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**FLUORIDE SOLID LUBRICANTS FOR EXTREME
TEMPERATURES AND CORROSIVE ENVIRONMENTS**

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION



FLUORIDE SOLID LUBRICANTS FOR EXTREME TEMPERATURES
AND CORROSIVE ENVIRONMENTS

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ABSTRACT

Fluorides of the alkali metals and the alkaline earth metals have an interesting combination of properties that make them promising candidates as solid lubricant materials for use at high temperatures and in corrosive environments. They are chemically inert in strong oxidizing or reducing environments; they are relatively soft and nonabrasive; and some of them, such as CaF_2 , have planes of perfect cleavage in their crystal structure suggesting low shear strength and good friction properties. Thin, fused fluoride coatings (0.001 in.) were applied to nickel-chromium alloys by spraying water slurries of the fluorides on the bearing surface, drying it, then firing it in a hydrogen atmosphere. Coatings of CaF_2 -LiF mixtures and of CaF_2 - BaF_2 mixtures were effective as solid lubricants in hydrogen to 1500°F and in air to 1200°F . CaF_2 - BaF_2 coatings were effective solid lubricants in liquid sodium at 1000°F and a sliding velocity of 2000 ft/min.

INTRODUCTION

Solid lubricants are of particular value under conditions where oils and greases by their very nature cannot be used. Severe lubrication problems are encountered whenever the conditions of extreme temperature and chemical reactivity are combined; perhaps the most common example is

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high-temperature air. In this environment, the lubricant must have both adequate physical properties (high melting points, low vapor pressures, etc.) and good oxidation resistance. High temperature oxidation-resistant lubricants are of current interest for use in present or proposed supersonic aircraft. It has been reported that in the Mach 3 RS70 airplane solid lubricants are used in 1000 applications (ref. 1). Another severe problem area in the aerospace field is the lubrication of bearings submerged in corrosive thermodynamic working fluids such as liquid sodium.

Because of these present and anticipated needs, a research program was conducted at Lewis Research Center to find solid lubricant materials with exceptionally good chemical and thermal stability. The primary analytical approach was the use of thermochemical calculations to determine the probable reactivity of candidate materials at the temperatures and in the environments of interest. The results of these studies indicated that the fluorides of calcium, barium, lithium, and sodium should be quite stable in both strong oxidizing atmospheres (e.g., air to at least 1500^o F) and in strong reducing atmospheres (e.g., liquid sodium). Other attractive properties of these fluorides are their adequately high melting points (all above 1500^o F) and their nonabrasive property.

Fluoride coatings were bonded to nickel-base alloys such as Inconel-X and René 41 in two ways:

(1) Ceramic bonding - the coatings were applied by spraying followed by firing a mixture of a fluoride with an oxide ceramic binder in an air atmosphere at a temperature above the melting point of the binder but below that of the fluoride (ref. 2).

(2) Fused fluorides - the coatings were applied by spraying followed by firing a mixture of fluorides in a hydrogen atmosphere at a temperature above the eutectic melting point of the mixture. In this case, the lubricating components were self-bonding. This method was originally used to obtain an oxide-free coating for liquid sodium exposure (ref. 3).

The friction, wear, and endurance properties of ceramic-bonded calcium fluoride (CaF_2) coatings were evaluated in air from 80° to 1900° F. The lubricating properties of fused fluoride coatings were evaluated in hydrogen and in air from 80° to 1500° F. All experiments in liquid sodium were at 1000° F.

APPLICATION AND PROCEDURE

Coating Procedure

The detailed procedure for applying ceramic-bonded CaF_2 is given in reference 2. The procedure for the fused fluoride coatings is given in reference 3. In general, as illustrated in Fig. 1, the coating material is prepared from carefully weighed and mixed powders made into an aqueous slurry that is sprayed on the metal substrate. Spraying was continued until the thickness of the unfired coating was 0.0015 ± 0.0005 inch. The ceramic-bonded coatings were fired in an air atmosphere at 2200° F.

