Chapter 13
Tribology of Solid Lubricants

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Abstract Over the last seven decades, extreme operating conditions encountered in many industrial and engineering applications—particularly those within the aerospace industry—have driven the evolution of more advanced commercial lubricants. While many long-standing lubrication techniques utilize liquid or grease-type lubricants, new tribological applications have developed over the last 70 years that have led to the development of lubricants derived from solid materials and coatings with self-lubricating properties. Many tribological applications require two surfaces to slide over one another in relative motion, resulting in friction and wear, such as in cutting and forming operations, gears, bearings, and engine parts. Increasingly, more of these applications are operating in extreme environments (such as high vacuum, microgravity, high/low temperatures, extreme pressure, space radiation, and corrosive gas environments) that are beyond the tolerable and usable domain of liquid and grease-based lubricants. This has propelled the development of dry/solid lubricants that are nonvolatile and can withstand such extreme environmental conditions. In this chapter, a review of the state of solid lubrication and the utilization of solid lubricants as powder transfer films, thin film coatings, colloidal mixtures, and composite matrices are presented for the field of tribology.

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P.L. Menezes et al. (eds.), *Tribology for Scientists and Engineers: From Basics to Advanced Concepts*, DOI 10.1007/978-1-4614-1945-7_13,

1 Introduction

Solid lubricants were first introduced as commercial products in the 1940s to meet the demands of the aerospace industry to control friction and wear. As many of the applications became specialized and oriented towards conditions of extreme environments (e.g., high or low temperatures, vacuum, radiation, and high contact pressures), they began reaching beyond the tolerable domain of conventional liquid and grease-type lubricants. In the early developments of solid lubricants, much of the research was performed by government organizations such as the National Aeronautics and Space Administration (NASA) and was under proprietary restrictions. However, as solid lubricants have become more prevalent and understood by commercial lubrication engineers, much of the research and data has become readily available and the technology has become commercialized with the information being disseminated through the scientific community. Solid lubricants offer a variety of advantages when compared to conventional liquid or grease-type lubricants. As described in Table 13.1, they have a high resistance to abrasion, lower rates of deterioration, and are less volatility than conventional lubricants. Applications of solid lubricants involve their use as dry lubricants, thin films, and as dispersants in water, oils, and greases. Combinations of solid and liquid lubricants also play an important role in the synergetic effect of controlling friction and wear performance in specialized sliding interfaces where

Table 13.1 Advantages and disadvantages of solid lubricants [8]

Advantages	Disadvantages
• Are highly stable in high-temperature, cryogenic temperature, vacuum, and high-pressure environments • Have high heat dissipation with high thermally conductive lubricants, such as diamond films • Have high resistance to deterioration in high-radiation environments • Have high resistance to abrasion in high-dust environments • Have high resistance to deterioration in reactive environments • Are more effective than fluid lubricants at intermittent loading, high loads, and high speeds • Enable equipment to be lighter and simpler because lubrication distribution systems and seals are not required • Offer a distinct advantage in locations where access for servicing is difficult • Can provide translucent or transparent coatings, such as diamond and diamond-like carbon films, where desirable	• Have higher coefficients of friction and wear than for hydrodynamic lubrication • Have poor heat dissipation with low thermally conductive lubricants, such as polymer-base films • Have poor self-healing properties so that a broken solid film tends to shorten the useful life of the lubricant (however, a solid film, such as a carbon nanotube film, may be readily reapplied to extend the useful life.) • May have undesirable color, such as with graphite and carbon nanotubes

the combined properties enhance the lubricant performance [1]. Solid lubricants behave and function similar to liquid or grease type lubricants in sliding contact, by adhering to the lubricating surfaces and forming a protective boundary layer that minimizes contact between opposing surface asperities to prevent wear. The protective boundary layer acts as a lubricant in sliding contact by easily shearing and accommodating the relative surface velocities. This allows the lubricious protective layers or coatings to provide low friction and minimal wear thus facilitating lubrication. Solid lubricants are often used in environments where their ability to resist the detrimental factors that render conventional liquid or grease-type lubricants ineffective—such as operation within cryogenic temperatures. The advantages to using solid lubricants include their ability to lubricate components for the duration of their life; perform dry lubrication; maintain non-volatility; lubricate where the presence of vapors from fluids or greases are unacceptable; and resist attraction to dust or dirt. Despite the many accolades received by solid lubricants, there are still some limitations, where environmental conditions such as atmospheric conditions, temperature, radiation, and load can influence their performance. In this chapter, the many contributing factors to the rise in solid lubricant usage as well as their lubricating performance are discussed in detail.

2 History of Solid Lubrication

2.1 *Introduction to Solid Lubricants*

The history of solid lubricants dates back to the invention of the wheel and has since grown into one of the largest industries in the world. Even now, it is estimated that one-third to one-half of all the energy produced is still lost through friction due to inefficient lubrication practices. Early applications of lubricants include the use of animal fats and vegetable oils until the first oil well was drilled in Titusville, PA, USA in 1859. This brought rapid advances in lubrication technology with the advent of petroleum-based oils. During the mid-1930s, the use of petroleum-based oils was significantly improved through the use of additives (some being solids) to enhance the load carrying capacity, lubricity, corrosive protection, and thermal-oxidative stability of the oils. As industrial applications became more complex, this required the use of lubricating components at higher temperatures and extreme environments. In many applications petroleum oils became inept, which led to the development of synthetic lubricants in the late 1930s. However, even synthetic lubricants encountered problems involving extremely high temperatures of supersonic aircraft, spacecraft, and other advanced industrial applications. This problem forced lubrication engineers to develop lubricants that do not evaporate at high temperatures and can withstand the various environmental and operational conditions, thus the solid lubricant was born in the 1940s. Solid lubricants are often

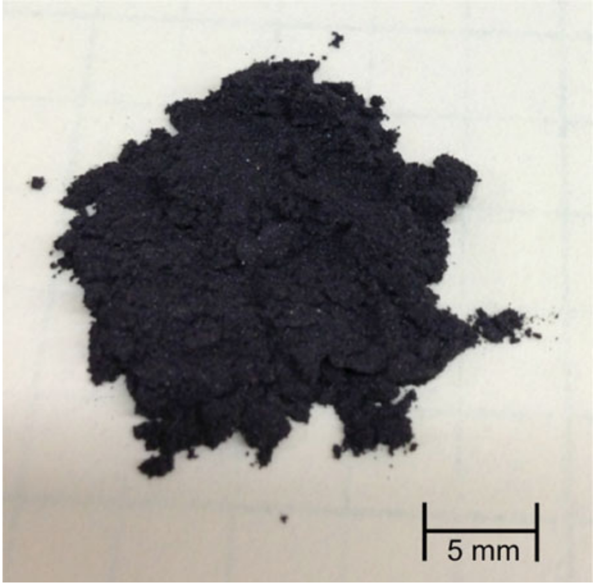


Fig. 13.1 Photograph of 50 nm graphite powder

described as substances that provide lubrication between two surfaces in relative motion under dry conditions. In preliminary studies, solid lubricants were effective at providing adequate lubrication of bearing surfaces at high temperatures and low pressures. The two best known and most popular solid lubricants are graphite and molybdenum disulfide. This is due to their slippery nature and low friction qualities. Photographs of graphite and molybdenum disulfide powders are shown in Figs. 13.1 and 13.2, respectively. Graphite is one of the oldest solid lubricants and has been used as a lubricant for centuries. Molybdenum disulfide was first used as a solid lubricant when travelers in Colorado employed pulverized rock to lubricate their wagon wheels. Coincidently, this also happens to be where the world's largest mineral deposit of molybdenite is located at Climax, CO, USA. Other types of solid lubricants consist of soft metals, metallic oxides, sulfides, selenides, tellurides, polymers, and composite materials, all of which have differing properties making them advantageous in various applications. A brief history of solid lubricants and their applications can be seen in the literature [2–4].

2.2 Advantages and Disadvantages of Solid Lubricants

Solid lubricants offer many advantages over liquid lubricants in applications (see Table 13.1) involving high vacuum, high temperature, cryogenic temperature, radiation, extreme dust, or corrosive environments [2, 3, 5, 6]. Figure 13.3 depicts the many operating conditions in which fluid lubricants are undesirable or ineffective, thus requiring the use of solid lubricants [7]. More specifically, Fig. 13.3 illustrates the

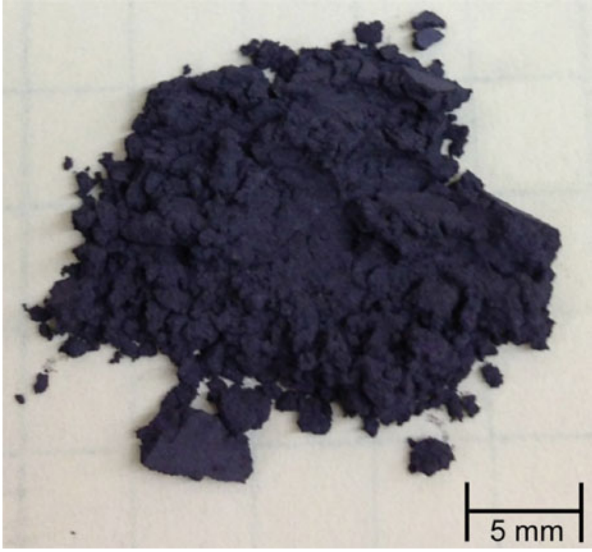


Fig. 13.2 Photograph of 2 μm molybdenum disulfide (MoS_2) powder

environmental applicability of solid and liquid lubricants in radiation, extreme temperature, and vacuum environments. In extreme pressure applications (i.e., high to ultrahigh vacuum conditions—a vacuum of ~10^{-2} Pa or higher or a gas density of ~10^{-12} molecules/cm^3 or lower) liquid lubricants can vaporize [2]. For example, in space, a liquid lubricant would vaporize, thus contaminating the device it is lubricating and potentially damaging it. This example could occur in the case of an optical or electronic equipment application. On the contrary, if a solid lubricant were used this problem would no longer exist. In high temperature applications extending beyond 523 K, liquid lubricants often vaporize or decompose, limiting their use as a lubricant. In contrast, when compared to liquid lubricants, solid lubricants at these temperatures can maintain relatively low coefficients of friction. Liquid lubricants can also solidify or become highly viscous and may not be effective at cryogenic temperatures. For this reason, solid lubricants are used when operating at temperatures as low as 0 K. In radiation environments, liquid lubricants tend to decompose at 10^6 rads (radiation dose absorbed of 10^4 J/kg), whereas solid lubricants demonstrate better radiation resistance and relatively low friction. In extreme dust areas, dust particles would ordinarily adhere to liquid lubricants, forming a grinding paste. This paste can cause abrasive wear and damage surfaces and sensitive equipment. In such a case, hard solid lubricants, such as diamond-like carbon and boron nitride films are preferred. In aerospace applications (e.g., weight-limited spacecraft and rovers) where weight limits are critical, solid lubrication is advantageous. Solid lubricants weigh substantially less than liquid lubricants and their use eliminates the need for recirculatory oil systems with pumps and heat exchangers [2, 3]. Moreover, the limited use of liquid lubricants and their replacement by solid lubricants would reduce spacecraft weight and therefore, have a dramatic impact on mission extent and spacecraft

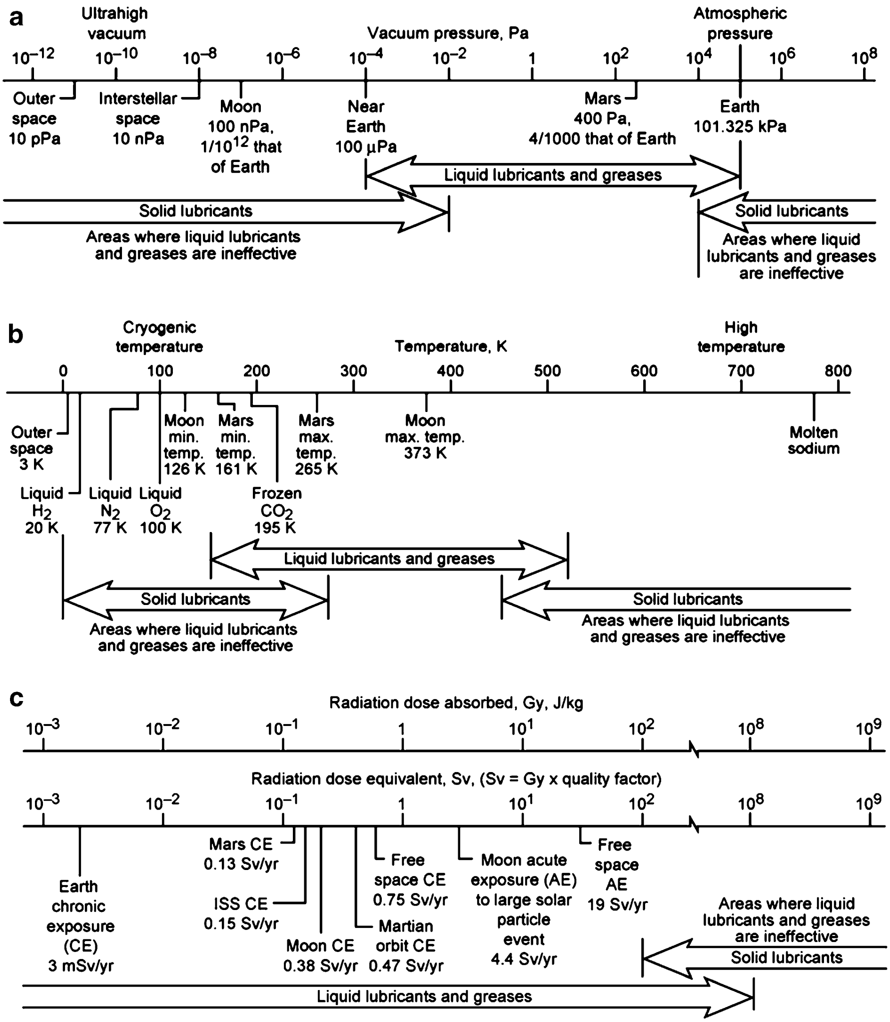


Fig. 13.3 Variations in environmental conditions for adequate usage for liquid, solid, and grease type lubricants: (**a**) vacuum environments; (**b**) cryogenic and high temperature environments, (**c**) radiation environments [7]

maneuverability. Under intermittent loading conditions or in corrosive environments, liquid lubricants can become contaminated, lose their lubricity, and lead to seizure of components. Changes in critical service and environmental conditions such as loading, time, contamination, pressure, temperature, and radiation, also affect liquid lubricant efficiency. When equipment is stored or is idle for extended periods, solid lubricants provide permanent satisfactory lubrication by maintaining their physico-chemical attributes unlike liquid lubricants.

