ~ 600 m min^{-1} velocity) was below 0.2 from 25 °C to 815 °C with a minimum of 0.06 at 600 °C. These values are somewhat below those of the all-fluoride composite. The wear rate of the Ca_2SiO_4–CaO modified composite was 1000 times lower than that of the unlubricated substrate alloy (Ni-Cr).

Monoaluminium phosphate $\{Al(PO_3)_3\}$ has been investigated as a bonding agent in fluoride-based composites [58]. Lavik *et al.* found that the addition of aluminium phosphate to a CaF_2–BaF_2 composite significantly improved the adhesion of the sintered film to metallic substrates. The results indicate that the addition of 6 vol% aluminium phosphate produces a coefficient of friction of 0.09 at 705 °C.

5. Oxide solid lubricants

Oxides have been known to facilitate relative motion between contacting metallic surfaces by reducing the coefficient of friction and lowering the wear rate [59, 60]. Friction and lubrication tests show that several oxides and double oxides are potentially useful in wear-related applications at high temperature [61]. Lead oxide (PbO) appears to be an effective lubricant up to 675 °C, with a friction coefficient of 0.07 at 675 °C. The good lubricity is thought to arise from viscous flows of the soft PbO [15, 62, 63]. It has also

TABLE I Friction coefficient of oxides, oxide mixtures, and double oxides

Lubricant	Test Temp. (°C)	Load (kg)	Velocity (cm sec^{-1})	Coefficient of friction (μ)	Reference
PbO	704	7.70	0.76	0.12	67
PbO	427	1.00	218.40	0.05	63
	676	1.00	218.40	0.12	63
PbO	593	14.50	2.54	0.10	68
PbO–4%PbO–SiO_2	25–650	9.80	> 600.00	< 0.20	10
95%PbO–5%B_2O_3	25–537	1.00	218.40	0.14	63
93%PbO–5%SiO_2–2%Fe	25–650	1.00	50.00	0.40 at 25 °C 0.20 at 650 °C	55
B_2O_3	650	7.70	0.76	0.14	67
	> 700	1.75	0.10	0.20	69
	593	14.50	2.54	0.18	68
MoO_3	704	7.70	0.76	0.20	67
	593	14.50	2.54	0.38	68
WO_3	704	7.70	0.76	0.55	67
	537	18.10	2.90	0.41	62
	593	14.50	2.54	0.56	68
CdO	704	7.70	0.76	0.48	67
	537	18.10	2.90	0.34	62
SiO_2 (quartz)	760	6.00	3.00	0.55–0.75	56
	1093	6.00	3.00	0.40	56
ZnO	704	1.88	0.76	0.33	67
	537	6.00	3.00	0.70	56
Co_2O_3	704	7.70	0.76	0.28	67
	704	6.00	3.00	0.45	56
CoO	704	6.00	3.00	0.38	56
Cr_2O_3	870–1093	6.00	3.00	0.25	56
	650	14.50	2.54	0.40	70
NiO	815	6.00	3.00	0.35	56
	593	14.50	2.54	0.69	68
Fe_3O_4	593	14.50	2.54	0.40	68
Fe_2O_3	593	14.50	2.54	0.42	68
Cu_2O	704	7.70	0.76	0.44	67
	593	14.50	2.54	0.48	68
CuO	593	14.50	2.54	0.18–0.22	68
V_2O_5	676	6.00	3.00	0.52	56
	593	14.50	2.54	0.32	68
Bi_2O_3	537	18.10	2.90	0.32	62
	815	6.00	3.00	0.18	56
	> 815	6.00	3.00	0.10	56
BaO	871	6.00	3.00	0.22	56
Sb_2O_3	537	18.10	2.90	> 0.41	62
SnO	704	7.70	0.76	0.42	67
Re_2O_7	316	14.50	2.54	0.23	68
ReO_2	593	14.50	2.54	0.27	68
PdO	537	18.10	2.90	> 0.41	62
TiO_2	704	7.70	0.76	0.50	67
MnO_2	704	7.70	0.76	0.41	67
CuO–Re_2O_7	580	–	–	0.18	68
CuO–MoO_4	580	–	–	0.35	68
CoO–Re_2O_7	580	–	–	0.20	68
CoO–MoO_4	580	–	–	0.34	68
Re_2O_7–B_2O_3	580	–	–	0.15	68
$PbMoO_4$	704	7.70	0.76	0.29	67
K_2MoO_4	704	7.70	0.76	0.20	67
$NiMoO_4$	704	7.70	0.76	0.29	67
Ag_2MoO_4	704	7.70	0.76	0.28	67
$FeMoO_4$	704	7.70	0.76	0.42	67
$CaMoO_4$	704	7.70	0.76	0.52	67
$Cr_2(MoO_4)_3$	704	7.70	0.76	0.80	67
Na_2WO_4	704	7.70	0.76	0.17	67
Pb_2WO_4	704	7.70	0.76	0.35	67
$CuWO_4$	704	7.70	0.76	0.41	67
$FeWO_4$	704	7.70	0.76	0.43	67
$CaWO_4$	704	7.70	0.76	0.45	67
$Cr(WO_4)_3$	704	7.70	0.76	0.49	67
$NiWO_4$	704	7.70	0.76	0.51	67
Cr_2O_3–Fe_2O_3	650	1.20	0.50	0.13	71
NiO–Fe_2O_3	650	1.20	50.00	0.15	71