The all-fluoride coatings were fired in a dry hydrogen atmosphere. The firing time and temperatures for the various compositions are given in Table 1.

Friction and Wear Apparatus and Experimental Procedure

The type of apparatus used in the friction and wear experiments in hydrogen and in air is shown in Fig. 2. Different equipment was used for

sodium but the design differences were those required to contain the particular environment involved. In the basic design, a rotating disk is placed in sliding contact with a hemispherically tipped rider (3/16-in. rad.) under a normal load of 500 or 1000 grams. When coatings are used, they are applied to the disk specimen only. The rider describes a 2-inch-diameter wear track on the disk. Sliding is unidirectional. The sliding velocity is variable; friction torque is continuously recorded.

Before each friction experiment, the rider specimen was carefully cleaned with acetone and then scrubbed with a paste of levigated aluminum oxide and water. The specimens were rinsed with distilled water and then dried. The disks were cleaned in the same manner before the coatings were applied; after firing, the coatings were not cleaned further.

Selection of Chemically Stable Metal Fluorides

As previously indicated, the primary analytical approach to the selection of chemically stable solid lubricant materials was the use of thermochemical considerations. The chemical reactivities of compounds with oxygen, hydrogen, and sodium were estimated from the standard free energy changes (ΔF°) involved in the assumed reactions of the candidate materials with these environments. The equilibrium constants (k) were calculated from the values of ΔF° .

The assumed chemical reactions of a divalent metal fluoride (CaF_2) and a monovalent metal fluoride (LiF) with oxygen, hydrogen, and sodium are given in Table 2. The reactions of two oxides (NiO and Cr_2O_3) with hydrogen and sodium are also included. Expressions for the equilibrium constants applicable to each reaction are given. The terms that appear

in the equilibrium constant expressions for the solid plus gas reactions are the equilibrium partial pressures (in atmospheres) of any gases appearing in the chemical equations. The terms appearing in the equilibrium constant expressions for the solid plus liquid metal reactions are the equilibrium concentrations (in mole fractions) of the liquid metal and the compounds that are soluble in the liquid metal. The neglect of other terms is based on the thermochemical convention that pure solids and pure liquids are in a reference state in which their effective concentrations (more rigorously, the activities) are equal to unity at all temperatures and over a wide range of pressures.

The calculated values of ΔF° for selected fluorides and oxides are given in Table 3. The reactive environments considered are oxygen, hydrogen, and liquid sodium at 500°K (440°F), 1000°K (1340°F), and 1500°K (2240°F).

Positive values of ΔF° indicate that the assumed chemical reaction will not occur under standard conditions, that is, when all reactants are at a pressure of 1 atmosphere (for ideal gases) or a mole fraction of 1 (for pure liquids and solids), and react to form gaseous products at 1 atmosphere or to form pure liquid or solid products. For more realistic conditions the equilibrium constant (k) is more meaningful. A small value of k indicates that the numerator (which contains the pressure or concentrations of the reaction products at equilibrium) is small compared to the denominator (which contains corresponding terms for the reactants) and hence that the formation of products is not favored. The relation of ΔF° to k is given by the equation

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

where

- ΔF cal per gm atomic weight of reactive environment
R universal gas constant, 1.987 cal per $^{\circ}\text{K}$ per mole
T absolute temperature, $^{\circ}\text{K}$

According to this equation, k will have a finite value for any value of ΔF° and, therefore, any chemical reaction has the theoretical potential to occur to at least an infinitesimal extent. However, a large positive value of ΔF° indicates that the equilibrium constant is small and, therefore, that conditions for the formation of reaction products are not favorable.

In Table 3, the large positive values of ΔF° and the correspondingly small equilibrium constants for the reactions of CaF_2 , BaF_2 , LiF , and NaF with oxygen indicate that these fluorides should all be chemically stable in air at elevated temperatures.