Some of the disadvantages of solid lubricants are their higher coefficient of friction and wear rates when used in hydrodynamic lubrication processes. Many solid lubricants maintain poor heat dissipation with low thermal conductivity when compared to liquid lubricants. For this reason, applications that require heat dissipation generally resort to liquid lubricants that can be pumped or circulated to remove heat. In cases where a solid lubricant is used and minimal heat generation is required, alternative techniques must be implemented to dissipate the heat. Additionally, solid lubricants have poor self-healing properties in the sense that a broken solid film can cause a decrease in the useful life of particular mechanical components.

2.3 Applications of Solid Lubrication

When solid materials were first being used as lubricants, much of the industry knowledge was primarily constrained to individuals within the lubrication industry and commissioned by government agencies such as the National Aeronautics and Space Administration (NASA), the Department of Defense (DOD), and the Department of Energy (DOE). As solid lubricants gained acceptance, other aerospace and commercial industries began utilizing them. Currently, knowledge of the applicability and use of solid lubricants is widespread and disseminated through publications in numerous scientific journals and conferences worldwide. The acceptance of solid lubricants to become a viable lubricant in the larger lubrication market was slow and encountered much reluctance, because of the frequent misuse and lack of knowledge in their early days. As more information was learned in the last several decades, their potential has been fully realized. Table 13.2 lists applications of solid lubricants that are utilized in various environments and operating conditions.

Solid lubricants received their start in the aircraft industry on both military and commercial aircraft as indicated by the numerous aerospace applications in Table 13.2. Solid lubricants were used in missiles and space vehicles as well as being exploited in these industries for their ability to lubricate under extreme conditions. Solid lubricants were initially used in only a few components in the 1900s fighter planes, however with time solid lubricants were eventually adopted and utilized in over 1,000 components on the North American Rockwell XB-70 bomber. Here, over 95 % of the plain bearings were lubricated with a plastic or thin-film-ceramic solid lubricant. The North American Rockwell Corporation was well known for its ceramic-bonded lubricant, “Vitrolube” which was used on bushings or plain spherical type bearings in applications from room temperature up to 644 K [3]. Aircraft components that require solid lubrication are ejection seat parts, canopy linkages, and control lever components. In these safety devices the movement is limited but it is critical that these mechanisms perform when needed. Other aerospace applications of solid lubricants include missiles, satellites, and spacecraft components [8]. Solid lubricant coatings have also been used in space

Table 13.2 Applications of solid lubricants [2, 7]

(a) Areas where fluid lubricants are undesirable	
Requirements	Applications
Resist abrasion in dirt-laden environments	Space vehicles (rovers) Lunar base Martian base Aircraft Automobiles Agricultural and mining equipment Off-road vehicles and equipment Construction equipment Textile equipment Dental implants
Avoid contaminating product or environment	Space telescopes Equipment in lunar base Equipment in Martian base Microscopes and cameras Spectroscopes Medical and dental equipment Artificial implants Food-processing machines Optical equipment Metalworking equipment Surface-mounted equipment Hard disks and tape recorders Textile equipment Paper-processing machines Business machines Automobiles
Maintain servicing or lubrication in inaccessible or hard-to-access areas	Space vehicles Satellites Aerospace mechanisms Nuclear reactors Consumer durables Aircraft
Provide prolonged storage or stationary service	Space telescope mounts Space antenna mounts Aircraft equipment Railway equipment Missile components Nuclear reactors Heavy plants, buildings, and bridges Furnaces

(continued)

Table 13.2 (continued)

(b) Areas where fluid lubricants are ineffective

Environment		Applications
High vacuum	Room temperature or cryogenic temperatures	Vacuum products Space mechanisms Satellites Space telescope mounts Space platforms Space antennas
	Cleanroom	Biomedical equipment Analytical tools Coating equipment Semiconductor manufacturing equipment
	High temperature	Space nuclear reactors X-ray tubes X-ray equipment Furnaces
High temperature	Lunar environments	Space vehicles Space mechanisms Lunar bases
	Air atmosphere	Furnaces Metalworking equipment Compressors
	Molten metals (sodium, zinc, etc.)	Nuclear reactors Molten metal plating equipment
Cryogenic temperatures		Lunar and Martian bases Space mechanisms Satellites Space vehicles Space propulsion systems Space telescope mounts Space platforms Space antennas Turbo pumps Liquid nitrogen pumps Butane pumps Freon pumps Liquid natural gas pumps Liquid propane pumps Refrigeration plants
Radiation (gamma rays, fast neutrons, X-rays, beta-rays, etc.)		Lunar and Martian bases Nuclear reactors Space mechanisms Satellites Space vehicles Space platforms Space antennas

(continued)

Table 13.2 (continued)

(b) Areas where fluid lubricants are ineffective

Environment	Applications
Corrosive gases (chlorine etc.)	Maneuvering Semiconductor manufacturing equipment
High pressures or loads	Metalworking equipment Bridge supports Plant supports Building supports
Fretting wear and corrosion (general)	Space antennas Space platforms Aircraft engines Turbine blades Landing gear Automobiles

vehicle components such as the gimbal bearings, tie-down clamps, camera parts, gears, bearings, sliding tracks, and valves.

In military applications, the US Army utilizes tremendous amounts of solid lubricants in a variety of forms for weapons and ground-handling equipment such as ball sockets, sliding covers, hand wheels, bearing-support points, slide dust covers, hand brakes, chain and sprocket drives, plungers, screw threads, telescoping-tube assemblies, warhead-mating fixtures, trailer elevating mechanisms, torsion bar suspensions, bearing areas, rifle mounts, rocket launchers, ammunition, firing mechanisms, breech mechanisms, and Trunnion bearings [9]. The US Army also utilizes solid lubricants in helicopter gearboxes and antifriction bearings. In these applications, the solid lubrication system serves as an auxiliary backup lubrication system in the event that the liquid oil lubrication system failed during an aircraft's flight. Other branches of military also utilize solid lubricants, such as the US Navy for applications involving aircraft and ships where greases with molybdenum disulfide additives are used to prevent seizure of gears, bearings, and joints.

The secondary adoption of solid lubricants began when commercial industries such as automotive, heavy electrical, metalworking, marine, household-appliance, toy, farming, and solid-waste disposal industries realized the value of such lubricants. Their applications are vast with some applications shown in Table 13.2. Other applications of solid lubricants include convex draw dies, solenoids, arc-furnaces guides, core-oven wheel bearings, conveyor wheels, railroad centerplates, helicopter gear boxes, cold extruder (wire), roller chains, turntable 45 rpm spindle (music), air-cooled four cylinder engines, cold hobbing (with steel dies), rolling mills, conveyor parts, brake air cylinders, oil pipeline valves, bullets, boat hulls, roll-extruded cylinders, wire rope (wire strand), aircraft landing gear, oxygen-furnace bearings, pressurized tee connectors on gas mains, small arms, ball joints and front suspensions (automobiles), air cylinder tubing, three-jaw chucks, plug valves, racecar axle threads, timing mechanisms, fuel pump mechanisms, rear axle assemblies (tractors), electrical connectors (space), cylinder walls (gasoline engines), gear trains, clutch brakes, hinge bolts, pylon-hinge pins (copters), rocket bellows, bearing-link assemblies, clock springs, camera shutters (space flight), root ribs (aircraft), rocket engines, fasteners, valves, bushings, rolling-mill couplings, self-aligning ball bushings, composite brushes, thrust bearings, draw and blanking punches, drilling and tapping machines, wheel bearings and kingpins (truck fleets), and sliding-tandem trailers (trucks) [3].

3 Quantification of Lubricants

3.1 Classifications

Lubricants are classified into two categories by (1) lubricating film type and (2) physiochemical properties. When categorizing lubricants as lubricating films, they are organized into three types: solid films, fluid films, and thin films. Solid films can be adsorbed, bonded, or deposited on lubricating surfaces. Solid lubricants are generally classified as solid films because of their ability to adhere to surfaces through various adsorption and deposition processes. Fluid films are thick films that completely separate two surfaces moving in relative motion with each other, whereas thin films only provide partial separation. Both fluid and thin films are typically composed of liquid lubricants. Table 13.3 shows the classification according to lubrication film with the addition of gas films, which consist of a pressured mass of gaseous atoms. In Table 13.3, fluid films are subclassified into several categories:

(a) Hydrodynamic films, which are defined as films formed by the motion of the lubricating surfaces through a convergent zone creating sufficient (hydrodynamic) pressure to support a normal load and thus maintaining separation of the surfaces without the aid of an external pumping apparatus;
(b) Hydrostatic films, which are fluid films that occur when pumping a fluid or film between the two lubricating surfaces that are in relative motion; and
(c) Squeeze films, which are fluid films that occur when lubricating surfaces move towards each other.

The second method of quantifying lubricants is through their physiochemical properties. This method classifies them based on their chemistry, crystal structure, and lubricity. Table 13.4 presents the most widely used and most recently developed lubricants by their subclasses as well as providing their coefficient of friction range. The ranges in the coefficient of friction are due to the fact that friction is a system dependent property that is dependent upon test environment, operating conditions, and surface geometrical configuration. Ambient conditions such as temperature and humidity as well as the type of counter face materials and surface texture also affect the friction coefficient of a given solid lubricant. Moreover, even the physical nature (i.e., powder, thin film, bulk, composite, and crystalline or amorphous state), deposition method, and/or application method of the solid lubricant can cause variations in the friction and wear properties.

Table 13.3 Types of lubricating films [2, 7]

Type	Lubricating film
Solid films	Nanotubes, nano-onions, and other nanoparticles (C, BN, MoS_2, and WS_2)
	Nanocomposite coatings (WC/C, MoS_2/C, WS_2/C, TiC/C, and nanodiamond)
	Diamond and diamond-like carbon coatings (diamond, hydrogenated carbon (a-C:H), amorphous carbon (a-C), carbon nitride (C_3N_4), and boron nitride (BN) films)
	Superhard or hard coatings (VC, B_4C, Al_2O_3, SiC, Si_3O_4, TiC, TiN, TiCN, AlN, and BN)
	Lamellar film (MoS_2 and graphite)
	Nonmetallic film (titanium dioxide, calcium fluoride, glasses, lead oxide, zinc oxide, and tin oxide)
	Soft metallic film (lead, gold, silver, indium, copper, and zinc)
	Self-lubricating composites (nanotubes, polymer, metal-lamellar solid, carbon, graphite, ceramic, and cermets)
	Lamellar carbon compound film (fluorinated graphite and graphite fluoride)
	Carbon
	Polymers (Polytetrafluoroethylene (PTFE), nylon, and polyethylene)
	Fats, soap, wax (stearic acid)
	Ceramics and cermets
Fluid film	Hydrodynamic films:
	Thick hydrodynamic film
	Elastohydrodynamic film
	Hydrostatic film
	Squeeze film
Thin film	Mixed lubricating film
	Boundary lubricating film
Gas film	Hydrodynamic film
	Hydrostatic film

3.2 *Lamellar Solid Lubricants*

Lamellar or layered solid lubricants are some of the most widely used class of lubricants by engineers. A significant amount of research and development has been performed to understand the tribological characteristics of these lubricants as well as determining the optimal lubricant for specific applications. A few examples of lamellar lubricants are graphite (shown in Fig. 13.1), transition metal dichalcogenides (compounds consisting of at least two molecules from Group 16 of the periodic table) such as MoS_2 (Fig. 13.2) or WS_2 (Fig. 13.4), hexagonal boron nitride (hBN) (Fig. 13.5), and boric acid (H_3BO_3) (Fig. 13.6). These lamellar solid powders all have similar molecular structures composed of layers of atoms bonded together with covalent bonds. These layers are held together by the weak

Table 13.4 Solid materials with self-lubricating capabilities [16]

Classification	Key examples	Typical range of friction coefficient
Lamellar solids	MoS_2	0.002–0.25
	WS_2	0.01–0.2
	hBN	0.150–0.7
	Graphite	0.07–0.5
	Graphite fluoride	0.05–0.15
	H_3BO_3	0.02–0.2
	GaSe, GaS, SnSe	0.15–0.25
Soft metals	Ag	0.2–0.35
	Pb	0.15–0.2
	Au	0.2–0.3
	In	0.15–0.25
	Sn	0.2
Mixed oxides	$CuO–Re_2O_7$	0.3–0.1
	$CuO–MoO_3$	0.35–0.2
	$PbO–B_2O_3$	0.2–0.1
	$CoO–MoO_3$	0.47–0.2
	$Cs_2O–MoO_3$	0.18
	$NiO–MoO_3$	0.3–0.2
	$Cs_2O–SiO_2$	0.1
Single oxides	B_2O_3	0.15–0.6
	Re_2O_7	0.2
	MoO_3	0.2
	TiO_2 (sub-stoichiometric)	0.1
	ZnO	0.1–0.6
Halides and sulfates or alkaline earth metals	CaF2, BaF_2, SrF_2	0.2–0.4
	$CaSO_4$, $BaSO_4$, $SrSO_4$	0.15–0.2
Carbon-based solids	Diamond	0.02–1
	Diamond-like carbon	0.003–0.5
	Glassy carbon	0.15
	Hollow carbon nanotubes	–
	Fullerenes	0.15
	Carbon-carbon and carbon-graphite-based composites	0.05–0.3
Organic materials/polymers	Zinc stearite	0.1–0.2
	Waxes	0.2–0.4
	Soaps	0.15–0.25
	PTFE	0.04–0.15
Bulk or thick-film (>50 μm) composites	Metal-, polymer-, and ceramic-matrix composites consisting of graphite, WS_2, MoS_2, Ag, CaF_2, and BaF_2	0.05–0.04
Thin-film (<50 μm) composites	Electroplated Ni and Cr films consisting of PTFE, graphite, diamond, B_4C, etc., particles as lubricants	0.1–0.5
	Nanocomposite or multilayer coatings consisting of MoS_2, Ti, DLC, etc.	0.05–0.15

