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FUNDAMENTAL CONSIDERATIONS FOR FUTURE SOLID LUBRICANTS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ABSTRACT

There are many properties important to the performance of solids as lubricants. Those properties include shear characteristics, coherence between particles, resistance to cold flow, adherance to the substrate, applicable chemical thermodynamics and kinetics of materials and environments, polymorphism, rheology. Several of the above properties are discussed with the intent of stimulating more general concern for fundamentals in the study, selection, and application of solids as lubricants.

Chemical thermodynamics and kinetics have been used effectively to predict stability and thereby to guide the application and use of solid lubricants. Those in the forefront of lubrication cannot afford to disregard this available technology.

Low shear strength can most generally be anticipated based on bonding force criteria which is reflected in crystal structure. Intercalation compounding and radiation exposure are means to expand critical lattice spacings and achieve reduced friction.

Rheology of constituents and formulations such as effects of high pressure and shear rates on shear force as well as viscoelasticity to enhance life merit careful attention. Adherance and mobility of films can be enhanced by use of surface energy (wetting) relationships and materials or methods that provide chemical bonding. Vacuum deposition by sputtering gives very adherant films. The nonstoichiometric intercalation compound graphite fluoride has good adherance in varied environments as well as useful shear properties and stability.

INTRODUCTION

During the last 25 years much effort has been directed to the study of solid lubricants (refs. 1 to 6). Those materials have solved many unique problems. Numerous studies of solid lubricating materials have been sufficiently fundamental to provide some basic understanding. Most of the efforts, however, have been rote empiricism and of very little significance with regard to considerations for future solid lubricants.

The more significant recent studies of solid lubricants (ref. 3) have strongly emphasized the importance of environment on the performance of solid lubricants. Dramatic differences have been found in the performance of graphite and molybdenum disulfide. It is quite apparent that when properly utilized they are complementary rather than competitive materials. One functions well where the other does not although they have significant commonalities in crystal structure. There are, however, significant differences in the atomic bonding of graphite and molybdenum disulfide. Much of our understanding of what is required for effective solid lubricants comes from examinations of the performance of graphite and MoS_2 in varied environments.

Work on methods of application has comprised a major part of the total recent effort; little of that work will have lasting significance because there has been an inadequately developed technical background. Exceptions worthy of special note are (1) attempts to use surface energy relations (e.g., wetting) in achieving better binders for lubricating solids and (2) their deposition by sputtering in vacuum systems. Examination of those cases can give us valued insight.

The work of many investigators suggest a number of properties are important to the performance of solids as lubricants. They are (1) low shear strength, (2) coherent bonding forces between crystallites, (3) high compressive stability under sustained normal load

(resistance to cold flow), (4) adherance (bonding) or film forming prop-
erties of lubricating solid on the lubricated substrate, (5) chemical
thermodynamics of the lubricating material with the adjacent materials
(e. g. , metal substrate, it oxides, contaminants, and bonding materials,
if any) and the environment (e. g. , vacuum or air and moisture at high
temperatures and high pressures), (6) polymorphism with changes in
temperature, pressure, etc. , (7) rheology including the effects of pres-
sure, shear rate and orientation during the shear processes. Experience
at the NASA Lewis Research Center has confirmed the importance of
the above properties to the functioning of solid lubricants. Further,
there can be no doubt that many present and most future technological
stresses dictate the very real necessity for the lubricant to be one
facet of conceptual design. Solid lubricants, in particular, should
always be specifically designed into future applications.

It is the purpose of this paper to further suggest the relevance
of several of the above properties of solid lubricants to their per-
formance. Such discussion includes speculation and is intended to
help guide the future study, selection, and application of solids as
lubricants. Information was drawn from several recent general pub-
lications and from more specific reports that mostly cover studies
at the NASA Lewis Research Center.

The Use of Chemical Thermodynamics and Kinetics

in Solid Lubrication Research

An obvious design approach to increasing the thermodynamic
efficiency of future propulsion and power generation equipment is
to increase the maximum temperature in the thermodynamic cycle
involved. Limitations of materials including lubricant and bearing
materials often restrict the temperatures that may be safely included
within the design. At high temperatures, high rates of chemical
reaction, thermal dissociation, and crystallographic transformation

as well as changes in physical and mechanical properties are to be expected. Therefore, in considering the future of solid lubricants, it is appropriate to give attention to techniques for predicting and for measuring the thermal and chemical stabilities of candidate lubricants and bearing materials.

Chemical thermodynamics. - An important tool, which has been used for predicting the chemical reactivity of solid lubricants, is the thermodynamic property known as the free energy of reaction (refs. 7 to 9). The free energy of reaction is a measure of the chemical potential for a reaction in terms of the energy change (excluding pressure-volume work) which occurs in the reaction. If free energy is lost during an assumed reaction (ΔF is negative), the implication is that the reacting system assumes a lower energy state and the reaction has the thermodynamic potential to occur.

An early example of the usefulness of the free energy concept in explaining the chemical behavior of solid lubricants was described in reference 7. Free energy calculations indicated that in air, the oxidation of a high temperature solid lubricant, lead monoxide (PbO), to form nonlubricating red lead oxide (Pb_3O_4) is favored below 350° F, but PbO is the more stable compound at higher temperatures (fig. 1). This was experimentally corroborated in X-ray diffraction studies (ref. 10) in which no oxidation of PbO to Pb_3O_4 occurred at 900° F, but complete conversion to Pb_3O_4 occurred at 880° F. This experiment therefore checked with the thermochemical predictions within 30° F.

In reference 8, the free energy relationships of solid lubricants were used to predict chemical reactivity of the candidate lubricant coatings with the substrate metals. On the basis of rolling disk experimental results, softness and thermodynamic properties were judged to be important criteria in the selection of candidate lubricants. With a few exceptions those compounds which were both soft and thermodynamically favorable for chemical reaction with the substrate provided the lowest friction and wear. It was postulated by

the authors that adherent solid lubricant films may be formed and maintained by chemical bonding with the substrate metal. Presumably, a tacit assumption in this postulate is that the reactivity is sufficient to form an adherent reaction layer but not sufficient to cause lubricant depletion, excessive corrosion, or bond disruption by volatile reaction products.