The corresponding data for a hydrogen atmosphere indicate that these fluorides should also be resistant to chemical attack by a strong reducing environment. It is interesting to compare equilibrium conditions at 1000°K (1340°F) for CaF_2 in hydrogen with the equilibrium conditions for the following oxides:

- (1) NiO , which is readily reduced by hydrogen
- (2) Cr_2O_3 , which can be reduced with difficulty, and
- (3) Al_2O_3 , which cannot be reduced by hydrogen

Illustrative calculations of equilibrium concentrations for these reactions are given in the appendix. The results demonstrate that CaF_2 should

be almost as inert to reaction with hot hydrogen as Al_2O_3 , and that CaF_2 should be more inert to hydrogen than chromium oxide (Cr_2O_3), which can be reduced only by careful exclusion of water vapor from the hydrogen atmosphere.

Sodium is a stronger reducing agent than hydrogen as indicated by the larger equilibrium constants and smaller positive values of ΔF° for reduction by sodium. An analysis for sodium reactions similar to the previously mentioned analysis for hydrogen is also given in the appendix. The results indicate that CaF_2 should be much more resistant to sodium than NiO and have a stability intermediate between that of Cr_2O_3 and Al_2O_3 . Cr_2O_3 should be at least superficially reduced. However, there is evidence (ref. 9) that Cr_2O_3 , although eventually reduced by pure liquid sodium, protects sliding surfaces immersed in the liquid metal for a limited time. Therefore CaF_2 , with an even smaller equilibrium constant than Cr_2O_3 may be expected to be reasonably stable.

The calculations do indicate that at 1000°K (1340°F) a small amount of Ca and NaF would be dissolved in liquid sodium in equilibrium with CaF_2 . However, thermodynamics tells us nothing about the rates at which reactions approach equilibrium. For small equilibrium concentrations and where the approach to equilibrium is slow, the concentration of dissolved NaF and Ca may never reach a level at which it would be a problem.

RESULTS AND DISCUSSION OF FRICTION AND WEAR STUDIES

Ceramic-Bonded CaF_2 in Air

CaF_2 coatings with a cobaltous oxide (CoO) base binder lubricated certain nickel-base super alloys at high temperatures (ref. 10). Rider

wear and friction coefficients for cast Inconel sliding against coated Inconel X at a sliding velocity of 430 feet per minute are given in Fig. 3. The friction coefficients were 0.20 or lower at temperatures from 250° to 1500° F. The coating has a tendency to flake off at 1600° F; sliding was rough and coating life was low at 500° F and lower temperatures. Therefore, the useful temperature range for the lubrication of Inconel X with this coating is from about 500° to 1500° F. The coating does not have a spalling tendency above 1500° F when bonded to René 41. This coating has effectively lubricated René 41 to 1900° F.

From 500° to 1000° F, the initial friction coefficients were sometimes objectionably high (>0.20) and erratic in nature. After a preliminary run-in period, the friction coefficients stabilized at the values indicated in Fig. 3. Recent studies have shown that the run-in characteristics of the coating can be improved (although at reduction in the melting point of the ceramic binder) by the addition of 3 percent molybdenic oxide (MoO_3) to the coating composition (ref. 2). Coatings that have been modified by the addition of 3 percent MoO_3 lubricate René 41 to a maximum temperature of 1600° F because of the reduced melting point.

Fused Fluoride Coatings in Air

A fused all-fluoride coating bonded to Inconel X and René 41 was also studied (ref. 3). This coating was originally formulated for use in liquid sodium. In order to avoid any oxide that might react with the liquid metal, the ceramic binder was eliminated and, the all-fluoride coatings were fused in a hydrogen atmosphere to prevent oxidation of the base metal during firing.

The friction and wear properties in air of fused fluoride coatings of the composition 38 percent CaF_2 - 62 percent BaF_2 are given in Fig. 4. The rider wear and friction coefficients of uncoated specimens are included for comparison. Separate 1-hour experiments were conducted to obtain each of the data points shown over a range of temperatures from 75° to 1500° F and at two sliding velocities, 455 and 2000 feet per minute. Rider wear is expressed as wear per foot of sliding so that wear at the two sliding velocities can be compared directly.