Fig. 13.4 Photograph of 0.6 μm tungsten disulfide (WS_2) powder

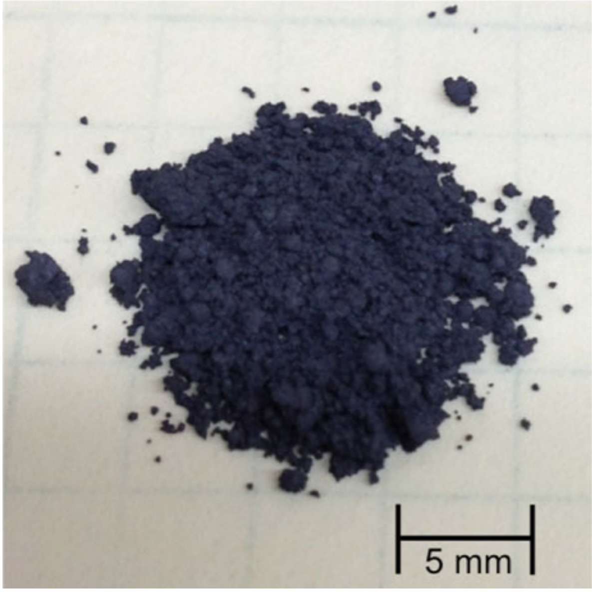
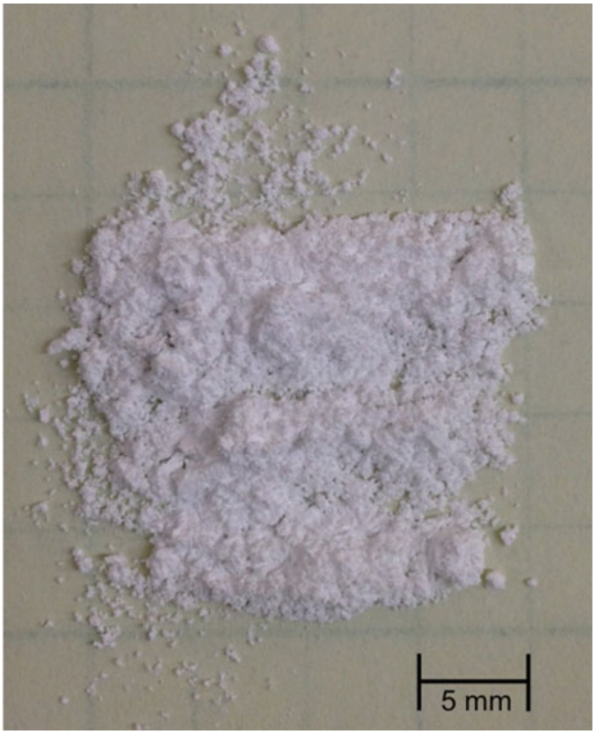


Fig. 13.5 Photograph of 70 nm hexagonal boron nitride (hBN) powder



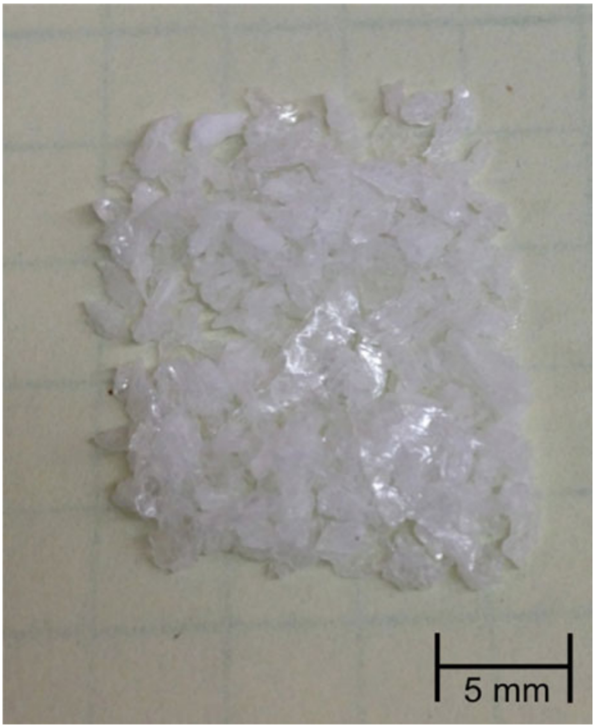


Fig. 13.6 Photograph of micron-sized boric acid (H_3BO_3) powder

van der Waals force and maintain different distances between the layers for different molecules. Figures 13.7, 13.8, 13.9, and 13.10 show a schematic representation of the layered crystal structure of graphite, MoS_2, hBN, and H_3BO_3 molecules, respectively. Some of the more widely used solid lubricants are derived from natural minerals, extracted from deposits found in the earth such as MoS_2, graphite, and boric acid. Other solid lubricants are synthetic, for example WS_2, hBN, fluorinated graphite, and transition metals diselenides (consist of two selenide molecules) and ditellurides (consist of two telluride molecules). The use of diselenides and ditellurides as solid lubricants is significantly less common than the use of graphite and MoS_2. As with many lamellar lubricants, transition metal dichalcogenides gain their lubricity from their layered crystal structure caused by the low intra-layer shear resistance due to the weak van der Waals force.

In the case of lamellar solids such as molybdenum disulfide (MoS_2), the friction coefficient varies from 0.002 to 0.25 due to the film microstructure, chemistry, test environment, ambient temperature, contact pressure, film thickness, stoichiometry, and purity. Due to the porous columnar structure, MoS_2 films deposited by conventional sputtering methods such as physical vapor deposition tend to exhibit higher friction and lower wear rates than films deposited by ion-beam-assisted deposition (IBAD) or closed-field unbalanced magnetron sputtering techniques. The effect of the different film deposition methods results in some films having near perfect

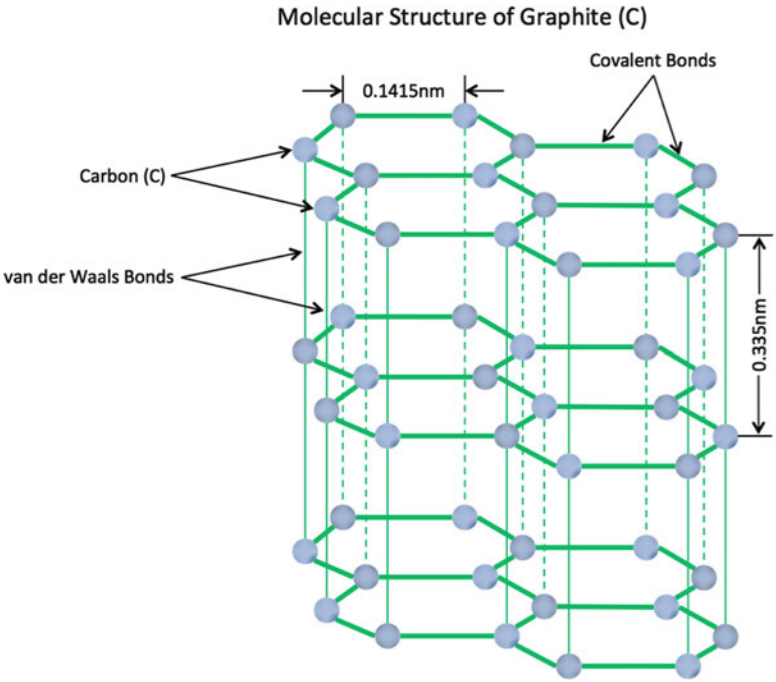


Fig. 13.7 Illustration of the layered crystal molecular structure of graphite (C)

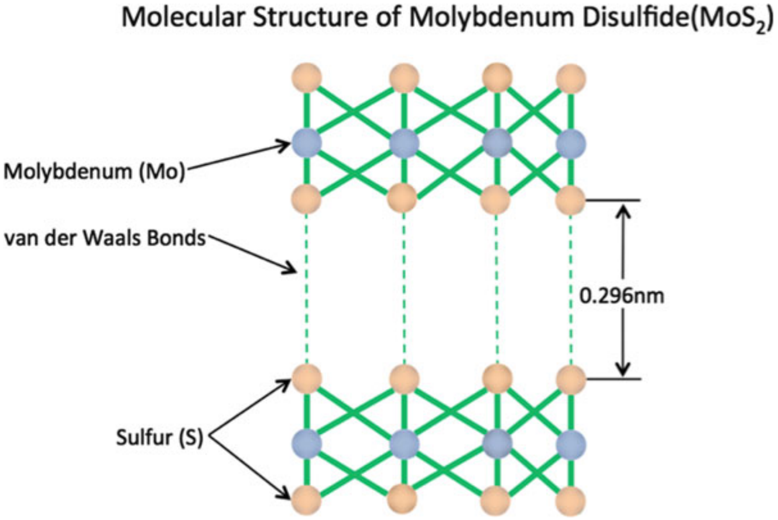


Fig. 13.8 Illustration of the layered crystal molecular structure of molybdenum disulfide (MoS_2) a dichalcogenide

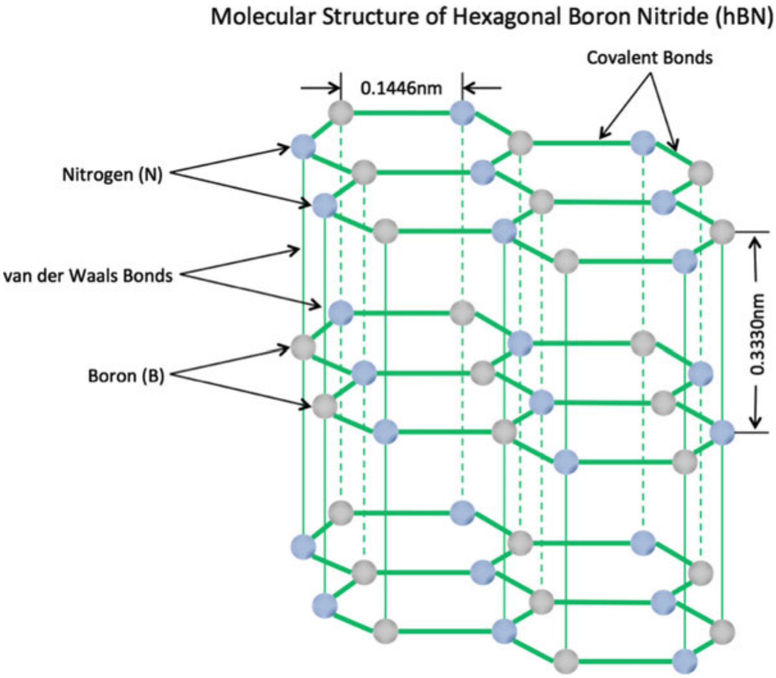


Fig. 13.9 Illustration of the layered crystal molecular structure of hexagonal boron nitride (hBN)

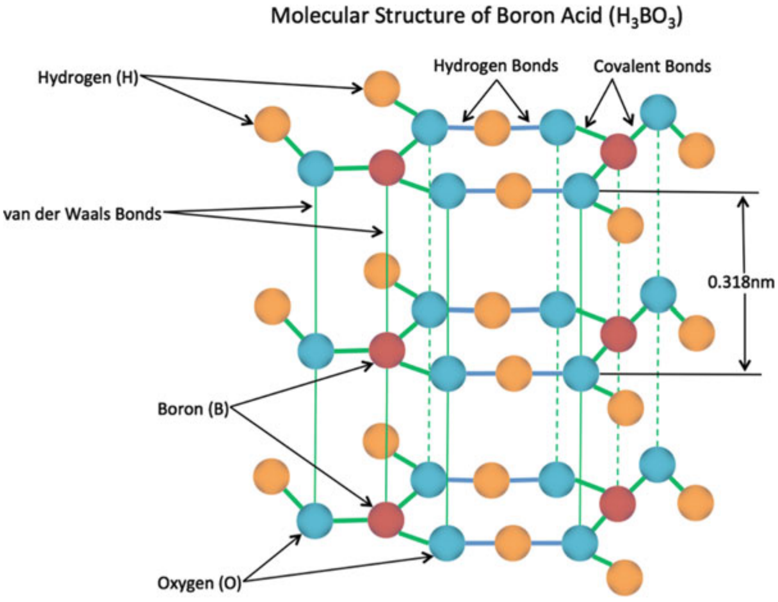


Fig. 13.10 Illustration of the layered crystal molecular structure of boric acid (H_3BO_3)

stoichiometry, purity, and basal plane orientation to the lubricating surface and the direction of motion, thus facilitating extremely low friction coefficients. In fact, in the presence of an ultrahigh vacuum, these deposited MoS_2 films can have friction values as low as 0.002 [10, 11]. All of the aforementioned factors affect the shear rheology and frictional properties of MoS_2, as the coefficient of friction is test dependent. Furthermore, not a single lubricant, including solid lubricants, can provide both low and consistent friction coefficients over a wide variety of test conditions, temperatures, environments, and deposition methods. Therefore, it is customary for lubrication engineers to optimize a lubricant for a specific application with a defined set of operational and environmental conditions.

Due to the sensitivity of each lubricant to its environment, many techniques have been developed to optimize a particular lubricant for a specific application. In extreme environments consisting of vacuum or high/low temperatures MoS_2, WS_2, and hBN are preferred as solid lubricants [12, 13]. Graphite and H_3BO_3 are superior lubricants in moist air environments; however, they are poor lubricants in dry or vacuum environments. As a modification, tribologists have learned that if graphite is fluorinated through a process of electrolysis in a solution of hydrogen fluoride, this creates graphite fluoride. Graphite fluoride has larger spacing between the carbon–carbon layers in graphite resulting in easier shear and hence better lubricity in dry environments. Among the lamellar solids, MoS_2 and WS_2 have some of the best overall load-carrying capacities when used as thin films. Most lamellar solids have good wetting capability and chemical affinity for ferrous surfaces [14]. On a rough or porous sliding surface, MoS_2 and WS_2 accumulate in the valleys between asperities, thus providing a smoother surface finish. When applied properly, these solid lubricants can withstand extreme contact pressures without being squeezed out of the load-bearing surfaces. WS_2 is preferred over MoS_2 when applications involve relatively higher temperatures [15]. However, WS_2 is a synthetic lubricant and therefore it is more expensive than MoS_2, which is derived from a natural mineral known as molybdenite. Selenides of molybdenum (Mo), tungsten (W), and niobium (Nb) can provide even higher temperature capabilities than their sulfide counterparts, and have demonstrated greater electrical conductivity, however, they too are expensive and hence they are used less frequently [16].