The equilibrium constant is another extremely useful value which can be derived from the thermochemical considerations. It is related to the standard free energy of reaction by the equation:

$$\log_{10} \frac{1}{k} = \frac{\Delta F^O}{2.3\, RT}$$

where ΔF^O Standard free energy of reaction

R = Universal gas constant, 1.987 cal/K per mole

T = Absolute temperature, K

The equilibrium constant k, is a function of the ratio of the concentrations of products to reactants at equilibrium (when no further net forward reaction will occur). A small value of k indicates that the reaction comes to equilibrium in the presence of only small amounts of reaction product and that the postulated reaction is not favored.

In reference 9, equilibrium constants were used to predict the resistance of CaF_2, BaF_2, LiF, and NaF to chemical reaction with air, hydrogen, and liquid sodium. The results indicated that these fluorides should be stable in air to temperatures well above their melting points. It was also shown that these fluorides should be more resistant to chemical reduction by hydrogen and liquid sodium than nickel or chromium oxides and comparable to aluminum oxide in this regard. Experimental verification was provided when these fluorides showed no change in chemical composition after friction and wear studies in air and in hydrogen to 1500° F and in sodium at 1000° F.

These tools must be used with an understanding of the assump-

tions and limitations involved. For example, small equilibrium constants on the order of 10^{-3} or 10^{-4} indicate that very small concentrations of reaction product will bring the system to equilibrium and in a closed system, the reaction will not proceed to any significant extent. However, if one of the reaction products is a gas and is continuously removed by natural or forced convection (by a sweep gas) the system cannot equilibrate and surprisingly rapid decomposition of the lubricant may occur. If such is the case, the lubricant may be stable in a sealed system but not acceptable in an open or a flowing system. The influence of air flow rate on the reaction rates of lubricants will be discussed in the following section.

Chemical kinetics. - Although thermochemical calculations are useful, ultimately, experimental studies are required to more completely characterize chemical and thermal stabilities. This is essential for determining reaction rates because thermodynamics gives little insight into reaction kinetics.

Thermal dissociation rates of molybdenum and tungsten disulfides, diselenides, and ditellurides in vacuum have been systematically studied (ref. 11). The method of thermogravimetric analyses (TGA) was used to continuously monitor sample weight during the experiments. A mass spectrometer was used to detect and characterize the volatile products of dissociation. Nonvolatiles were analyzed by X-ray fluorescence and diffraction. The major results are summarized in table I. The data indicate that the disulfides are the most stable to thermal dissociation, the diselenides are intermediate and the ditellurides are the least stable. However, the diselenides provided effective lubrication in vacuum to a higher temperature (1400° F) than the disulfides. The friction-temperature characteristics were determined for very thin, unreplenished, burnished films. The diselenides, because of their higher densities, evaporate more slowly than the disulfides and apparently, for these very thin films, the evaporation rates were the controlling factor in determining the maximum temperatures for effective lubrication.

The author did not consider the ditellurides to be candidates as high temperature lubricants because of their low (1300° F) thermal dissociation temperature.

Lavik has studied the air oxidation of the dichalcogenides by TGA (ref. 12). He gives data for the oxidation of fifteen dichalcognides. He gives no kinetic data but threshold temperatures for rapid oxidation are derived from the thermograms. Tantalum disulfide (TaS_2) and diselenide ($TaSe_2$) exhibited the best oxidative stability in dry air with "most of the oxidation occurring above 1100° F." Next in order of oxidative stability were WSe_2, WS_2, and $MoSe_2$. Unfortunately, no lubrication experiments were reported. Because of the good oxidation resistance of TaS_2 and $TaSe_2$ it would be very interesting to know their effectiveness as solid lubricants.

More recently, Moore (ref. 13) has determined the oxidation rates of $MoSe_2$ over the temperature range of 375° - 530° C. Moore's technique also employed TGA but weight loss curves were measured under isothermal conditions so that oxidation rate constants could be derived from the data. The results satisfactorily conformed to the Arrhenius equation which requires a linear relationship of the logarithm of the reaction rate constant with the reciprical of the absolute temperature. The slope of the Arrhenius plots gave an activation energy of about 25 kilocalories per mole for the oxidation of $MoSe_2$.

The chemical reaction kinetics in air for powder compacts of WS_2, MoS_2, PbS, PbO, and CaF_2 have been studied by X-ray diffraction techniques (ref. 10). The diffraction data gives information concerning composition within a thin surface layer of the compacts (~ 0.0002-to 0.0010-in. for compounds of heavy metals). Bulk average reaction rates for 0.0300 inch thick compacts were also determined by chemical methods.

In figure 2, the oxidation-time relationships at various temperatures for thin X-ray layer of WS_2 powder compacts are shown. At all temperatures, the reaction rate decreased with time in a manner suggesting that WS_2 oxidized by a parabolic rate mechanism. If a reaction is truly parabolic, it should conform to the rate equation:

$$(G_x)^2 = Kt \tag{1}$$

where G_x is the fraction reacted in time t, and K is the parabolic rate constant. To test this relation $(G_x)^2$ was plotted against time with the results shown in figure 3. At all temperatures, a straight line passing through the origin was obtained thus verifying a parabolic oxidation rate mechanism for WS_2. The slopes of the lines are K, the oxidation rate constants.

Therefore, for any value of G_x and t, K can be determined from equation (1). A helpful way of presenting these data is to show the effect of temperature on the time required to oxidize some arbitrary fraction of the material. It is convenient to give the time required to oxidize one-half of the starting material and may be defined as the "oxidation half-life $t_{1/2}$," where from equation (1)

$$t_{1/2} = \frac{(0.5)^2}{K} \, 0.25 \left(\frac{1}{K} \right) \tag{2}$$

A plot of $t_{1/2}$ against temperature for the data of figures 2 and 3 is given in figure 4.

The effect of compact thickness on the oxidation rate of WS_2 is also given in this figure. It is clear that the oxidation rate of the thin surface layer is considerably higher than the average oxidation rate of a 0.030 inch thick compact.

The oxidation half-lives of the thin films of WS_2 and MoS_2 are compared in figure 5. Above about 730° F, MoS_2 oxidized more rapidly than WS_2.