Over the entire temperature range and at both sliding velocities, the coatings were responsible for very significant reductions in friction and wear relative to the uncoated metals. At a sliding velocity of 455 feet per minute, the friction coefficient of the coated specimen was high (0.4) at 75° F, but rider wear was low; from about 500° to 1500° F the friction coefficients were within acceptable limits (0.11 to 0.20). At 2000 feet per minute, the friction coefficients were within acceptable limits (0.10 to 0.22) over the entire temperature range 75° to 1500° F.

Significantly, the coatings did not wear through to failure in any of the experiments in an air atmosphere. One hour represents 52,200 cycles at the lower speed and 229,000 cycles at the higher speed.

Because all coatings were fired in a dry hydrogen atmosphere, all the specimens were unoxidized prior to the air runs. During the experiment in air, at temperatures above 1000° F, the nickel-chromium substrate oxidized slowly. Up to 1200° F, this oxidation had no detrimental effect, although a gray or pale green discoloration of the coating was observed. At 1500° F, the originally white coating became dark green and rough as oxides derived

from the base metal diffused into the coating. No lubrication failure occurred, however, at 1500° F during the 1-hour experiments. These results indicate that, while the coatings may be expected to remain serviceable in air for an extended period of time at 1200° F, they may be useful for only 1 or 2 hours at 1500° F.

X-ray diffraction studies of the coatings after a 3-hour exposure to air at 1500° F indicated that little or no conversion of CaF₂ or BaF₂ to the corresponding oxides had occurred. The changes in coating composition were caused by contamination with base metal oxides, primarily Cr₂O₃.

In comparing ceramic-bonded CaF₂ coatings with the fused BaF₂-CaF₂ coating for use in air it appears that ceramic-bonded CaF₂ would be superior where optimum performance is required above about 1200° F and fused fluoride coating would provide better wear resistance from room temperature to 1200° F.

Fused Fluoride Coatings in 10 Percent Hydrogen - 90 Percent Nitrogen Atmosphere

Several compositions of fused fluoride coatings were evaluated in a 10 percent hydrogen - 90 percent nitrogen atmosphere. Most of the lubrication experiments were performed at a specimen temperature of 1000° F, but some were also performed at other temperatures from 75° to 1500° F. The results are summarized in Table 4.

At a sliding velocity of 2000 feet per minute, the friction coefficients, with a few exceptions, were in the range 0.15 to 0.20 at temperatures from 75° to 1500° F for the following compositions: 80 percent CaF₂ - 20 percent BaF₂, 38 percent CaF₂ - 62 percent BaF₂, 77 percent

CaF_2 - 23 percent LiF, 100 percent LiF, and 81.4 percent CaF_2 - 18.6 percent NaF. At a lower sliding velocity of 1000 feet per minute, the friction coefficient for one of the coatings (77 percent CaF_2 - 23 percent LiF) was 0.24 at 500° and at 1000° F. The friction coefficients were not significantly affected by load. Therefore, at least within the limits of the temperatures, sliding velocities, and loads used, the only variable that had a significant effect on the friction coefficient was sliding velocity. A sliding velocity of 2000 feet per minute or faster is considered realistic for face-type rotating seals. It is encouraging that, at these high sliding velocities, the friction coefficients for the fused fluorides are below the usually accepted maximum (0.2) for thin-film lubrication under severe sliding conditions.

The same coating compositions for which low friction coefficients were observed also were effective in reducing metallic wear. The photomicrographs and surface profiles in Fig. 5 show the surface details of the worn areas on the uncoated metals. The worn surfaces are characterized by gross metal transfer from the rider to the wear track on the disk. Transferred particles up to 0.003-inch thick were welded to the disk. Metal transfer of this serious proportion would readily close the clearances on bearings or cause leakage in sliding contact seals. The corresponding photomicrographs and surface profiles of specimens lubricated with CaF_2 - BaF_2 and CaF_2 -LiF coatings are shown in Fig. 6. No metal transfer or welding has occurred. The wear scars generated on the hemispherical riders are small and glazed over with a thin film of lubricant coating material. The wear tracks penetrate to a depth approximately equal to the original thickness of

the coating, but the bottoms of the tracks are also glazed over with a very thin film of coating material. In one track, two narrow scratches extend down into the substrate metal, but any metallic contact that may have occurred was not indicated by a measurable increase in friction coefficient.