3.3 Transition-Metal Dichalcogenides

Transition-metal dichalcogenides are among the lowest-friction materials known for their use in dry, vacuum, and cryogenic environments. They comprise of MX_2 structure, where M is a transition metal consisting of molybdenum (Mo), tungsten (W), niobium (Nb), or tantalum (Ta) and X_2 refers to a chalcogenide consisting of two atoms from Group 16 in the periodic table, most notably consisting of sulfur (S), selenium (Se), or tellurium (Te). MoS_2 and WS_2 are among the most widely used transition-metal dichalcogenides and photographs of

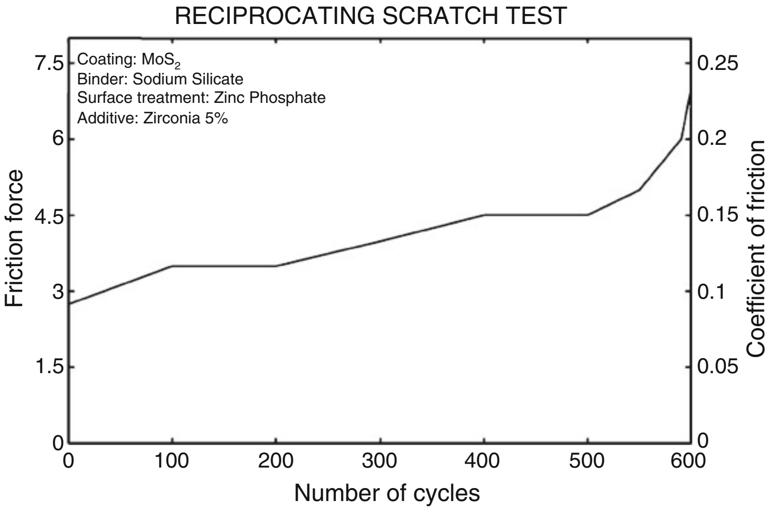


Fig. 13.11 Variation of friction force and coefficient of friction with number of cycles when a steel ball is slid against a zinc phosphated steel specimen coated with the MoS_2 and 5 % zirconia additive [19]

these powder particles are shown in Figs. 13.2 and 13.4, respectively. Dichalcogenides are chemically stable and resist attack by most acids with the exception of aqua regia (also known as nitro-hydrochloric acid), hydrochloric acid (HCL), sulfuric acid (H_2SO_4), and nitric acid (HNO_3). At room temperature in ultrahigh vacuum, these solid lubricants can provide the lowest coefficient of friction values ranging from 0.002 to 0.2. Their shortcomings occur in the presence of moisture environments, which have a detrimental effect on their lubricity [17, 18]. Oxidation of MoS_2 begins when temperatures reach about 648 K and at approximately 773 K, rapid oxidation occurs resulting in MoO_3 and SO as byproducts. The thermal-oxidative stability of WS_2 is better than that of MoS_2 and thus it is used in higher temperature application.

An investigation of MoS_2-based solid lubricant mixtures containing zirconia and graphite on the contact surface during sliding against a steel ball was made [19]. In this study, Zirconia, a ceramic material, was studied because it offers superior tribological properties such as a high resistance to wear. Experiments were conducted to measure the friction force for various numbers of cycles using a reciprocating scratch tester. Figure 13.11 shows the variation of friction force and coefficient of friction with number of cycles when a steel ball is slid against a zinc phosphated steel specimen coated with the MoS_2 and 5 % zirconia additive. The MoS_2-based lubricant with a 5 % zirconia additive has an average wear rate of 0.018 μm/cycle and an initial coefficient of friction value of 0.1. A similar coating containing 8 % of zirconia in the lubricant demonstrated an average wear rate of 0.0125 μm/cycle with an initial coefficient of friction value of 0.11.

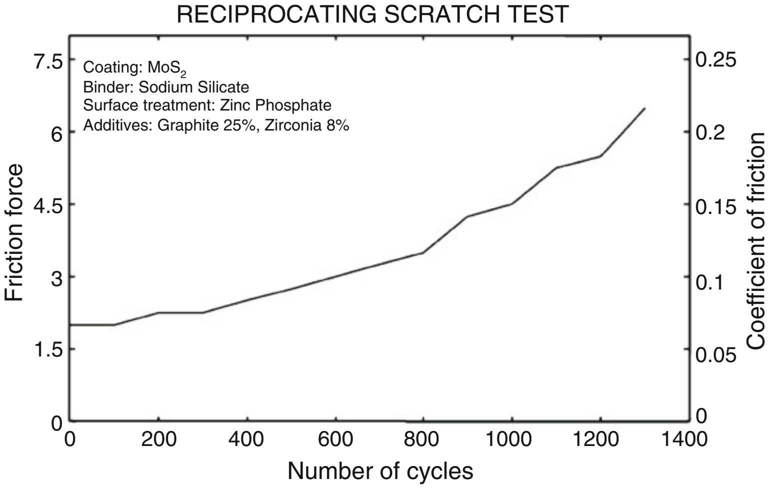


Fig. 13.12 Variation of the friction force and the coefficient of friction with the number of cycles when a steel ball is slid against a zinc phosphated steel specimen coated with MoS_2, 8 % zirconia, and 25 % graphite as additive [19]

Although the addition of zirconia improved the wear properties, it also increased the initial friction value when changing from 5 to 8 % of zirconia. This problem of an increased coefficient of friction value was overcome by the addition of graphite into the lubricant. Graphite, as previously discussed, is an excellent solid lubricant to use in humid conditions because it maintains its low-friction behavior when it is contaminated by water vapor or other condensable vapors. Here, the MoS_2-based lubricant was prepared with a combination of 25 % graphite and 8 % zirconia as additive material. Figure 13.12 shows the variation of the friction force and the coefficient of friction with the number of cycles when a steel ball is slid against a zinc phosphated steel specimen coated with MoS_2, 8 % zirconia, and 25 % graphite as additive. The experiment revealed an average wear rate of 0.003 μm/cycles and an initial coefficient of friction value of 0.06. The addition of 8 % of zirconia and 25 % of graphite to the lubricant increased the wear resistance of the film by about 72 % and reduced the friction coefficient from 0.11 to 0.06.

To understand the influence of moisture on friction and wear, the tests were conducted at a high temperature of 473 K. Figure 13.13, shows the variation of friction force and coefficient of friction with number of cycles when a steel ball is slid against manganese phosphated steel specimens coated with MoS_2 and 8 % zirconia and 25 % graphite as additive at 473 K. The behavior of the MoS_2 film in the presence of moisture at ambient temperatures was found to be poor. On the contrary, at high temperatures, the moisture evaporated and thus enhanced the film performance. The results of scratch tests conducted for 5,500 cycles at 473 K had not shown any signs of failure and maintained a friction coefficient of 0.05. The temperature of the specimen that were maintained at 473 K, were then decreased to room temperature. The results showed a failure of the films occurring as low as

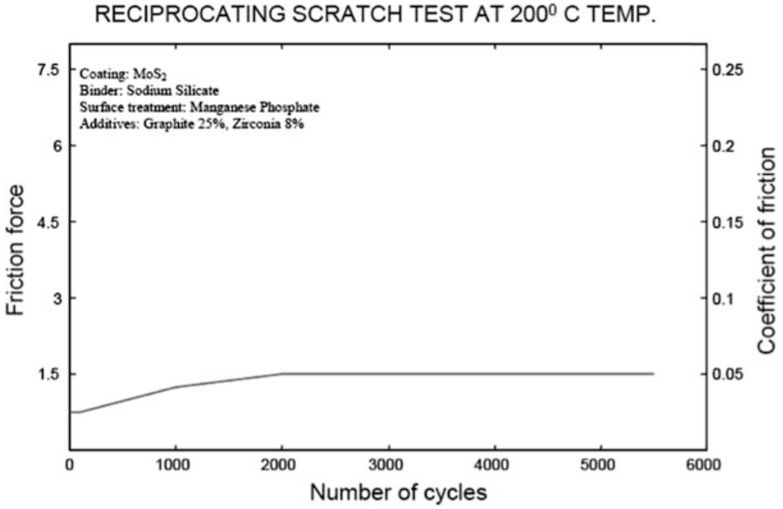


Fig. 13.13 Variation of friction force and coefficient of friction with number of cycles when a steel ball is slid against manganese phosphated steel specimens coated with MoS_2 and 8 % zirconia and 25 % graphite as additive at 473 K [19]

600 cycles and as high as 3,000 cycles. These tests demonstrate the effect of moisture on MoS_2 film. In summary, the results showed that the addition of zirconia and graphite into the MoS2-based lubricant has improved its properties in terms of both friction and wear. In addition, it was observed that the presence of moisture in the air affects the life of the lubricating film increasing the coefficient of friction and wear rate. It was shown that at high temperatures the moisture evaporation enhanced the coating performance of the film.

3.4 Metal-Monochalcogenides

Metal-monochalcogenides, such as GaS, GaSe, or SnSe are similar to transition-metal dichalcogenides by nature of their crystal structures. Monochalcogenides are composed of a MX structure, where the M is a metal consisting of gallium (Ga) or tin (Sn) and the X refers to a single chalcogenide atom such as sulfur (S) or selenium (Se). These solid lubricants are well-known sandwich semiconductors in solid-state physics for their superior electrical and optical properties [20]. Tin and germanium-based monochalcogenides represent a group of layered compounds that also consist of sulfides (SnS and GeS) and selenides (SnSe and GeSn). Similarly, another class of layered metal-monochalcogenides consist of an indium metal-base and have been explored with sulfides (InS) and selenides (InSe). Pin-on-disk experiments, as well as electron microscopy inspection of metal-monochalcogenides, have revealed that the interlayer bonding and the crystal chemistry are responsible for the lubricity and

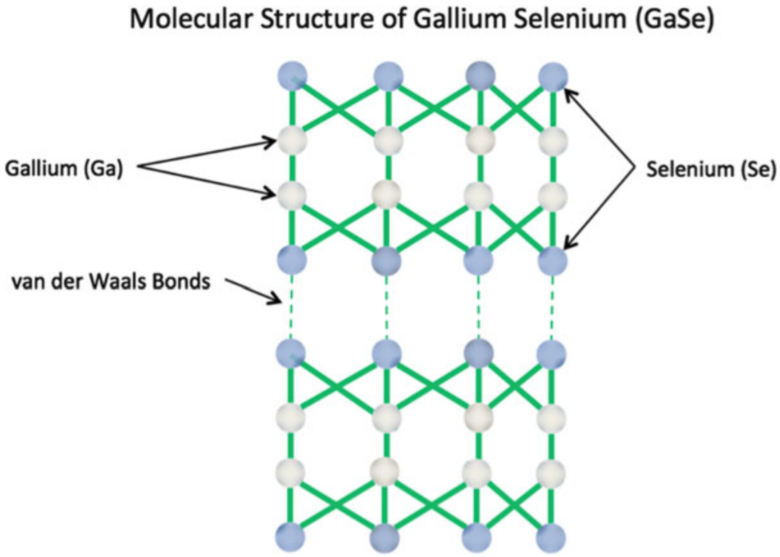


Fig. 13.14 Illustration of the layered crystal molecular structure of Gallium Selenium (GaSe) a Monochalcogenide

self-lubricating mechanisms [21]. Chalcogenide are known for obtaining their low friction and high wear resistance to sliding surfaces due to their lamellar structure in which strongly bonded atoms form extensive rigid sheets. Unlike dichalcogenides such as MoS_2 or $MoSe_2$ whose crystal structure creates a monolayer of Mo ions trapped between layers of S or Se ions, monochalcogenides such as GaS or GaSe have a crystal structure composed of a double layer of Ga sandwiched between S or Se ions. Figure 13.14 illustrates a schematic of the layered crystal structure of GaSe molecules.

3.5 Graphite

Another lamellar solid that offers superior friction reduction and wear resistance properties is graphite. A photograph of graphite powder is shown in Fig. 13.1. Graphite occurs naturally from deposits in the earth and can be synthesized by heating petroleum coke to temperatures of 2,973 K beyond that of graphitization, which converts carbon to graphite. Graphite has been used in many industrial applications due to its good lubricity, abundance, low cost, and resistance to both acids and bases. Graphite can be used as a lubricant in a variety of forms such as a powder, bulk, thin film, colloidal dispersion, solid, and composite forms to combat friction and wear. In some applications, it is used as a dispersant in water, solvents, oils, and greases to achieve better lubricity under extreme application conditions such as lubrication of molds and dies in metal forming; flange on rails; and railcar wheels. Graphite has even found uses as a self-lubricating filler in various metal, ceramic, and polymer matrix composites used in various engines, aircraft components, and seal applications [22–24]. Graphite is one of the softest materials with a relatively poor thermal conductivity but a good electrical conductor. The structure of graphite is sheet-like crystals where carbon atoms are strongly bonded in a plane to form a layer and the layers are weakly held together by van der Waals forces. The layered crystal molecular structure of graphite is shown in Fig. 13.7. In dry air, inert atmospheres, or vacuum, the lubricity of graphite degrades quickly, causing it to be removed from the contacting surfaces. In contrast, the tribological properties of graphite are superior in moist or humid environments. Research has shown that the lubricity of graphite is not solely due to its layered crystal structure, but depends strongly on the quantity of water vapor in the environment. Graphite requires a small amount of condensable vapor to allow the atomic layers to slide with ease thus improving its lubricity. The thermal-oxidative stability of graphite allows it to lubricate in open-air environments where the temperature is below 773 K, however the friction does tend to increase as the temperature rises. Beyond this temperature threshold, graphite begins to rapidly oxidize and lose its lubricity. In vacuum environments, the trends are reversed for graphite. For example, it has an initially higher coefficient of friction of 0.4 at lower temperatures in vacuum, however when the temperature increases, the coefficient of friction decreases. At a maximum temperature of 1,573 K, the coefficient of friction decreases to about 0.2 and beyond this temperature, graphite begins to decompose and lose its lubricity.