The importance of oxygen availability is demonstrated in figure 6 where oxidation half-life of MoS_2 is given for two air flow rates, 333 cubic centimeter per minute and 2000 cubic centimeters per minute. Oxidation was more rapid at the higher air flow rate. The dependence of oxidation rate on oxygen availability to the reacting surface is therefore clear.

Arrhenius plots of the oxidation data for WS_2 and MoS_2 gave acti-cation energies of 29 kilocalories per mole for WS_2 and 54 kilocalories per mole for MoS_2. These values along with Moore's value for $MoSe_2$ show the greater temperature sensitivity of reaction rate for MoS_2 compared to $MoSe_2$ and WS_2.

It was also reported in reference 10 that tetragonal PbO and Pb_3O_4 were rapidly converted to orthorhombic PbO at 1000° F. Oxidation of PbO to Pb_3O_4 occurred at 880° F, but was very sluggish. This study of lead oxides demonstrated one of the advantages of the X-ray dif-fraction technique: crystallographic transformations, which involve no change in chemical composition can be readily detected and charac-terized. Lead sulfide PbS, reacted in air at 800° F to 900° F to form volatile tetrabasic lead sulfate (4 $PbO\cdot PbSO_4$). At higher temperatures PbS decomposition products were mixtures of lead oxides and sulfates. No sign of reaction was observed for CaF_2 in air up to the maximum temperature employed (1200° F).

Shear of Solids

The importance of cyrstalline structure on the shear properties (and therefore friction) has been recognized for many years (ref. 3). Lamellar crystal structures are found in a large number of inorganic compounds (ref. 1). Generally, the layer lattice compounds have small positive ions and large negative ions. Crystallites of such compounds shear between well defined adjacent planes of similarly charged (negatively) atoms. The cleavage planes and shear plane of graphite and MoS_2 are the same, however, that is not true for some other solid lubricants (i.e., CaF_2).

Graphite and boron nitride are considered to have identical lamellar crystal structures. Their performance as solid lubricants however, depends on extraneous adsorbates to reduce the shear resistance between adjacent surface layers. The same adsorbates can have adverse influence on shear with more ionic compounds like MoS_2 and WS_2.

The structural hypothesis for shear of solid lubricants is predicted on the anisotropic nature of such materials. To properly understand structural processes it is necessary to study the shear process of pure materials with no or controlled adsorbates present as in ultra-high vacuum facilities (ref. 14).

Systematic studies of friction with crystalline materials of several types including single crystals (ref. 15) has provided convincing evidence that frictional anisotropy is indeed related to lattice structure and to orientation. Metals, covalent crystals, and ionic crystals, and ionic crystals all show anisotropic shear properties. Crystals with minimum numbers of slip systems show the best friction properties (e.g., Co has 3 systems and Ni has 12 systems). The preferred slip planes for lowest shear force (friction) is generally on the greatest atomic density planes where sliding in the direction of the most closely packed planes (ref. 16). With hexagonal metals, friction has been related to C/a (fig. 7) and it has been possible to alloy for the purpose of achieving useful structure. For example, as shown in figure 8 alloying to expand the C/a lattice parameter of titanium caused marked reduction in shear force. The shear process achieves orientation of crystallites.

One approach for achieving low shear strength solid lubricants might be similar to that described for metals. For example, there are many intercalation compounds of graphite that increase lattice spacing without destroying the lamellar structure (ref. 18). Such compounding should be analogous to the alloying of aluminum in titanium to achieve greater C/a ratios. In fact, the effects may be greater in the case of graphite since the initial metallic bonds are stronger than Van der Waals bond forces.

An example of compounding to expand lattice spacing for potential use as a solid lubricant is found in the case of graphite fluoride. Figure 9 shows the spacings between the layer planes of graphite are expanded from 3.4 Å to between 6 and 9 Å by intercalation of fluoride ions. The material functions well as a solid lubricant in the absence or presence of moisture with useful friction and endurance properties (table II). Although, there are only limited data available, it is clear

that graphite fluoride is a promising material for use as a solid lubri-
cant.

Nuclear radiation damage to some solid lubricating materials might
also be expected to improve lubricating properties. With graphite,
irradiation produces lattice defects such as the introduction of atoms
interstitially that cause increase in spacing between hexagonal layers.
For example, 5×10^{20} nVt irradiation will expand the interlammelar
spacing (C_0) by more than 6 percent and C_0 for boron nitride will be
similarly expanded (ref. 20).

If those amounts of increased lattice spacing have similar effects
to the effects observed for metals (figs. 7 and 8) the friction (shear
force) with irradiated graphite and boron nitride may be less than
half that for the undamaged material. With weaker initial bonds (Van
der Waals) of lubricating materials as compared with metals, the
reductions in shear resistance with increased lattice spacing may be
even greater. Such changes should correspond to some power func-
tions of the lattice spacing that can be verified experimentally. At
elevated temperatures (e.g., $>900^{\circ}$ F) however, radiation induced
changes can be annealed from the structures of graphite. Thus, we
must be concerned that the ambient temperatures and the pressures
and temperatures of friction processes may also anneal radiation
changes from lubricant crystallite. It appears, however, that ir-
radiation is one way of treating some solid lubricants that might
enhance their lubricating properties.

Rheology

Rheology of organic fluids is being subjected to closer examination
as an approach to explain the vagaries in lubrication of concentrated
contacts. Emerging from a myriad of considerations is the opinion
that viscoelasticity according to several theoretical models may pro-
vide much needed clarification (ref. 21).

Similarly, rheology in solid film lubrication may be very important.

High pressure viscosity measurements indicate that the nominally liquid lubricants may in fact be functioning in transient concentrated contacts as solid or semisolid films formed by high pressures. Shearing of even a solid high-pressure film would likely provide a liquidus shear plane. The plastic shear hypothesis has been explored by Smith (ref. 22) and later by Johnson and Cameron (ref. 23).

Solid lubricants have been specifically formulated to form glasslike structures capable of viscoelastic behavior and subject to shear melting. An example of such films is the fused $PbO - SiO_2$ composition reported in reference 1. The standard Kelvin or Voigt models (ref. 24) represents nonhomogeneous or homogeneous viscoelastic solids and may be useful to explore solid lubricant phenomenological behavior where structural considerations cannot be defined.