An indication of coating wear can be derived from the coating wear life expressed as cycles to failure in Table 4. Coating failure was detected as a sudden and large increase in friction coefficient.

The wear life of the coating was sensitive to load. On the average, longer coating life was obtained with a 500-gram load than with a 1000-gram load. At 1000° F, with a 500-gram load, no coating failures were obtained during experiments of 1-hour duration (229,200 cycles). The unit loads during these experiments varied from a maximum of about 120,000 pounds per square inch (theoretical initial Hertz stress for a 3/16-in.-rad. steel hemisphere on a steel flat) down to a final apparent unit stress of about 500 pounds per square inch. The final unit stress was obtained by dividing the 1.1-pound (500-g) normal load by the area of a typical wear scar on the rider at the conclusion of an experiment. Face-type sliding contact seals are generally designed to operate at unit loads of 30 pounds per square inch or less. Therefore, the experiments reported herein may be considered accelerated tests of coating life relative to conditions customary to seal technology.

Fused Fluoride Coatings in Liquid Sodium

Coating compositions that had given favorable results in hydrogen were evaluated in sodium. The compositions evaluated in sodium were 80 percent CaF_2 - 20 percent BaF_2 , 38 percent CaF_2 - 62 percent BaF_2 , 77 percent CaF_2 -

23 percent LiF, 100 percent LiF, and 81.4 percent CaF_2 - 18.6 percent NaF.

These experiments were conducted with the disk specimen and the rider submerged in liquid sodium held at a temperature of 1000° F. The disk was rotated at 3820 rpm for 1 hour before the start of the friction and wear experiment. The duration of the friction experiment was another hour. In addition to being a friction and wear experiment, this was a severe test of the sodium compatibility of the coatings. If the coating failed before 1 hour under load, the rider was retracted and the disk was allowed to rotate until a total sodium exposure time of 2 hours had elapsed. In this manner, uniform sodium exposure time and conditions were maintained so that the resistance of the various coating compositions to sodium could be directly compared even when the durations of the actual friction experiments were not the same.

X-ray diffraction was used to detect any changes in the thickness or composition of the coatings caused by sodium exposure. Any serious reduction in coating thickness caused by sodium exposure was indicated by a decreased intensity in the diffraction peaks for the compounds in the coating relative to the diffraction peaks of the substrate metal. Also, when one compound in a binary composition was leached out and the other was not, the diffraction peaks for the compound that had been attacked would disappear or decrease in intensity with respect to the peaks for the other compound.

The friction and wear observed in the sodium experiments are summarized in Fig. 7. Data for some coatings in 10 percent hydrogen - 90 percent nitrogen are also given for comparison. In sodium, the friction coefficients of four of the coating compositions were between 0.15 and 0.20, and rider

wear was reduced by a factor of at least 100 relative to the uncoated metals. Photomicrographs and surface profiles for unlubricated nickel-chromium slider specimens and for specimens lubricated with 62 percent BaF_2 - 38 percent CaF_2 coatings are shown in Fig. 8. The results obtained with the coated disks correlate well with the results that had been observed in the preliminary experiments in 10 percent hydrogen; however, friction and wear of the unlubricated, uncoated specimens were different in the two environments. In 10 percent hydrogen, the friction coefficient was 0.47 compared with 0.35 in sodium. In 10 percent hydrogen, wear of the uncoated metals was primarily a matter of metal transfer from the rider to the disk; in sodium, wear was equally severe on both rider and disk. (Compare Fig. 5 with Fig. 8.)