3.6 Hexagonal Boron Nitride

A lamellar solid with similar structural and lubricating properties as graphite is hexagonal boron nitride (hBN), also referred to as “white graphite” [25]. A photograph of hBN powder particles is shown in Fig. 13.5 and the layered crystal structure is shown in Fig. 13.9. It can be seen that the molecular structure resembles other lamellar solid lubricants such as graphite. This soft, white, lubricious powder is derived from the reaction of boric oxide or boric acid with urea or ammonia at high temperatures ranging between 1,073 and 1,273 K. There are two crystal structures of boron nitride, cubic and hexagonal. Cubic boron nitride is extremely hard and wear resistant like diamond and is very abrasive. Hexagonal boron nitride, a synthetic inorganic solid lubricant, is a highly refractory and thermochemically stable material that maintains its lubricious qualities at high temperatures with negligible oxidation occurring below 1,273 K. Moreover, hBN is chemically inert and resists attack by molten metals, oxides, glasses, slags, and fused salts. It is environmentally friendly and displays excellent electrical insulating properties, even under vacuum. The lubricating properties of hBN arise from its graphitic-like crystal structure where atomic planes arranged in two-dimensional arrays of

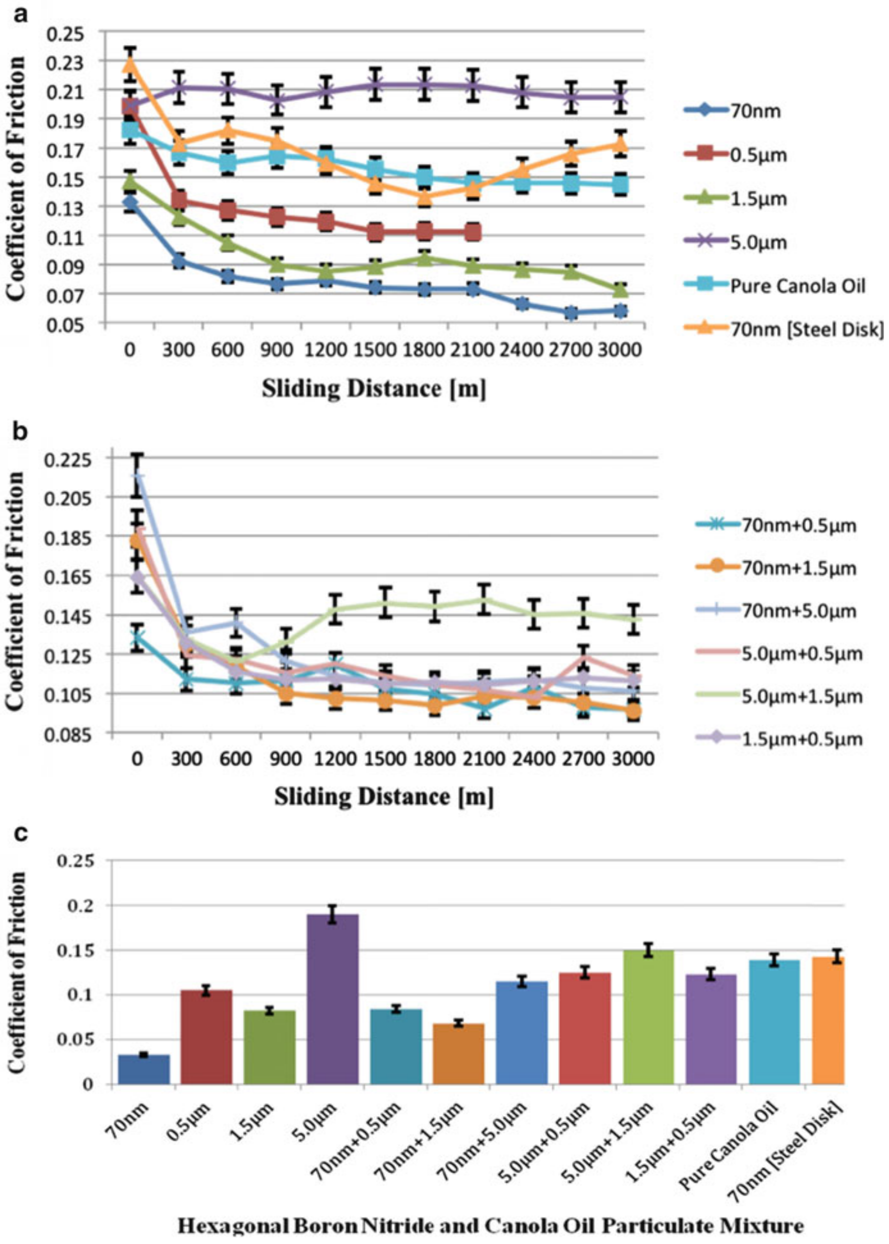


Fig. 13.15 (**a**) Variation of coefficient of friction with sliding distance for single particle-size particulate mixtures, (**b**) Variation of coefficient of friction with sliding distance for multiple particle-size particulate mixtures, (**c**) Coefficient of friction for various particulate mixtures at the end of the experiments

boron and nitrogen atoms, configure in a honeycomb lattice as illustrated in Fig. 13.9. The bonding between atoms in a plane is the strong covalent bond and the bonding between each planar layer is the weak van der Waals bond.

Lubrication applications of hBN include compaction through hot pressing to create dense solid pieces or prepared as a solid polymer composite structure. Hexagonal boron nitride has been used as a dispersed additive to oils and greases to improve antiwear and antifriction properties as well as a self-lubricating coating where it is plasma/thermal-sprayed with ceramics [1, 26–28]. It can be used as metal–ceramic electro-deposition coatings, constituent in epoxy coatings, and has found uses in aqueous and oil dispersions as release agents in metalworking operations. The physical and chemical properties of hBN are similar to graphite, which allows it to function in a variety of similar applications under sliding contact in conditions involving high-load, high-temperature, and extreme pressure [29, 30].

In a recent study, the size effect of hBN particles in canola oil was investigated using a pin-on-disk apparatus [1]. Here, various sizes of hBN particles were combined into colloidal mixtures containing canola oil and 5 % by weight of hBN particles. The sizes investigated were 70 nm and 0.5, 1.5, and 5.0 μm. Figure 13.15a shows the variation of coefficient of friction with sliding distance for the single particle-size particulate mixtures; Fig. 13.15b illustrates the variation of coefficient of friction with sliding distance for multiple particle-size particulate mixtures; and Fig. 13.15c shows the coefficient of friction for all the particulate mixtures at the end of the study. Figure 13.16(a) shows the variation of the pin wear volume with sliding distance for the all the particulate mixtures and Fig. 13.16(b) depicts the variation of pin wear volume for various particulate mixtures at the completion of the test. It was determined that the nanometer-sized particulate mixtures outperformed micron- and submicron-sized particulate mixtures in terms of friction and wear performance, and provided a smoother surface finish to the metallic substrates. Furthermore, the tribological response of canola oil containing micron- and submicron-sized particles was found to be significantly enhanced by the addition of nanometer sized particles, where friction and wear rates were reduced by 40 % and 70 % respectively.

Furthermore, this research study [1] revealed that the tribological performance was influenced by the particle shape. In this study, the larger particles had a plate-shaped geometry and the smaller particles exhibited a spherical geometry. The scanning electron micrographs of the various sized hBN particles are shown in Fig. 13.17. Figure 13.18 demonstrates the size and shape effects that the various hBN particles have on the tribological properties. Larger particles behave more abrasively than smaller particles due to their plate-shaped geometry. Additionally, particles having a size on the same order of magnitude as the initial surface roughness resulted in high stress concentration scenarios (Fig. 13.18), which diminished their tribological performance.

Figures 13.17 and 13.18, illustrate the importance of choosing an appropriately sized solid particle lubricant to enhance the lubricity and minimize wear of the tribo-interface. By optimizing the particle size and by selecting an appropriate carrier fluid, a sustainable lubricant can be developed that has properties that will lower friction and wear, thereby improving system efficiency and ultimately conserving energy.

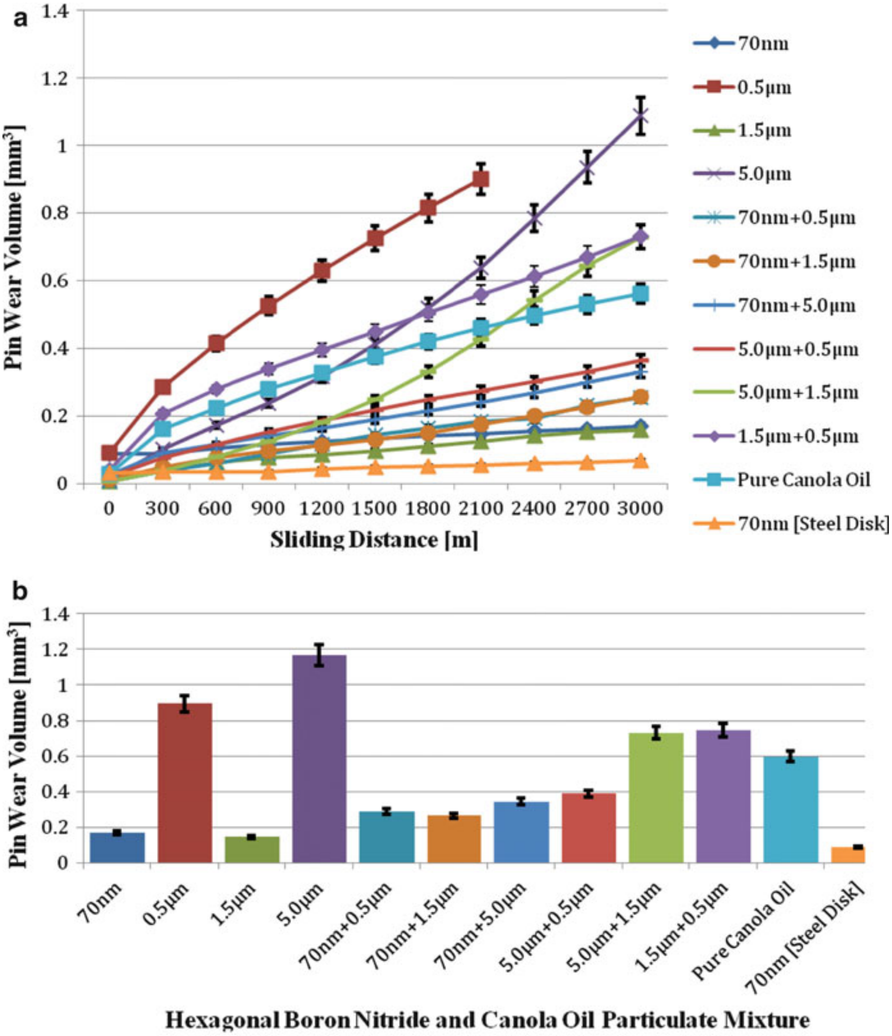


Fig. 13.16 (**a**) Variation of pin wear volume with sliding distance for particulate mixtures, (**b**) Variation of pin wear volume for various particulate mixtures at the end of the experiments

3.7 *Boric Acid*

Boric acid (H_3BO_3) is another lamellar solid lubricant with a layered crystal structure closely related to that of graphite and hBN [31]. Figure 13.6 shows a photograph of boric acid crystals in a powder form and Fig. 13.19 shows scanning electron micrographs of the lamellar structure of the boric acid powder. Boric acid has a triclinic crystal structure and is composed of boron, oxygen, and hydrogen atoms arranged to form atomic layers parallel to the basal plane. Figure 13.10 is an

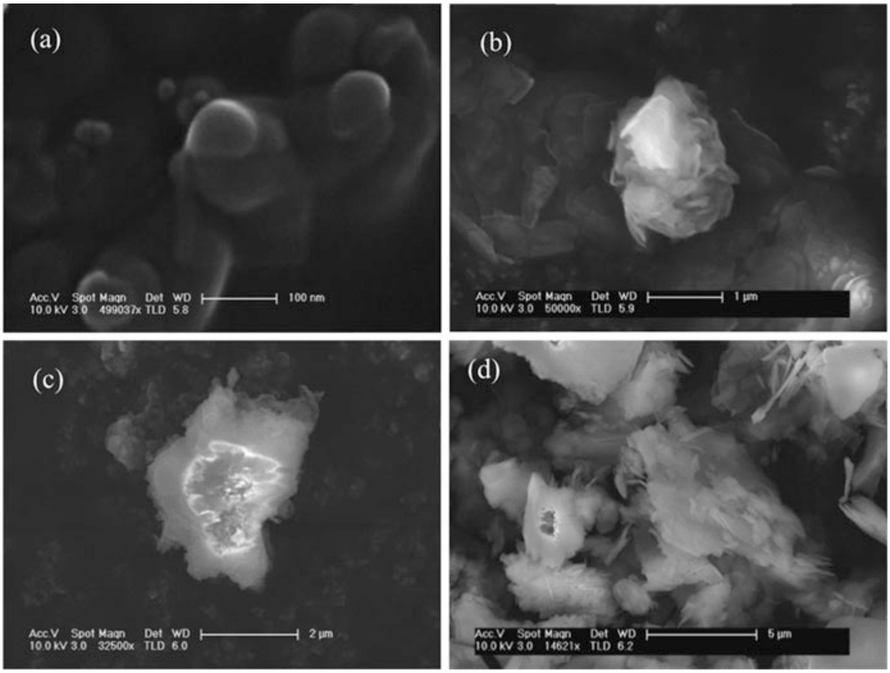


Fig. 13.17 SEM micrographs of hexagonal boron nitride (hBN) particles with size (**a**) 70 nm, (**b**) 0.5 µm, (**c**) 1.5 µm, (**d**) 5.0 µm