Early studies of carbon bonded solid films incorporating MoS_2 by NACA (ref. 3) utilized relatively thick films. The investigators including one of the present authors observed unexplained friction trends with those films as a function of load and surface speed that now seem to suggest viscoelastic behavior. Such effects were not so noticeable with the thin films (0.0002 in.) that quickly gained acceptance and are most widely used today.

The use of organic plastics as lubricating solids (e.g., Teflon) and as bonding media (e.g., phenolics and polyimides) for other lubricating pigments encompasses a very broad phase of solid lubricant technology. A body of information defining the viscoelastic behavior of solid organic materials is being developed (ref. 25). Many of the bonding agents are organic resins or glasses. In their use with lubricating pigments, the property of viscoelasticity should be extremely important. Reference 26 is an example of research considering the role of viscoelasticity in friction of solids during sliding and rolling. Lubrication problems are often most critical at concentrated contacts; the localized stresses may be upwards of 100,000 psi. A degree of viscoelasticity in thin surface layers is one of the factors that can reduce fracture of asperities on the solid surface during shear. Also,

the stress concentrations are reduced by providing effective film areas much greater than the nominal Hertzian contact. Viscoelasticity should be sought in binder-solid-lubricant systems and can be studied by the same methods used for measurement of thin liquid films. For example, measurements of shear atoms at high pressure should be made with varied shear rates into the range of real engineering problems.

These observations suggest the extended utilization of rheological concepts in research on solid film lubricants. Viscoelasticity may have a similar role in solid film lubrication to that now being suggested for liquids.

It has been indicated in reference 27 that a sound basis now exists for analytical treatment of the frictional properties of dry film lubricants. That treatment is depends on the availability of experimental data describing the effect of pressure on shear strength for the solid lubricants of interest. The well known works of P. W. Bridgeman (ref. 24, vol. 2, p. 339) provide the best data on pressure-shear effects that are now available. It is also suggested that data are needed at widely varied shear rates.

Surface Adherance and Migration

A lubricant cannot perform its functions without a capability to adhere to and deform with one of the bearing surfaces. For solid lubricants, moisture is commonly present as an adsorbate on both the surface to be lubricated and the lubricating particle. It has been well documented that moisture enhances adherance, shear properties and hence lubrication by graphite and impares lubrication by moly-bdenum disulfide. Similarly, the roles of other contaminants have been cited for many lubricating compounds.

The primary method by which surface adherance has been gained for solid lubricant films is to disperse the lubricating pigment in an organic or glass-like bonding agent. After suitable thermal processing to carbonize, cross-link, polymerize, fuse, or drive off volatiles the

pigment is bonded to the surface in an encapsulating matrix. Micro-fibrous boehmite has been used as a nonencapsulating binder (ref. 28). While other physical and chemical effects are likely, it is generally thought that mechanical bonding is the primary means by which film adherance is achieved.

It was mentioned earlier that wetting of bonding agents or pigments has been a factor in the formulation of solid film lubricant compositions (ref. 29). That consideration is sound. The surface energy state of the surface to be coated, should, however, be also considered. For ex-ample, it is known (ref. 30, vol. 2, p. 5) that even at high temperatures (e.g., 1000° C), dispersion forces are insufficient to make molten glass spread on a metal surface unless an oxide is first formed on the metal. Pretreatment of surfaces to provide oxide or other high surface energy reaction films that enhance physical and/or chemical adhesion of the bonding agent should be sought. Chemical effects must be carefully controlled to prevent corrosion and thereby structural deterioration of the substrate. Present concern for surface pretreatment is mostly to achieve optimum surface topography.

Where coatings are applied to hydrophillic surfaces, formulation constituents to displace water or other contaminants from the solid should be utilized. For example, as reference 30 suggests, butanol and liquids of similar polarity displace water from the solid surface during the spreading process. Optimum binder to solid adherance re-quires that the binder should completely wet the solid before the bonding agent becomes nominally solidified.

Wear and fatigue are the factors usually considered to give a fin-itely limited endurance life to solid lubricant films. In addition to re-ducing stresses, viscoelasticity may enhance surface mobility that can provide self-repair of surface films and extend real life. Addition-ally, however, diffusion or other transport phenomena in solids can be such that trace or minor constituents in the bulk of metals may be present in major concentrations on surfaces. Trace amounts of carbon in pure ion (65 ppm) can migrate as an interstitial through the lattice to have

disproportionate influence on metallic adhesion (ref. 31). Reference 32 also indicates that such diffusion against a concentration gradient in iron with 200 ppm carbon formed surface carbide particles which are 25 A/o carbon (25,000 ppm carbon). Conversely, as shown in figure 10 small amounts of aluminum ($<$1 percent) in copper gives copper the less desirable adhesion properties of pure aluminum in vacuum (ref. 33). While aluminum has an adverse effect on adhesion, if the transport mechanism (believed to be preferential segregation of aluminum to the surface by vacancy transport) can be resolved, other metal systems may be formulated that provide for the transport of useful lubricating constituents (i.e., metallic solid lubricants) to the surfaces. This situation is physically similar to the disproportionate concentrations of refractory metal oxides (e.g., chromium) found in the surface scale of steel after exposure to high temperatures in air.

The composite materials including solid lubricants use a more simple transport mechanism to maintain surface films. In the case of composites the skeletal matrix wears away exposing fresh lubricating material. Subsequently, the lubricant is carried by the contacting member to other surface areas. Such transport was demonstrated in the ball bearing experiments with solid lubricants of reference 34 employing calcium fluoride based compositions at temperatures to 1500° F.

Burnishing of solid lubricant films on to bearing surfaces has been a very common method of application. For MoS_2, if the burnishing is accomplished with a rotating metal brush in an inert environment using modest surface pressure, good adherance is achieved. In the experiments of reference 35 electron diffraction showed that a surface reaction between MoS_2 and steel can occur in that iron sulfide was present. Such coatings have relatively good endurance life but somewhat higher friction than comparable coatings containing bonding agents. The transfer of solid lubricants from one surface to another as cited above for CaF_2 in ball bearings (ref. 34) is essential for sustained operation. That action is similar to a burnishing application, and would be enhanced by all factors contributing to surface adherance. Surface adherance permitting

intercrystalline shear or cleavage of lubricating substances should be sought. That is, for solid lubricants the energy of adhesion to the substrate surface should be greater than the cohesion of the lubricant film; for bearing materials the opposite is sought.