The differences in the modes of wear of the uncoated nickel-chromium specimens in 10 percent hydrogen - 90 percent nitrogen and in sodium are considered to be caused by the difference in the heat-transfer capabilities of the two environments. Thus, the good thermal conductivity of liquid sodium tends toward equalization of the temperature of the rider and the disk. Wear is therefore, to a first approximation, equally distributed between the rider and the disk. In the gaseous atmosphere, frictional heat is not as readily dissipated, and the wear surface of the rider (because it is in continuous sliding contact) becomes hotter than the wear track of the disk. The rider wear surface is then of lower shear strength than the disk wear surface, and it seems reasonable that this difference in shear strength accounts for the predominance of metal transfer from rider to disk.

Coating failure in liquid sodium was detected by a simultaneous increase in the friction force and in the wear rate. A representation of friction and

wear recorder traces is given in Fig. 9. Wear life data for the coatings evaluated in sodium are given in Fig. 10. No one composition showed an outstanding superiority in wear life in these experiments; however, only the CaF_2 - BaF_2 coatings were unaffected by sodium exposure. In light-load long-duration applications, the sodium compatibility of the coating may be the determining factor in coating life rather than the resistance of the coating to repeated mechanical stresses.

Wear life of 100 percent LiF coatings was about the same as that of the 38 percent CaF_2 - 62 percent BaF_2 coatings. However, LiF was slowly eroded or dissolved by flowing sodium and therefore would not be suitable for prolonged sodium exposure.

The wear life of 77 percent CaF_2 - 23 percent LiF coatings was the longest life observed; however, X-ray diffraction studies indicated that LiF was leached out of the coating and, further, that the degree of sodium attack was greater near the rim than near the center of the disk. Since the relative velocity of the coated surface with respect to the liquid metal increases with radial distance from the center of the disk, it is evident that, where sodium attack occurred, it was seriously influenced by the flow rate of liquid metal over the surface of the coating. After a friction experiment, the CaF_2 remaining on the disk was adherent until rinsed with water or alcohol. It appears that the pores in the coating caused by loss of LiF become filled with sodium. Hydrogen gas is formed within the voids in the leached coating when the entrained sodium reacts with alcohol or water and the bond between the remaining coating material and the substrate metal is completely destroyed.

X-ray analysis of the 81.4 percent CaF_2 - 18.6 percent NaF coating after exposure to flowing sodium showed that NaF was completely removed from the

coating. In contrast to the experience with the 77 percent CaF_2 - 23 percent LiF coatings, removal of the non- CaF_2 component resulted in immediate lubrication failure.

The very large range of environments in which fluoride coatings of the alkali metal and the alkaline earth metals can be used may be illustrated by the fact that they have shown promise for use in cryogenic fluids such as liquid oxygen and liquid fluorine (ref. 11) as well as the environment discussed in this paper. One of the principal reasons these coatings can be used in such a variety of extreme conditions is their extremely good chemical stability in either strong oxidizing or reducing atmospheres.

CONCLUDING REMARKS

1. With the aid of some theoretical principles of thermochemistry, the chemical resistance of candidate solid lubricant materials to both strong oxidizing or strong reducing environments were estimated. Good correlation between theoretical prediction and experiment were obtained except where some physical phenomena, such as the solubility of LiF in liquid sodium, overshadowed chemical considerations.

2. Ceramic-bonded CaF_2 lubricated a nickel-base alloy (René 41) in air at temperatures up to 1900°F . Inconel X was lubricated to 1500°F , but coating adhesion was unsatisfactory at higher temperatures.

3. Fusel all-fluoride coatings (e.g., 62 percent BaF_2 - 38 percent CaF_2) have lubricated in a wide variety of environments including air from 75° to 1200°F , hydrogen from 75° to 1500°F , liquid sodium at 1000°F , and in cryogenic fluids such as liquid oxygen and liquid fluorine.

4. The most apparent limitation of the fluoride coatings is that, at low sliding velocities, they have a high friction coefficient at ambient temperatures below about 500° F. At high sliding velocities (e.g., 2000 ft/min), low friction coefficients (<0.20) were obtained at low ambient temperatures.