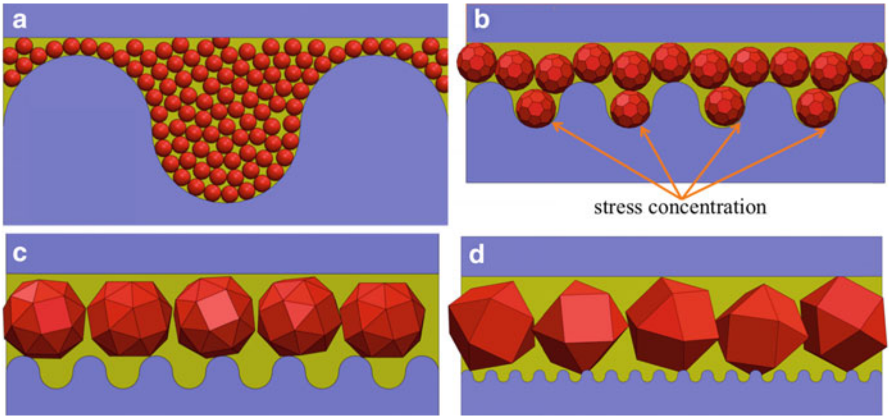


Fig. 13.18 Schematic diagram of boron nitride and canola oil particulate mixtures with size (**a**) 70 nm, (**b**) 0.5 µm, (**c**) 1.5 µm, (**d**) 5.0 µm at the tribo-interface

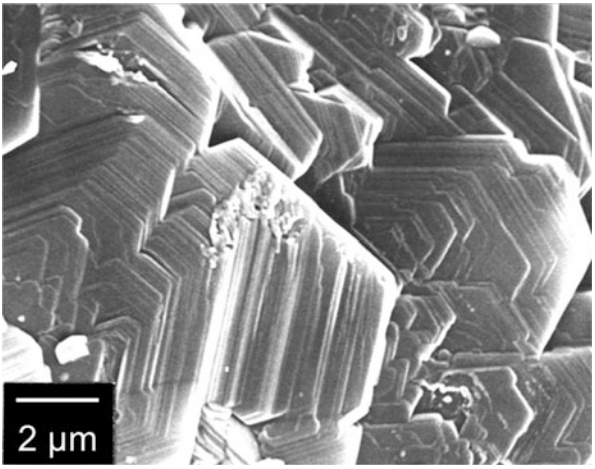


Fig. 13.19 SEM micrograph of the lamellar structure of boric acid

illustration of the layered crystal structure of the boric acid Atoms on the same plane are closely packed and the bonding between the atoms is of the strong covalent type for boron and oxygen and of the hydrogen type. The weak van der Waals force holds adjacent planes together. The bonding types present in boric acid allow it to dissolve in water and other solvents, making it a useful additive in many lubricants. Two forms of boric acid that exhibit the layered crystal structure are the orthoboric and orthorhombic metaboric acids. The lubricious nature of boric acid arises from its ability to align its plate-like crystals parallel to the direction of relative motion under shear stress [32]. Once aligned, these layers can slide over one another with relative ease, thus providing the low friction and self-lubricating properties similar to that of MoS_2, graphite, and hBN. The limitation of boric acid is that it decomposes at temperatures over 443 K, turning into B_2O_3, losing its layered structure, and thus its lubricious nature. At temperatures over 723 K, B_2O_3 begins to melt where it can possibly react with the surfaces of the underlying substrate. If the underlying substrate is metallic, the reactions can be negligible and low friction can be maintained due to viscous-flow lubrication. On the contrary, if the underlying substrate is ceramic, the liquid B_2O_3 produces an oxide film that worsens the tribological properties due to high corrosive wear and high friction. Despite minimal drawbacks, boric acid has found a place in various applications, for example in metal-forming, boric acid films have been shown to bond to metallic surfaces to provide excellent lubricity [33]. Boric acid has also been used as fillers in polymers and dispersed in oils and greases to enhance lubricity, wear resistance, and extreme pressure capabilities [34–36].

An investigation by Lovell et al. studied the size effect of boric acid powder particles used as a performance enhancing additive when mixed with canola oil to form a multifunctional biolubricant [35]. The effect of nano- (20 nm), submicron- (600 nm), and micron-sized (4 mm) boric acid powder additives combined with canola oil in a vortex generator to establish a colloidal mixture were investigated for

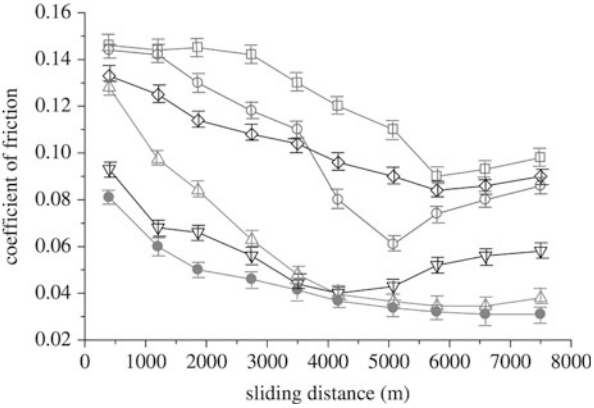


Fig. 13.20 Variation of coefficient of friction with sliding distance for various lubricants (*open square*, boric acid 4 mm; *open circle*, boric acid 600 nm; *open triangle*, boric acid mix (4 mm and 600 nm); *open inverted triangle*, MoS_2 5 mm; *open diamond*, canola oil; *filled circle*, boric acid 20 nm) [35]

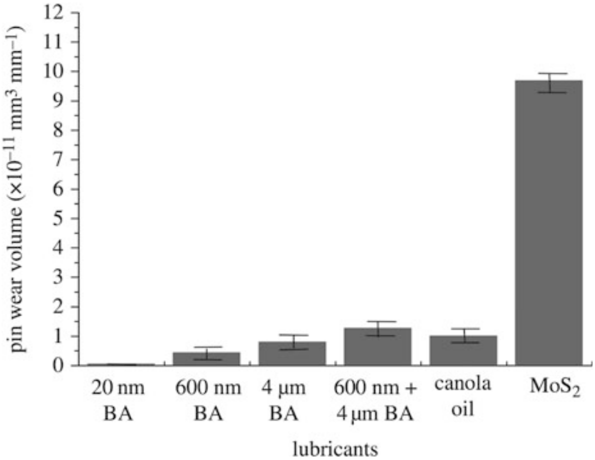


Fig. 13.21 Variation of wear rate of the Cu pins slid against Al disks in the presence of various additives in canola oil-based lubricants at the interface. *BA* boric acid [35]

their influence on tribological properties. As a basis for comparison, lubricants of pure canola oil and canola oil mixed with MoS_2 powder (ranging from 0.5 to 10 µm) were also prepared. Friction and wear experiments were carried out on the prepared lubricants using a pin-on-disk apparatus under ambient conditions. Figure 13.20 shows the variation of coefficient of friction with sliding distance for lubricants containing various particulate additives. Figure 13.21 shows the variation of wear rate of the Cu pins slid against Al disks in the presence of various sized boric acid additives in canola oil-based lubricants at the interface. Based on the experiments, the lubricant mixtures containing the nano-sized boric acid particulate additive significantly outperformed all of the other lubricants with respect to friction and wear performance. In this study, the nano-sized boric acid powder-based lubricants exhibited a wear rate more than an order of magnitude lower than the MoS_2 and larger sized boric acid additive-based lubricants. It was also discovered that the oil mixed with a combination of submicron- and micron-sized boric acid powder additives exhibited better friction and wear performance than the canola oil mixed with submicron- or micron-sized boric acid additives alone.

3.8 Soft Metals

Soft metals such as silver, gold, platinum, indium, tin, and lead are used as lubricants because of their low shear strength, rapid recovery, and recrystallization properties that allow them to exhibit low friction in sliding contacts [37, 38]. Many soft metals are used in place of typical solid lubricants because they offer properties that are not offered by many solid lubricants such as excellent electrical and thermal conductivity, oxidation resistance, good transfer-film-forming tendency, and relatively high melting point than liquid lubricants. Soft metals traditionally have low hardness values between 1 and 3 in the Mohs hardness scale and coefficients of friction between 0.1 and 0.4 depending on material and testing conditions as shown in Table 13.4. The applications of soft metals are limited by their physical properties; lead (Pb), indium (In), and tin (Sn) have lower friction coefficients than silver (Ag), gold (Au), and platinum (Pt). However, in applications involving high temperatures, lead, indium, and tin tend to oxidize and melt, for this reason silver, gold, and platinum are more commonly used in high temperature applications due to their high melting points and thermal-oxidative stability [39–41].

Soft metals are applied to substrates as thin films through various deposition techniques. During these processes, the film-to-substrate adhesion is important for long-term durability, improved lubricity, and antiwear properties [42, 43]. Electroplating and vacuum evaporation processes can be used to deposit most soft metals on substrates as thin self-lubricating films. However, to obtain high density and strong adherent soft metal films, ion plating, sputtering, and ion-beam-assisted deposition techniques are utilized [44]. The thickness of a deposited soft metal film is critical to friction and wear performance. The optimal thickness of a soft metal film is between 0.5 and 1.0 μm, where the film can maintain a low coefficient of friction and minimize the wear rate under a high contact pressure [38, 45, 46]. If the film is too thin (<0.5 μm), it can degrade quickly and become ineffective at lowering friction and minimizing wear. In contrast, a thick film (>1.0 μm) exhibits a higher coefficient of friction and wear rate due to an increase in contact area caused by plastic deformation as a result of softening of the film. In some instances, the physical and mechanical properties of soft metals change due to environmental interactions that result in variations in the tribological performance. The coefficient of friction decreases in most soft metals as the ambient temperature increases due to initial softening of the material and rapid recovery from strain hardening [5]. At very high temperatures, the coefficient of friction increases due to softening of the material causing the material to flow with increased ductility and a larger real area of contact, which results in stronger adhesion between the surfaces. In instances of high frictional or ambient heating, silver and gold are ideal solid lubricants due to their high thermal conductivity, low shear strength, and chemical inertness, resulting in lower adhesion and a lower coefficient of friction when compared to other soft metals. Moreover, when highly thermally conductive films are used such as silver and gold, the wear rate tends to decrease because frictional heat is dissipated rapidly from the sliding interface.

Applications of soft metals consist primarily of dry and oil-lubricated sliding contact conditions where effective dissipation of frictional heating is necessary. Extensive usage of soft metals is limited by their affinity to react with sulfur and chlorine and undergo corrosive wear. Despite this deficiency, soft metals do have their optimal applications. Silver, for instance, is often used to lubricate the high-speed ball bearings of rotating anode X-ray tubes, satellite parts, ball bearings, bolts, and sliding parts in nuclear reactors. Bronze and Babbitt components prepared by alloying soft metals with aluminum, zinc, and copper have been used to lubricate bushings, bearings, and many other mechanical components.

3.9 Polymers

Polymers are a common solid lubricants in tribology because they are lightweight, inexpensive, easy to produce, corrosion resistance, and biocompatible. They are often combined with other solid lubricants to create self-lubricating composite materials that can be used in bulk and thin-film forms as well as binding agents for other solid lubricants [5, 47–49]. Some of the better-known polymers are ultrahigh-molecular-weight polyethylene (UHMWPE), polyimide, nylon, and polytetrafluoroethylene (PTFE). Polymer coatings can be deposited on surfaces by spraying or dusting a powder form on a substrate, then curing it at high temperatures. UHMWPE is a popular polymer for its use in joint replacements, because it has long entangled molecular chains that provide improved wear resistance [50, 51]. Polyimide is a polymer known for having low friction and good thermal stability. It can be combined with self-lubricating inorganic fillers at high temperatures to enhance the mechanical and tribological properties of composite structures [52, 53]. PTFE is the most well known polymer by its trade name Teflon (an E.I. DuPont de Nemours and Company product). PTFE is a “nonstick” surface coating that is commonly used in cookware, seals, and gaskets to facilitate release and separation in applications below 523 K. Less common forms of PTFE are powder, composite, and colloidal dispersion in oils and greases to lower friction [54]. Its coefficient of friction ranges between 0.04 and 0.2 depending on the materials and testing conditions.

4 Lubrication Mechanisms of Layered Solids

The lubrication mechanisms that govern solid lubricants are controlled by intrinsic and extrinsic parameters. There are no solid lubricants that can provide both low friction and wear in all environments. The friction and wear performance of solid lubricants is influenced by inherent properties, environmental parameters, and application usage. Solid lubricants can be used as dry lubricants by themselves in which their physiochemical properties are dominant. They are used as additives in oils and greases where their physical properties prevail and in coatings in which physiochemical reactions and adherence become critical. This section discusses the viability of solid lubricants based on their lubrication mechanisms and the lubricating environment.

Layered solid lubricants include lamellar solids (i.e., graphite, hBN, and H_3BO_3), transition-metal dichalcogenides (i.e., MoS_2 and WS_2), and metal-monochalcogenides (i.e., GaS, GaSe, or SnSe). The lubrication mechanisms of these various solid lubricants are controlled by their affinity for interfilm sliding, intrafilm flow, and interface slip, which are all dependent on the material's interlayer shear properties. As previously discussed in this chapter, all of these solids have layered crystal structures where atoms lying on the same plane are closely packed and strongly bonded through ionic, covalent, or hydrogen bonds and the layers themselves are bonded through weak van der Waals forces. The lubricity, wear resistance, and durability of these solid lubricants are derived from their strong interatomic bonding and packing within each layer that allows for the high in-plane strength. Furthermore, when these lubricants are entrained between two surfaces in relative motion, they are able to align themselves parallel to the relative motion and slide over one another with relative ease providing lubrication. Moreover, many of these layered solids coalesce in surface asperities (see Fig. 13.18), creating a thin smooth transfer film that is able to accommodate the relative sliding velocity and dissipate frictional energy affording longer wear lives and greater performance.