Establishing chemical bonds such as those in the burnished MoS_2 films is very desirable. Experience with lightly burnished graphite fluoride films in reference 19 showed very good film adherance in the absence or presence of contaminating vapors (table II). The utilization of more frictional energy in the burnishing process would be likely to further improve film adherance.

It is suggested that nonstoichiometric solid lubricant compounds such as graphite fluoride (as with unsaturated organics) provide greater capability to form chemical bonds with substrate material. Chemical bonds strengths can then be used to postulate relative adherance of the compound to a known substrate. Such bonds occur with the surface atoms of the substrate. New tools such as the LEED and Auger spectrometer as well as field ion-emission microscopy may allow a less speculative appraisal of physical and chemical adherance mechanisms for lubricating films in the near future. Those tools allow study of surface atoms with the capability to build up by adsorption or strip successive atomic layers on surfaces. Pertinent mechanisms can only be explained on an atomistic mechanics basis.

The deposition of highly adherant surface films by vacuum methods has unusual promise (refs. 37 to 39). Either evaporation or sputtering processes in conjunction with an ionized plasma may be used to deposit pure metals and inorganic compounds that can provide lubrication. The combined conditions of an extremely clean substrate, accelerated high velocity coating material, and ionization of that material provides several of the requirements needed for strongly adherent films. In particular, it should be noted that mechanical bonding does not have a major influence on adhesion in vacuum film formation processes as it does when bonding agents are used. Much remains to be resolved with vacuum deposition methods. It has been demonstrated however,

that highly adherent coatings of desired stoichiometry can be deposited in closely controlled and uniform thickness. Coatings around 2000 A $(8\times10^{-6}$ in.) thick are sufficient for good performance with MoS_2 while the optimum thickness for films with bonding agents would be 200×10^{-6} inch or more (25 times greater thickness).

Special Effects

The preceding discussion has considered several special useful effects on solid lubricants by the environment of operations; for example, the varied roles that adsorbates like moisture can fill and the possible effect of radiation damage in expanding the crystal lattice. There also are chemical changes related to each environment that may influence the effective use of solids. One case in point was an experience at Lewis Research Center in the studies of vacuum deposition of solid lubricants.

The sputtering technique for the deposition of solid lubricants as described in reference 36 requires the use of solid targets of the lubricating material. The practice at Lewis has been to cold press the lubricant powders into cylindrical specimens as shown in the foreground of figure 11. Cylindrical slugs of WS_2 were wrapped in absorbent tissue and stored exposed to the atmosphere of an air conditioned laboratory for $2\frac{1}{2}$ months. During that storage period the body of the molded pieces crumbled. Also, the tissues in which they were wrapped were chemically attacked as shown in figure 11. It would appear that the modest amounts of moisture in the laboratory air reacted with the tungsten disulfide to form sulfuric acid. The acid was absorbed by and chemically attacked the tissue.

Analogous friction and endurance results have been obtained with sputtered films of WS_2 run in vacuum and in air (fig. 12). The endurance in air was 1500 cycles compared to lives of more than 1,000,000 cycles for similarly deposited films run in vacuum. Further, friction obtained in air (0.22) was much higher than that (0.06)

measured in vacuum. It would appear that, with activation by frictional energy, moisture in the air quickly reacted with the WS_2 film. The higher friction may have been a result of either or both the subsequent reaction product with the nickel-chrome alloy substrate or the deterioration of the film material.

The caution to be gained from this experience is the likelihood of similar harmful moisture effects with other potential solid lubricants in the family of lamellar compounds. The observations may also be quite relevant for molybdenum disulfide. It has been well documented that friction is higher and endurance life shorter for MoS_2 films in moist air than in dry air; and further that the best performance for MoS_2 is in vacuum. Thus, it is clear that both moisture and oxygen have harmful effects on MoS_2, WS_2, and possibly other solid lubricants. Therefore, the results with graphite monofluoride (table II) showing good performance in the presence or absence of moisture may be very significant. Also, the use of a continuous protective matrix (resin) binder system to encapsulate materials such as WS_2 would seem to be a good way to inhibit harmful moisture effects. That protection would not be effective, however, in the shear area where crystal forces of the the lubricating compound will be exposed.

Formulation of solid film lubricant compositions to more closely approximate the thermal expansion and thermal conductivity of the lubricated material can be very important. That fact can be demonstrated for temperature extremes (refs. 39 and 40) but is likely equally related to good endurance at all operating conditions for solid film lubricants.

Shear melting of lubricating films was mentioned earlier. That mechanism of action can be enhanced by maintaining a liquidus film on the surface. Practical implications are such that it is difficult to provide the desired liquidus film at the interface when required. One approach is for the solid film to be an eutectic composition (ref. 41) and another approach is the use of gallium rich films for use with corrosion resistant materials (ref. 42). Recent experience

indicates such films have particular promise for sliding electric contacts in vacuum (ref. 43).

Concluding Remarks

This discussion has attempted to focus attention on (in some cases speculate about) basic considerations important to the present status and future of solid lubricants. Speculative discussions are intended to stimulate research. Although primary data are drawn from research at the NASA Lewis Research Center, the following generalizations are based on the publications and experience of many research workers.

(1) Chemical thermodynamics and kinetics are powerful tools for use in determining the useful environments and methods of application for solid film lubricants. While only limited use of these methods have been made to date, researchers and developers of solid lubricants cannot afford to avoid this available technology.

(2) The primary requirement for a solid lubricant is low shear strength and that can be satisfied by crystal structure and bonding force factors. Intercalation compounding and radiation exposure are ways to investigate for expanding the lattice spacing between shear planes to reduce friction (shear strength) of solid lubricants.

(3) The rheology of solid film constituents and formulations is likely to be of vital importance to performance and life. The effect of pressure on shear and of shear rate on shear force are critical to friction. Viscoelasticity of the film can be important to stress distribution and hence endurance of the substrates and resiliance may contribute endurance to the films.