APPENDIX - DETERMINATION OF EQUILIBRIUM CONCENTRATIONS FROM
INFORMATION IN TABLES 2 AND 3

Reactions With Hydrogen at 1000° K

For CaF₂ and H₂

$$k = p_{\text{HF}} / (p_{\text{H}_2})^{1/2} = 9.6 \times 10^{-14}$$

$$p_{\text{HF}} = 9.6 \times 10^{-14} (p_{\text{H}_2})^{1/2}$$

Where $p_{\text{H}_2} = 1$ atmosphere, $p_{\text{HF}} = 9.6 \times 10^{-14}$ atmosphere. (The presence of an immeasurably small amount of reaction product, HF, is sufficient for equilibrium and no detectable reaction is likely to occur.)

For NiO and H₂

$$(p_{\text{H}_2\text{O}})^{1/2} / (p_{\text{H}_2})^{1/2} = 7.4$$

$$p_{\text{H}_2\text{O}} = 54.7 p_{\text{H}_2}$$

Where $p_{\text{H}_2\text{O}} + p_{\text{H}_2} = 1$ atmosphere, $p_{\text{H}_2} = 0.02$ atmosphere, and $p_{\text{H}_2\text{O}} = 1 - 0.02 = 0.98$ atmosphere. (The reaction should readily proceed even in the presence of a large partial pressure of water vapor.)

For Cr₂O₃

$$(p_{\text{H}_2\text{O}})^{1/2} / (p_{\text{H}_2})^{1/2} = 2.5 \times 10^{-3}$$

$$p_{\text{H}_2\text{O}} = 6.3 \times 10^{-6} p_{\text{H}_2}$$

Where $p_{H_2} = 1$ atmosphere, $p_{H_2O} = 6.3 \times 10^{-6}$ atmosphere. (The partial pressure of water vapor must be kept below 6 parts per million to reduce Cr_2O_3 with hydrogen at $1000^\circ K$.)

For Al_2O_3

$$(p_{H_2O})^{1/2} / (p_{H_2})^{1/2} = 1.1 \times 10^{-7}$$

$$p_{H_2O} = 1.2 \times 10^{-14} p_{H_2}$$

Where $p_{H_2} = 1$ atmosphere, $p_{H_2O} = 1.2 \times 10^{-14}$ atmosphere. (It would be just about impossible to maintain partial pressure of water vapor low enough to react Al_2O_3 with hydrogen.)

Reactions with Sodium at $1000^\circ K$

For CaF_2 and Na

$$k = (N_{Ca})^{1/2} N_{NaF} / N_{Na} = 1.5 \times 10^{-3}$$

where N is the mole fraction. The chemical reaction shown in Table 1 shows that 2 moles of NaF are formed for each mole of Ca. Therefore,

$$(N_{Ca})^{1/2} \cdot 2N_{Ca} = 2(N_{Ca})^{3/2} = 1.5 \times 10^{-3} N_{Na}$$

$$N_{Ca} = 8.3 \times 10^{-3} (N_{Na})^{2/3}$$

for nearly pure Na, $N_{Na} \sim 1$

$$N_{Ca} \sim 0.008$$

$$N_{NaF} \sim 0.016$$

and to iterate,

$$N_{Na} \sim 1 - (0.008 + 0.016) = 0.98$$

(A small, but measurable amount of reaction product may dissolve in the liquid sodium before equilibrium is reached.)

For NiO and liquid sodium

$$k = (N_{\text{Na}_2\text{O}})^{1/2}/N_{\text{Na}} = 1.8 \times 10^3$$

This corresponds to a mole fraction of $\text{Na}_2\text{O} = 0.99^+$. (Equilibrium cannot be attained before Na_2O solubility in liquid sodium is exceeded; therefore, NiO reduction by sodium will go to completion.)