When discussing solid lubricants, layered crystal structure is of interest, because layers can be composed of single or multiple atomic planes. Lubricants with single atomic planes per layer include graphite (Fig. 13.7), hBN (Fig. 13.9), and H_3BO_3 (Fig. 13.10), while transition-metal dichalcogenides consist of three atomic planes per layer such as MoS_2 (Fig. 13.8) and WS_2; and metal-monochalcogenides consist of four atomic planes in each layer, for example GaSe (Fig. 13.14). The three atomic planes in the transition-metal dichalcogenides are arranged where the metal atom is sandwiched between the chalcogen atoms in a planar array. For example in MoS_2, the atoms are arranged as S–Mo–S (Fig. 13.8), similarly, for WS_2, the planar array is arranged as S–W–S. The monochalcogenides atomic plane array differs slightly from dichalcogenides where the interior is composed of two metal atomic planes sandwiched between the chalcogen atoms. For example, GaSe has the atomic planar sequence of Se–Ga–Ga–Se (Fig. 13.14), likewise SnSe and GaS follow a similar atomic planar sequence of Se–Sn–Sn–Se and S-Ga-Ga-S, respectively.

The lubricity of solid lubricants is controlled by intrinsic properties, such as the layered crystal structure, interlayer distance, electrostatic attraction, and extrinsic parameters such as humidity, temperature, and environment. The intrinsic properties contribute to the tribological performance of solid lubricants because the layered crystal structure allows the solids to shear with minimal resistance. The interlayer distance between layers is also important because as the interlayer distance increases, the ability of the van der Waals force to hold adjacent layers together decreases, thus the shearing resistance between layers weakens enhancing lubricity. For graphite and MoS_2 the interlayer distances are 0.335 nm and 0.296 nm respectively. In humid air, graphite can have a lower friction coefficient than MoS_2; however, in dry and vacuum environments MoS_2 has the lower coefficient of friction [16]. This shows how the lubricity and tribological performance of solid lubricants are largely controlled by extrinsic factors. Electrostatic attraction between layers is another intrinsic parameter that affects the lubricity of solid lubricants. For this reason, when choosing metals and transition metals that could function as possible solid lubricants, one must consider the electrostatic attraction, which significantly reduces the number of potential options. For example, there are many dichalcogenides that have a layered crystal structure such as NbS_2, TiS_2, VS_2, TaS_2, MoS_2, and WS_2. However, based on molecular orbital and valence bond theories, it is speculated that NbS_2, TiS_2, VS_2, and TaS_2, are poor lubricants. The inferior lubricity is a result of these dichalcogenides having a region of negative electrical charge that is concentrated between the chalcogen atoms on a specific layer and in between chalcogen atoms of adjacent layers [55]. This affects the lubricity, because the spaces between atoms are positively charged due to the exposed ion cores surrounding the atoms. As a result, in these solids, there is an electrostatic attraction between layers that strengthens the shear resistance. To the contrary, MoS_2 and WS_2 exhibit superior lubricity because they have a region of negative electrical charge between the chalcogen atoms on a specific layer. Thus, the surfaces of the chalcogen atoms are positively charged, causing an electrostatic repulsion between neighboring layers that lowers the shear resistance and improves the lubricity.

The electronic states of atoms in each layer are important because they can affect the shear resistance of the solid lubricant. Graphite and hBN are similar in that they each have single atomic planes per layer and have similar electronic states. A major difference between the two is the bonding configuration. Graphite's π-bonding and π-antibonding bands overlap weakly at the Brillouin-zone boundary, providing it with good electrical conductivity [16]. In contrast, the hBN's π-bonding and π-antibonding bands are separated by an energy gap of several electron volts, thus causing it to be an insulator. Both graphite and hBN are examples of lamellar solid lubricants where high friction and wear occur if the π attractions between the atomic layers are not eliminated or reduced. Eliminating the π-bond interactions is performed in graphite through intercalation, the process of increasing the interlayer distance by incorporating another atom or molecule such as fluoride, thus creating graphite fluoride. Intercalation can be achieved through the use of alkali metals (known as donor) and metal chlorides (known as acceptor) [56, 57]. As a result of intercalation, the interlayer distance of graphite can expand from 0.335 nm to approximately 0.8 nm, thus decreasing the effectiveness of the weak van der Waals forces and reducing the shear resistance, thus minimizing friction and enhancing the lubricity [58]. Attempts to perform intercalation to hBN have been unsuccessful.

The dominating factor limiting friction and wear performance of solid lubricants in all environments are the detrimental effects caused by extrinsic factors such as humidity, temperature, and environment. The presence of humidity in the atmosphere plays a large role when selecting a lubricant for a particular application. As previously noted, graphite functions best in humid air, while MoS_2 performs best in dry and vacuum environments. Boric acid and hBN have similar properties to graphite. The presence of water molecules in the atmosphere is speculated to cause a weakening of the π-bonds between layers in hBN and graphite, thus increasing the lubricity. The poor lubricating property of MoS_2 in humid environments is related to the reaction of the water molecules, which alter the interatomic array bonding causing an increase in friction.

Solid lubricants can be applied as dry lubricants or as additives in oils or greases. In either case, the physical mechanisms that control their lubricity and wear resistance are the same. Lamellar solids are able to coalesce in the valleys between asperities on rough or porous sliding surfaces while withstanding extreme contact pressures without being squeezed out of the contacting interface. In these situations, the solid lubricant develops into a thin lubricating transfer film that can protect a surface by accommodating the relative motion by easily shearing and carrying a portion of the asperity contact load, thus decreasing friction and minimizing wear. This physical behavior allows lamellar solids to be used as solid lubricants whether they are in the form of a granular powder, compressed pellet, or colloidal solution.

5 High-Temperature Solid Lubricants

Many of the solid lubricants discussed in this chapter lose their lubricious qualities in open air and at temperatures above 773 K. Furthermore, most sliding metal surfaces and non-oxide ceramic surfaces become oxidized in these high temperature environments [59]. During oxidation, thin oxide films can develop on the sliding surfaces that can affect the friction and wear properties. Multiple oxide films can develop if the two opposing surfaces differ chemically or if there is a third body particulate in the sliding interface. When abrasive wear particles become trapped in the sliding interface, high wear can result. Investigations into the shear rheology of oxide films has focused on the development of lubricious oxides through the use of metal alloys and metallic composite structures that induce low shear strength oxide formation [60].

5.1 Oxides, Fluorides, and Sulfates

At elevated temperatures, various oxides, fluorides, and sulfates can become soft with minimal shear resistance and thus used as a lubricant. These oxide (e.g., Re_2O_7,

MoO_3, PbO, B_2O_3), fluoride (e.g., CaF_2, BaF_2, SrF_2, LiF, and MgF_2), and sulfate (e.g., $CaSO_4$, $BaSO_4$, $SrSO_4$,) solid layers can be deposited as highly lubricious thin films or coatings by plasma vapor, plasma spraying, and fusion bonding deposition techniques to provide lower friction coefficients and promote longer component lifetimes at higher temperatures [61–65]. Solid films can be mixed with themselves (for example in the case of oxides CuO–Re_2O_7, CuO–MoO_3, PbO–B_2O_3, PbO–MoO_3, CoO–MoO_3, Cs_2O–MoO_3, NiO–MoO_3) or with other solid lubricants to broaden the lubricants operable temperature range and durability [66, 67]. The drawbacks of oxide films are their inherently brittle nature and ease of fracture. Additionally, oxide films suffer from thermal instability as their tribological properties, particularly their lubricity, is dependent on temperature. At temperatures below room temperature (296 K) or if frictional heating is negligible, oxide films can develop defectively resulting in thin films that can wear out quickly or result in high shear resistance. Oxide films develop high shear resistance due to lack of heat causing them to solidify thereby retarding their lubricating properties. To remedy these low temperature problems, a zinc oxide film was synthesized by pulsed-laser deposition and has been shown to provide effective lubrication and wear resistance at room temperature due to its stoichiometry and microstructure [68]. Oxide, fluoride, and sulfate lubricants tend to find uses in high temperature seal, bearing, gear, valve, valve seat, variable stator vane, and foil bearing applications. At high temperatures, the oxide layer that forms on alloy surfaces is advantageous and desirable in comparison to traditional solid lubricant coatings, which have finite lifetimes. The extended lifetime of oxide layers is a result by the process where previously formed oxide layers are depleted from a surface due to wear and normal operation. The alloying ingredients within the material diffuse to the surface of the material where the oxygen potential is higher and begin to reoxidize. Thus, the surface is replenished with a new oxide layer that offers low shear strength and surface energy, which play a role in decreasing friction [60, 67].

5.2 *Composites*

Alternative approaches to combat friction and wear at high temperatures have been investigated through the use of plasma-sprayed composites and adaptive lubricants. Composite coatings consist of a self-lubricating component composed of silver or an alkaline halide such as calcium fluoride (CaF_2) or barium fluoride (BaF_2) and a wear resistant component composed of chrome carbide or oxide [69–72]. Deposited self-lubricating composite coatings can be as thick as 0.2 mm and have a coefficient of friction ranging between 0.2 and 0.5 depending on testing parameters and chemical composition. These composite coatings have demonstrated superior durability and frictional performance in high speed sliding bearing surfaces, such as foil bearing applications [73]. Composite coatings have a broad temperature range, as they are able to lubricate from room temperature to high temperatures due to their adaptive nature allowing them to chemically change with temperature variations. The ability of these coatings to adapt to their environment thermally is a result of their composition of multiple ingredients. At low temperatures, adaptive composites provide low friction, however, as the temperature increases, their ingredients begin to react with each other and with oxygen to form a new lubricious solid lubricant that provides low friction at high temperatures [74]. The largest concern with such a lubricant is that the reaction is not reversible, thus once oxidation has taken place and the composite has transformed, it cannot provide effective lubrication at low temperatures again. In an attempt to solve this problem, some tribologists have used thin diffusion-barrier layers to limit the extent of oxidation to the surface layers, thus allowing the bulk composite coating material to remain unreacted. An alternate solution utilizes capsules of high temperature adaptive lubricants in a low-temperature matrix. Here, the low temperature matrix can dominate the friction properties at low temperatures, while the capsules provide a protective shell on the surface reacting with the oxygen to produce a high-temperature lubricant.

5.2.1 Self-Lubricating Composite Structures

Self-lubricating composite structures thwart friction and reduce wear in sliding, rolling, and rotating applications. These composites are derived by dispersing self-lubricating solids (known as fillers) in a powder form into a metal, polymer, or ceramic matrix. Powder metallurgy processes are used to mix, compact, and sinter the fillers and matrix materials into functional parts that can be extruded, rolled, or hot/cold-pressed into various forms [16]. These techniques have been available for a long time and are extensively used in industrial applications. In some instances, parts are made to undergo centrifugal processes in which compositional gradients occur within the composite structure. Here, the core can be nearly a pure matrix material to yield high strength, hardness, and durability, while the exterior perimeter is enriched with the self-lubricating powder. In effect, the area where the sliding and relative motion takes place has enhanced lubricity due to the high concentrations of lubricating material on the exterior. Composite structures prepared in this manner are advantageous because of their ability to be used in a wide variety of applications such as bushings, bearings, gears, and traction devices. The increase in performance of self-lubricating composite structures is a result of the formation of a thin transfer layer on the exterior sliding surface caused by the rubbing against a counter material. This transfer layer is continuously replenished by the embedded self-lubricating lubricious powders dispersed in the composite matrix material that enter the area of sliding contact as a result of surface wear and subsurface deformation [22]. In some instances, when self-lubricating composite structures are used with polymers an increase in mechanical strength occurs yielding high wear resistance.

Copper–graphite and silver–graphite used in electrical brushes and contact strips and aluminum–graphite used in bearings, pistons, and cylinder engines are among the many examples of these self-lubricating metal–matrix composite structures [75, 76]. Investigations into composite structures have revealed that when the filler is mixed at the optimal concentration and particle size, there is a substantial enhancement to the mechanical and tribological properties of the matrix material. This has been shown with graphite, MoS_2, and boric acid fillers used with a nylon and PTFE-type polymer matrix material where an increase in wear resistance was observed [48, 53]. Moreover, aluminum-graphite composites have been shown to exhibit superior lubricity, durability, and resistance to galling in both lubricated and non-lubricated applications [22]. Transition-metal dichalcogenides such as WS_2 used as fillers have also shown to reduce the effects of galling as well as exhibit excellent lubricity and durability under high-vacuum environments, thus increasing component resistance to seizure and facilitating operation in higher loading conditions.

Self-lubricating polymer–matrix and ceramic–matrix composite structures have successfully exhibited properties that reduce friction, minimize wear, and decrease galling under extreme conditions for use in industrial applications [24, 77]. Alumina–graphite composites have been shown to minimize friction by more than 50 % in comparison to alumina–alumina composites and are being explored for the utilization in sealing applications [78]. Ceramic composites were created by drilling small holes in alumina and silicon nitride ceramics and filling them with $NiCl_2$ intercalated graphite under high pressure. The silicon nitride composites exhibited substantial friction coefficient reduction in comparison to the alumina composite due to the formation of a graphite-rich transfer film, which cannot be formed in the case of the alumina composite [24]. In more advanced self-lubricating composite structures, mixtures of fillers containing Sb_2O_3 and MoS_2 were shown to greatly improve friction and wear performance. There, the MoS_2 particles on the surface established the thin transfer layer and were influenced by oxidation. The presence of the Sb_2O_3 particles in the composite structure protected the subsurface MoS_2 particles from thermal and environmental degradation. Thus by minimizing the effects of tribo-oxidation the tribological properties can be improved [79].

In a new and expanding field, self-lubricating nanocomposite films and coatings are being developed due to the improvements in the tribological performance brought upon by using physical vapor and chemical vapor deposition techniques. These nanocomposites are based on self-lubricating solids (such as MoS_2, WS_2, DLC, graphite, and PTFE) that are deposited onto metal, ceramic, and metal nitride or carbide surfaces (such as Ti, TiN, TiC, Pb, PbO, ZnO, Sb_2O_3) as thin films or multilayered coatings. They have been shown to exhibit improved hardness, wear resistance, lower friction, and resistant to extrinsic parameters such as humidity in the most demanding tribological conditions [80–82]. These composite coatings have been proposed in various milling, drilling, and tapping processes; cold-forming dies and punches; stamping applications; bearings; and gears for aerospace and vacuum applications, among many other dry sliding and machine applications [16, 83, 84]. Furthermore, nanocomposite films have been shown to exhibit adaptive properties where they can provide superior lubrication in oxidizing environments both at room temperature and high temperature. In these environments the nanocomposite films react with atmospheric oxygen to produce lubricious oxide films that aid in minimizing friction [74, 85–87].