(4) Adherance and mobility of surface films is another primary requirement for long lived solid lubricants. Commonly utilized mechanical bonding can be strengthened by useful surface energy relationships between the substrate, the binder, and the lubricating solid. Chemical bonding of the lubricant to the substrate extends endurance; it can be achieved by some burnishing methods and by vacuum sputtering deposition. A nonstoichiometric intercalation compound, graphite fluoride, provided good adherance and low friction.

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

Compound	Probable onset of thermal dissociation as, ^{o}F (detected by TGA)	Dissociation products first detected by mass spectrometry, ^{o}F	Maximum temperature at which burnished films provided effective lubrication, ^{o}F
MoS_2	1700	2000	1200
WS_2	1600	1900	1350
$MoSe_2$	1400	1800	1400
WSe_2	1300	1700	1400
$MoTe_2$	1300	1300	1000
WTe_2	1300	1300	(a)

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

TABLE II. - COMPARISON OF FRICTION COEFFICIENT AND WEAR LIFE

OF BURNISHED FILMS OF GRAPHITE FLUORIDE, GRAPHITE,

AND MOLYBDENUM DISULFIDE IN THREE DIFFERENT

ATMOSPHERES AT 25°C

[Moisture content: moist air, 10,000 ppm; dry air, 20 ppm; dry argon, 20 ppm; linear sliding speed, 1.6 m/sec; load, 500 g; riders, 440-C stainless steel.]

Powder	Disk substrate (stainless steel)	Minimum friction coefficient			Wear life, min		
		Atmosphere			Atmosphere		
		Moist air	Dry air	Dry argon	Moist air	Dry air	Dry argon
$(CF_{1.12})_n$	301	0.35	0.02	0.025	700+	250	50
Graphite	301	.09	Immediate failure[a]	Immediate failure	350	0	0
MoS_2	301	----	Immediate failure	Immediate failure	-----	0	0
$(CF_{1.12})_n$	440-C	.06	.15	-----	1200	450	---
MoS_2	440-C	.15	.02	-----	30	70	---

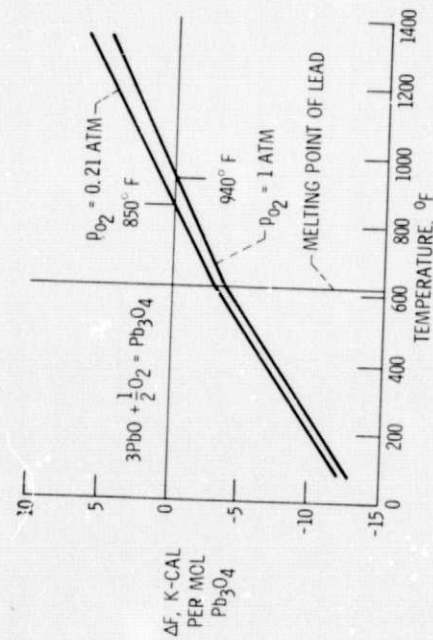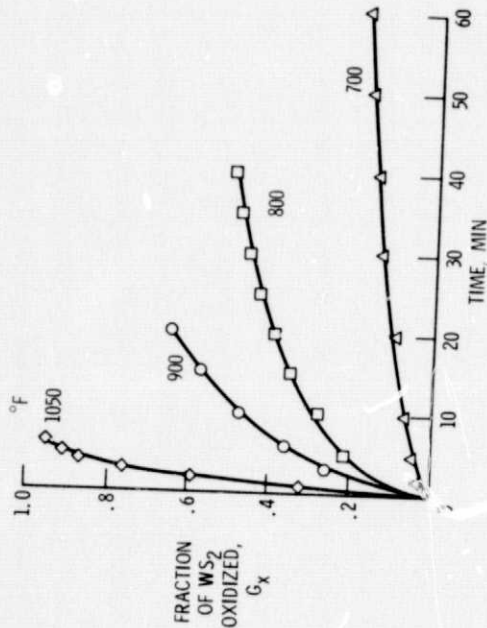[a]Criterion for failure was a frictional force equal to that of unlubricated metal combination.

Figure 2. - Oxidation kinetics for x-ray (surface) layer of WS_2 powder compacts exposed to air at various temperatures. Average powder particle size, 1.0 micron; density of compact, 50 percent of maximum; air flow rate through furnace chamber, 1/3 liter per minute.
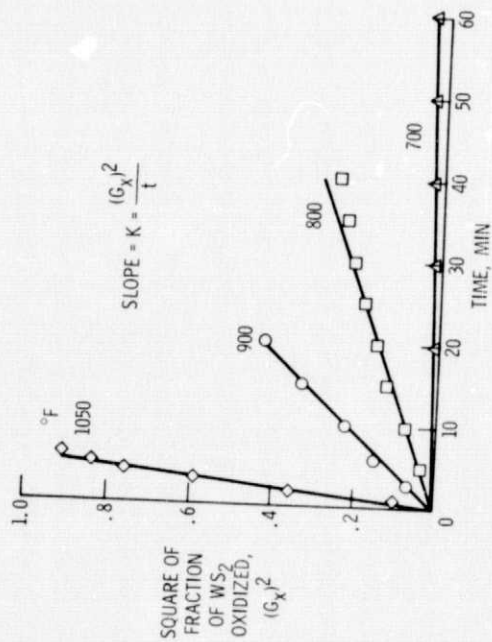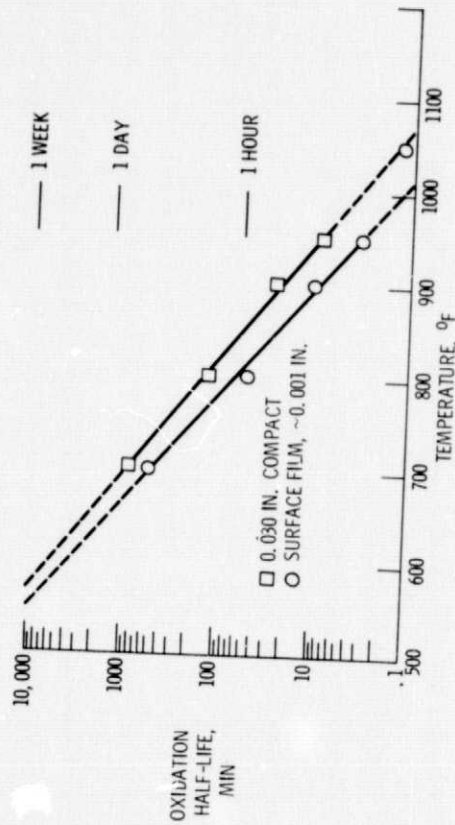
FRACTION OF WS_2 OXIDIZED, G_x