been found [48, 63–66] that the addition of small amounts of SiO_2, B_2O_3, and Fe_2O_3 to PbO to form a sintered ceramic coating can protect against oxidation of PbO and improve adhesion to substrates. The results of Peterson *et al.* [67] show that PbO, B_2O_3, MoO_3; potassium molybdate (K_2MoO_4), sodium tugstate (Na_2WO_4), as well as metallic lead and silver are most promising in providing low friction characteristics above 700 °C. Sliney [56] obtained a value of about 0.2 for the friction coefficient of a thin chromium oxide (Cr_2O_3) film on cast inconel between 870 to 1093 °C in air. Below 870 °C, the coefficient of friction ranges between 0.3 to 0.4 under the same conditions. Table I shows the coefficients of friction of a large variety of oxides, oxide mixtures, and double oxides at elevated temperatures.

6. Conclusions

This review discusses currently available information on solid lubricants, their properties and temperature capabilities, in an attempt to establish a systematic appraisal of the various classes of lubricants used at elevated temperatures.

The main groups of lubricants are polymers, laminar solids, fluorides, and metal oxides. The polymer group has the lowest temperature capability as they offer good lubrication up to 300 to 350 °C. They are usually soft and lack strength and dimensional stability. The best known example of a polymeric lubricant are the polyimides and polytetrafluorethelene (PTFE). Most polymer lubricants are used in the form of composites which utilize inorganic filler materials to improve their strength and wear properties. The most important materials in the second group are graphite and molybdenum disulphide. Graphite has more potential because of its higher temperature lubricating capability (450 °C compared to 300 °C for molybdenum disulphide) and because its oxidation products are gaseous species that should not cause abrasion or wear to metal or ceramic substrates. Other layered components, such as tungsten disulphide, boron nitride, and lead oxide, are useful lubricants up to about 600 °C. However, most of these materials oxidize at high temperature to form abrasive oxides.

Metal fluorides are more attractive solid lubricants than layered compounds or polymers because of their better high temperature lubricating properties. Most fluorides are chemically stable under oxidizing environments, they can withstand high loads, and provide good lubricity up to about 800 °C. Some rare earth fluorides have shown good lubrication up to 1000 °C in air. For extreme high temperature applications, oxides stand at the top of the list, though they perform poorly at room temperature. Chromium oxide (Cr_2O_3) offers good lubricity up to about 1000 °C.

It should be realized by designers and engineers that there is no "universal lubricant" that can operate under all environmental conditions. Solid lubricants that are efficient at high temperatures do not provide good lubrication at low temperatures. Conversely, lubricants that are efficient at low temperatures are unstable at high temperatures. For the lower temperature regimes, polymers or layered compounds may represent the best choice. For the more demanding high temperatures and aggressive chemical environments, the fluorides and oxides are probably the only choice. Among all materials discussed in this review, graphite occupies a unique place. It can provide excellent lubrication at both ambient temperature in the crystalline form, and at very high temperatures in the form of gaseous combustion products.

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