6 Methods of Evaluating Solid Lubricants

Characterizing the tribological properties and evaluating the surface properties are imperative to understanding the success and applicability of solid lubricants and coatings. Many of their properties such as friction, adhesion, bonding, abrasion, erosion, oxidation, corrosion, fatigue, and cracking are all affected by surface properties [2, 3, 5]. Lubrication engineers and tribologists can enhance the performance of solid lubricants by lowering their surface energy, adhesion, and friction, and increasing their resistance to abrasion, erosion, oxidation, corrosion, and cracking. Additionally, improving solid lubricants' compatibility with extraterrestrial environments by having a working knowledge and understanding of deposition techniques of thin films, production methods of multilayered coatings, and modification procedures of surfaces also improves their tribological performance [6, 88, 89]. The multidisciplinary knowledge required to understand the interaction between surfaces and lubricants demands an understanding of physical and chemical characteristics of a material surface and the lubricant. Many of these studies are performed using friction and wear testers and surface analysis tools.

6.1 Friction and Wear Testers

Methods of evaluating the tribological properties of solid lubricants are extensive. Many of the methods used in research laboratories, industries, and commercial applications try to replicate the physical contact geometry that the lubricant is going to be operated in by the use of a tribometer. A tribometer is an experimental apparatus used to evaluate wear-life, wear rate, coefficient of friction, and friction force of a lubricant or material pair over a broad set of parameters as well as examine lubricant film adhesion, fluid resistance, heat resistance, and corrosion resistance. Many of the methods to test solid lubricants are designed based on the intended application specifications of the lubricant. However, some of these testing procedures are standardized through the American Society for Testing and Materials (ASTM) International. Due to the wide variation in test results of solid lubricants the Coordinating Research Council (CRC) conducted a round-robin test program to determine a correlation between the most widely accepted tribometers. Their results indicated that there was no correlation between different machines and that little repeatability exists between identical tribotesters (due to the fact that friction is a system property). Table 13.5 is a brief compilation of tribotesters that are frequently used in the tribological characterization of solid lubricants.

Table 13.5 Examples of friction and wear test apparatus for solid lubricants [3]

Name	Specimen
Plain bearing tester	H-11 test shaft, M-2 steel bushing
Friction tester	Metal disk and rider
High temperature, high speed bearing performance apparatus	20 mm rolling contact bearing
Vacuum friction and wear apparatus	Metal disk and rider
Lubricant vacuum environment apparatus	20 mm rolling contact bearing
Modified 4-ball wear machine	½ in. diameter balls
High temperature, high speed rubbing wear apparatus	Rotating washer vs. stationary
Pellet friction machine	Pellet vs. tool steel track
Press-fit tester	Pin and bushing
Lubricant tester model LFW-1	Test block and 1 3/8 in. Timken® bearing outer race
Falex lubricant tester	Cylindrical pin and V-Blocks
Timken tester	Cylindrical cup rotating against a stationary rectangular block
Oscillating tester	Rotating ring vs. stationary blocks
Dry-film lubricant tester	Cylindrical pin and V-blocks
Sliding friction test apparatus	Cylindrical sleeve slider sliding on a cylindrical rod
Bearing test apparatus	20 mm rolling contact bearing
Fretting corrosion apparatus	Steel flat vibrating against steel flat
High temperature bearing radial and thrust rig	20 mm rolling contact bearing
Modified lubricant tester	Rotating ring vs. rectangular block
Modified Falex tester	Rotating ring vs. stationary V-blocks
Crossed cylinders friction apparatus	Vertical cylinder-carbon tool steel, horizontal cylinder-solid section
Model A-3 friction and wear tester	Timken test cup T-54148 and AISI-4130 steel blocks
Stick–slip slow-speed friction apparatus	½ in. diameter ball vs. flat block
Rolling and sliding contact specimen test machine	Ball and plate
A-6 friction and wear tester	Rotating ring vs. rectangular blocks
Galling machine	Flat plate vs. test cup

6.2 Surface Characterization

Surface analysis techniques are becoming more prevalent and necessary in the characterization process of solid lubricants. There are a number of ways to perform a surface analysis of any solid lubricant, thin film, or coating [90, 91]. Table 13.6, lists many of these surface analysis techniques that are being incorporated in scientific, industrial, and commercial fields [2, 7, 92–100]. Of these techniques, the most widely used for examining solid lubricants, thin films and coatings are optical microscopes, scanning electron microscopy, energy-dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, surface profilometry, X-ray

Table 13.6 Surface analysis techniques [2]

Technique	Main information	Use (popularity)
Light microscopy	Defects image and morphology	Extensive
Scanning electron microscopy (SEM)	Defects image and morphology	Extensive
Scanning tunneling microscopy (STM) nd atomic force microscopy (AFM)	Structure defects image and morphology	Medium
Transmission electron microscopy (TEM)	Phase structure defects image and morphology	Medium
Energy-dispersive X-ray spectroscopy (EDS)	Element composition image	Medium
Electron energy-loss spectroscopy (EELS)	Element composition chemical state image	Not common
Cathodoluminescence (CL)	Element composition defects	Not common
Electron probe X-ray microanalysis (EPMA)	Element composition image	Medium
X-ray diffraction (XRD)	Phase structure defects	Extensive
Low-energy electron diffraction (LEED)	Structure defects	Medium
Reflection high-energy electron diffraction (RHEED)	Structure defects	Medium
X-ray photoelectron spectroscopy (XPS)	Element composition chemical state image	Extensive
Auger electron spectroscopy (AES)	Element composition chemical state image	Extensive
X-ray fluorescence (XRF)	Element composition	Extensive
Photoluminescence (PL), or fluorescence spectrometry	Chemical state defects image	Medium
Variable-angle spectroscopic ellipsometry (VASE)	Film thickness	Not common
Fourier transform infrared spectroscopy (FTIR) chemical state defects	Chemical state defects	Extensive
Raman spectroscopy	Chemical state defects	Medium
Solid-state nuclear magnetic resonance (NMR)	Chemical state phase structure	Not common
Rutherford backscattering spectrometry (RBS)	Element composition structure defects	Medium
Elastic recoil spectroscopy (ERS)	Hydrogen content	Not common
Ion-scattering spectroscopy (ISS)	Element composition	Not common
Secondary ion mass spectrometry (SIMS)	Element composition chemical state image	Extensive
Mass spectrometries Sputtered neutral (SNMS) Laser ionization (LIMS) Spark source (SSMS) Glow discharge (GDMS) Inductively coupled plasma (ICPMS)	Element composition chemical state	Extensive to medium
Profilometers Stylus profiler Optical profiler	Surface roughness image	Extensive
Adsorption	Surface areas chemisorption	Medium

diffraction, Auger electron spectroscopy, ellipsometry, scanning probe microscopy, transmission electron microscopy, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy, confocal microscopy, and secondary ion mass spectroscopy. As industrial applications become more complex, the need to properly verify the surface preparation, coating, or treatment process will become imperative for understanding the performance of a solid lubricant. In many applications, these procedures are vital for identifying surface contaminants that can be detrimental to the performance of a solid lubricant or coatings. For this reason, it is imperative to select the correct surface analysis tool to gain the appropriate information for a particular application. The selection process depends on specific criteria such as specimen size, sampling area, sampling depth, spatial resolution, and detection sensitivity as well as quantitative or qualitative data acquired through destructive or nondestructive analysis [7]. Although there is no single tool that can provide a complete analysis, it is becoming more common to utilize a variety of tools to assess the performance of a lubricant.

7 Conclusion

The technology of solid lubricants has advanced rapidly over the last seven decades, primarily to meet the demands of the industrial and aerospace industries. Solid lubricants are used in environments that are beyond the tolerable domain of conventional petroleum-based and synthetic lubricants where temperatures and pressures are extremely high or low. In these environments, solid lubricants thrive, due to their resistance to many of the environmental issues that would ordinarily render an oil or grease type lubricant ineffective. Solid lubricants generally consist of materials with low shear strength and high wear resistance. When solid lubricants enter the gap between interacting surfaces in relative motion, they achieve lubrication by accommodating the relative surface velocities by easily shearing; coalesce in the surface asperities; carry a portion of the asperity contact load; and form a protective transfer layer. Solid lubricants can be applied as dispersants in oils and greases, as loose powders, or as coatings where they establish thin protective films on surfaces reducing friction and wear thus preventing unwarranted damage to the lubricating surfaces. As tribosystems continue to advance, the use of solid lubrication is expected to increase in the near future to meet the demands of these future systems. Although solid lubricants meet many of the necessary demands of a traditional lubricant, there is no one solid lubricant that provides both low friction and high wear resistance over a broad set of environments. Solid lubricants are severely influenced by intrinsic and extrinsic parameters and are used in a wide variety of lubricant application. When solid lubricants are used as coating or thin films, their performance is related to the thickness of the film and adherence of the film to the surface. This makes the study of deposition techniques critical for adequate usage of solid lubricant thin films. As technology evolves and industrial applications become more advanced, having a multidisciplinary approach to understanding the physical and chemical interactions that affect the tribological performance of solid lubricants will become increasingly more important. Additionally, the use of surface analysis tools will aid in the successful utilization of solid lubricants in the future.

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Exercises

1. What is a lamellar solid lubricant? Give an example and explain its lubrication mechanism.
2. Why are oxides, fluorides, and sulfates important? When are they applicable lubricants?
3. List five methods of surface analysis.
4. What are the subcategories when classifying solid lubricants as lubricating films and by physiochemical properties?
5. List five environments that solid lubricants thrive in and possible applications.
6. Explain the evolution of lubricants and why we began utilizing solid lubricants.

7. What are five apparatuses for evaluating the friction and wear of a solid lubricant?
8. Give three examples of a transition-metal dichalcogenides, metal-monochalcogenides, and a soft metal lubricant.
9. Provide examples of intrinsic and extrinsic parameters that affect the lubricity of solid lubricants.
10. Explain how self-lubricating composite structure function.
11. Explain how solid lubricant composites function.

Answers

1. A lamellar solid lubricant is a layered solid lubricant where the atoms on a single layer are held together via covalent, ionic, or hydrogen bonds and the layers are held together by the weak van der Waals force. Examples of lamellar solids are graphite, hexagonal boron nitride, boric acid, molybdenum disulfide, and tungsten disulfide. These lubricants function by coalescing within surface asperities, accommodating relative velocities, and establishing a thin monolayer that protects the surfaces with high lubricity.
2. At elevated temperatures, oxides, fluorides, and sulfates can act as high temperature solid lubricants. They function by softening at high temperatures that result in a lubricant with minimal shear resistance. Examples of oxide are Re_2O_7, MoO_3, PbO, and B_2O_3; examples of fluoride are CaF_2, BaF_2, SrF_2, LiF, and MgF_2; and examples of sulfates are $CaSO_4$, $BaSO_4$, and $SrSO_4$.
3. (1) Optical microscopes, (2) scanning electron microscopy, (3) energy-dispersive X-ray spectroscopy, (4) Fourier transform infrared spectroscopy, and (5) surface profilometry.
4. Solid lubricants are classified in two types by quantifying them as lubricating films and by physiochemical properties. When describing solid lubricants by lubricating films they are classified as three categories: solid films, fluid films, and thin films. When quantifying solid lubricants through their physiochemical properties, they are categorized based on chemistry, crystal structure, and lubricity.
5. (1) High vacuums environments with applications in satellites, space antennas, semiconductor manufacturing, or X-ray tubes. (2) High temperatures environments with applications in space vehicles, furnaces, and nuclear reactors. (3) Cryogenic temperature environments with applications such as space propulsion systems, turbo pumps, and liquid propane pumps. (4) Radiation environments with applications such as Lunar and Martian base stations, nuclear reactors and satellites. (5) Corrosive environments with applications such as maneuvering systems, semiconductor manufacturing, and all-purpose equipment.
6. Lubricants came into existence with animal fats and oils and were soon replaced with petroleum-based oils during the industrial revolution. Since the development of the aerospace industry, solid lubricants have been developed because many applications were requiring lubricants to operate in

environments that were beyond the tolerable domain of many petroleum-based lubricants. Currently, solid lubricants are becoming more prevalent as they are beginning to find uses in many more terrestrial applications such as additives to conventional automotive lubricants and gear oils.

7. (1) Plain Bearing Tester, (2) 4-Ball Wear Machine, (3) Pellet Friction Machine, (4) Dry-Film Lubricant tester, (5) Vacuum Friction and Wear Apparatus.
8. Transition-metal dichalcogenides: MoS_2, WS_2, and hBN
   Metal-monochalcogenides: GaS, GaSe, and SnSe
   Soft metals: Ag, Pb, and Au
9. The lubricity of solid lubricants is controlled by intrinsic properties such as the layered crystal structure, interlayer distance, electrostatic attraction, and extrinsic parameters such as humidity, temperature, and environment. These properties contribute to the tribological performance of solid lubricants because the layered crystal structure allows the solids to shear with minimal resistance, thus establishing their high lubricity.
10. Self-lubricating composite structures function by having solid lubricant powders known as fillers dispersed into a metal, polymer, or ceramic matrix allowing them to have superior lubricity and antiwear properties. The increase in performance of self-lubricating composite structures is a result of the formation of a thin transfer layer on the exterior sliding surface caused by rubbing against a counter material. This transfer layer is continuously replenished by the embedded self-lubricating lubricious powders dispersed in the composite matrix material that enter the area of sliding contact as a result of surface wear and subsurface deformation. In some instances, when self-lubricating composite structures are used with polymers an increase in mechanical strength occurs yielding high wear resistance.
11. Conventional composites consist of a self-lubricating component composed of silver or an alkaline halide such as calcium fluoride or barium fluoride and a wear-resistant component composed of chrome carbide or oxide. Composite coatings have a broad temperature range, where they are able to lubricate from room temperature to very high temperatures. The ability of these coatings to adapt and continually provide low friction despite a change in temperature environment is a result of their composition of multiple ingredients. At low temperatures, adaptive composites provide low friction and at high temperatures, their ingredients begin to react with each other and with oxygen in the atmosphere to form a new lubricious solid lubricant that provides low friction at high temperatures.