TIME, MIN

°F
1050
900
800
700

Figure 4. - Effect of temperature on time to oxidize one-half of initial weight of WS_2 to WO_3. Average particle size, ~1µ, compact density, 50 percent of maximum, air flow rate, 1/3 L/min.
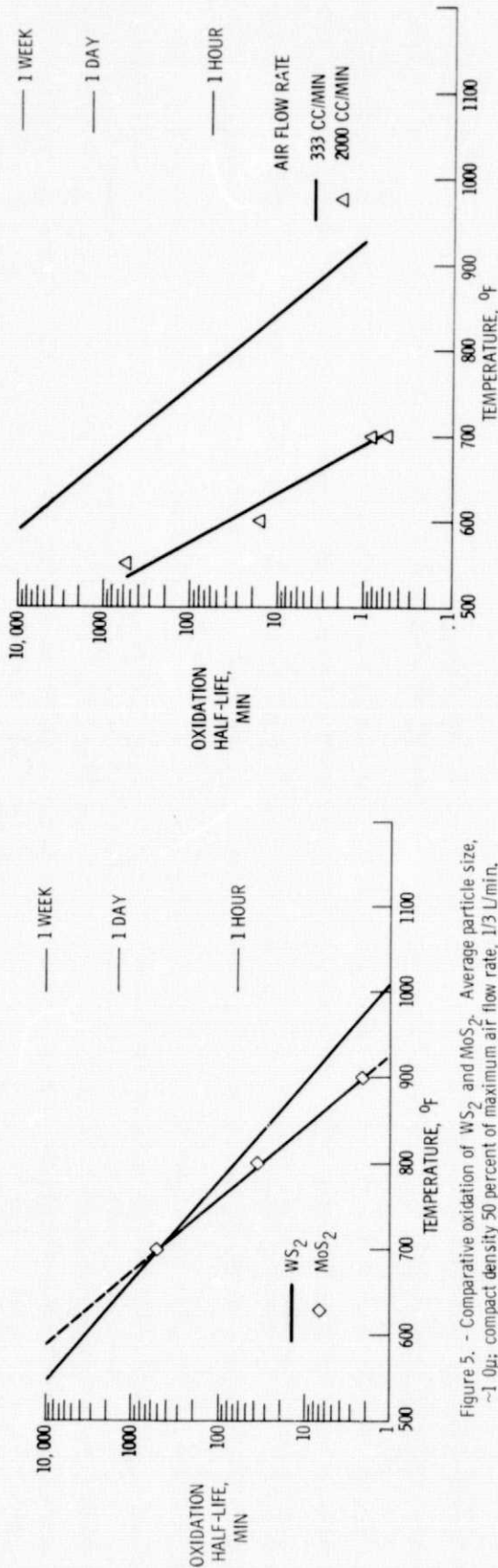
OXIDATION HALF-LIFE, MIN

TEMPERATURE, °F

1 WEEK
1 DAY
1 HOUR

□ 0.030 IN. COMPACT
○ SURFACE FILM, ~0.001 IN.

Figure 1. - Thermochemistry of PbO at various temperatures.

ΔF, K-CAL PER MOL Pb_3O_4

TEMPERATURE, °F

$p_{O_2} = 0.21$ ATM
850° F

$3PbO + \frac{1}{2}O_2 = Pb_3O_4$

940° F
$p_{O_2} = 1$ ATM

MELTING POINT OF LEAD

Figure 3. - Derivation of parabolic oxidation-rate constants K, for x-ray (surface) layers of WS_2 compacts.

SQUARE OF FRACTION OF WS_2 OXIDIZED, $(G_x)^2$

TIME, MIN

$SLOPE = K = \frac{(G_x)^2}{t}$

°F
1050
900
800
700

Figure 6. - Oxidation characteristics of MoS_2 at two air flow rates. Average particle size, ~1.0μ; compact density, 50 percent of maximum.

—— 1 WEEK
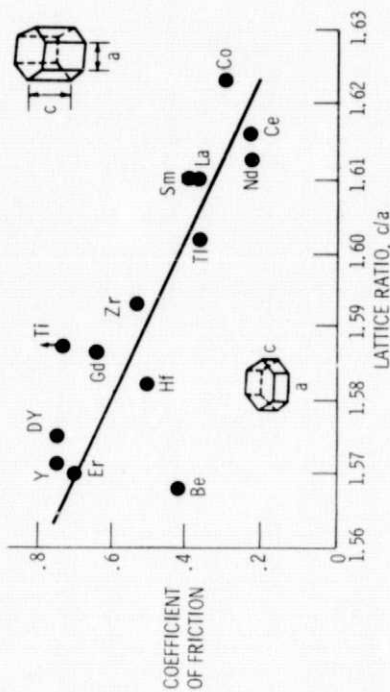—— 1 DAY
—— 1 HOUR

AIR FLOW RATE
333 CC/MIN
2000 CC/MIN

OXIDATION HALF-LIFE, MIN

TEMPERATURE, °F

Figure 7. - Friction of various hexagonal metals. 10^{-9} mm Hg; load, 1000 g; 390 ft/min, on 440C steel.

COEFFICIENT OF FRICTION

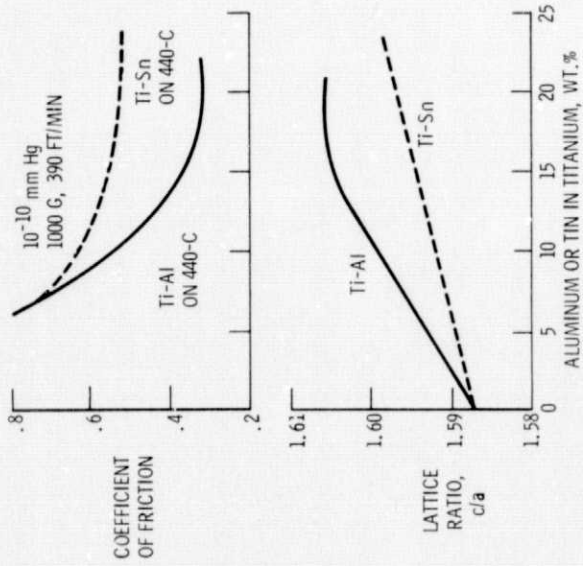LATTICE RATIO, c/a

Figure 5. - Comparative oxidation of WS_2 and MoS_2. Average particle size, ~1 0μ; compact density 50 percent of maximum air flow rate, 1/3 L/min.

—— 1 WEEK
—— 1 DAY
—— 1 HOUR

WS_2
MoS_2

OXIDATION HALF-LIFE, MIN

TEMPERATURE, °F

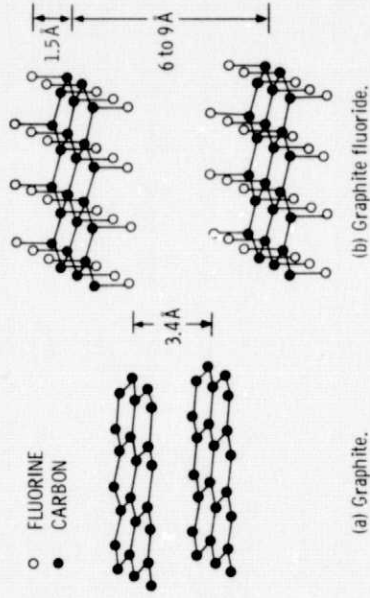E-5241

(a) Graphite.

(b) Graphite fluoride.

Figure 9. - Structure of graphite and proposed structure of graphite fluoride illustrating the expansion of the carbon layer planes due to the intercalation of fluorine atoms.

○ FLUORINE
● CARBON

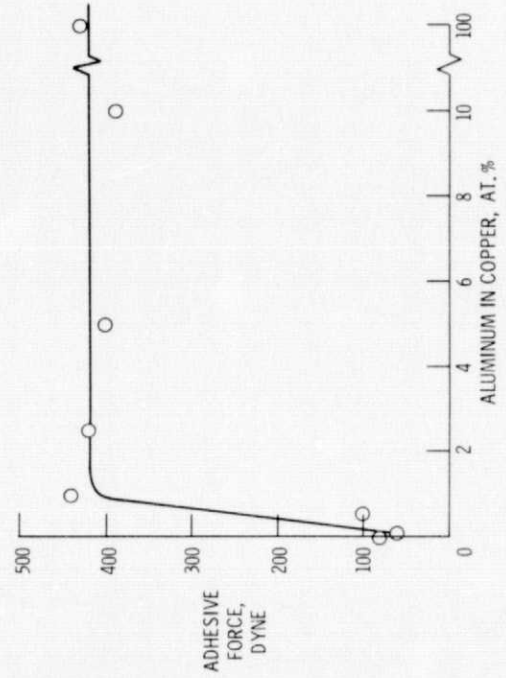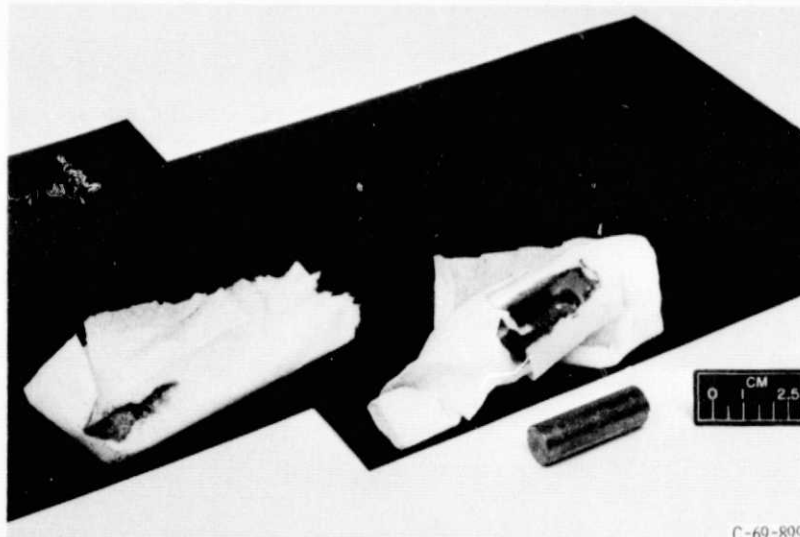Figure 8. - Friction and lattice ratio (c/a) for titanium alloys.

Figure 10. - Adhesion force of (111) gold to the (111) surface of copper, aluminum and various aluminum in copper alloys. Initial applied load, 20 dynes; contact time, 10 seconds.

C-69-899

Figure 11. - Tungsten disulfide cold pressed compacts stored in tissue in room atmosphere for $2\frac{1}{2}$ months. Moisture carried deterioration and acid formation with compacts. Compared with a newly formed compact.
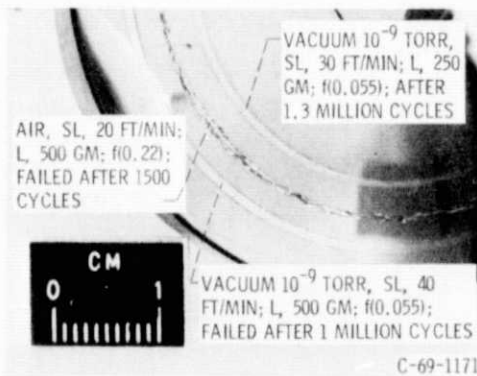

AIR, SL, 20 FT/MIN; L, 500 GM; f(0.22); FAILED AFTER 1500 CYCLES

VACUUM 10^{-9} TORR, SL, 30 FT/MIN; L, 250 GM; f(0.055); AFTER 1.3 MILLION CYCLES

VACUUM 10^{-9} TORR, SL, 40 FT/MIN; L, 500 GM; f(0.055); FAILED AFTER 1 MILLION CYCLES

C-69-1171

Figure 12. - Wear tracks on a (Ni-Cr) disk with sputtered WS_2 film (~2500 Å) after sliding against a 3/16 inch hemispherical nickel rider (SL, sliding velocity; L, load).