For Cr_2O_3 and liquid sodium

$$k = (N_{\text{Na}_2\text{O}})^{1/2}/N_{\text{Na}} = 0.61$$

$$N_{\text{Na}_2\text{O}} = 0.37(N_{\text{Na}})^2$$

$$N_{\text{Na}_2\text{O}} + N_{\text{Na}} \equiv N_{\text{Total}} \equiv 1$$

$$0.37(N_{\text{Na}})^2 + N_{\text{Na}} = 1$$

$$N_{\text{Na}} = 0.78$$

$$N_{\text{Na}_2\text{O}} = 0.22$$

(The appreciable mole fraction of reaction product Na_2O indicates that it is thermodynamically possible to reduce Cr_2O_3 with sodium at 1000°K .)

For Al_2O_3

$$k = (N_{\text{Na}_2\text{O}})^{1/2}/N_{\text{Na}} = 2.8 \times 10^{-5}$$

for nearly pure liquid,

$$N_{\text{Na}} \sim 1$$

$$N_{\text{Na}_2\text{O}} = (2.8 \times 10^{-5})^2 = 7.8 \times 10^{-10}$$

(No detectable reaction.)

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11. Hady, W. F.; Allen, G. P.; Sliney, H. E.; and Johnson, R. L.: Friction, Wear, and Dynamic Seal Studies in Liquid Fluorine and Liquid Oxygen. NASA TN D-2453, 1964.

Table 1 - Properties and firing of fused coatings

Composition, weight percent	Liquidus temper- ature, °F (a)	Eutectic melting point, °F (a)	Firing	
			Time, min	Temper- ature, °F
80 CaF ₂ - 20 BaF ₂	2400	1872	10	1950
38 CaF ₂ - 62 BaF ₂	1872	1872	10	1920
77 CaF ₂ - 23 LiF	2100	1416	7	1700
100 LiF	1558	----	6	1600
81.4 CaF ₂ - 18.6 NaF	2150	1490	6	1550

^aData from refs. 4 and 5.

Table 2 - Chemical reactions and equilibrium constant expression for some fluorides and oxides

Candidate material	Assumed chemical reaction in various environments	Equilibrium constant expression, k (a)
CaF ₂	$\text{CaF}_2 + \frac{1}{2} \text{O}_2 = \text{CaO} + \text{F}_2$	$P_{\text{F}_2} / (P_{\text{O}_2})^{1/2}$
	$\frac{1}{2} \text{CaF}_2 + \frac{1}{2} \text{H}_2 = \frac{1}{2} \text{Ca} + \text{HF}$	$P_{\text{HF}} / (P_{\text{H}_2})^{1/2}$
	$\frac{1}{2} \text{CaF}_2 + \text{Na} = \frac{1}{2} \text{Ca} + \text{NaF}$	$(N_{\text{Ca}})^{1/2} N_{\text{NaF}} / N_{\text{Na}}^b$
LiF	$2 \text{LiF} + \frac{1}{2} \text{O}_2 = \text{Li}_2\text{O} + \text{F}_2$	$P_{\text{F}_2} / (P_{\text{O}_2})^{1/2}$
	$\text{LiF} + \frac{1}{2} \text{H}_2 = \text{HF} + \text{Li}$	$P_{\text{HF}} / (P_{\text{H}_2})^{1/2}$
	$\text{LiF} + \text{Na} = \text{NaF} + \text{Li}$	$N_{\text{NaF}} N_{\text{Li}} / N_{\text{Na}}^b$
NiO	$\frac{1}{2} \text{NiO} + \frac{1}{2} \text{H}_2 = \frac{1}{2} \text{Ni} + \frac{1}{2} \text{H}_2\text{O}$	$(P_{\text{H}_2\text{O}})^{1/2} / (P_{\text{H}_2})^{1/2}$
	$\frac{1}{2} \text{NiO} + \text{Na} = \frac{1}{2} \text{Ni} + \frac{1}{2} \text{Na}_2\text{O}$	$(N_{\text{Na}_2\text{O}})^{1/2} / N_{\text{Na}}$
Cr ₂ O ₃	$\frac{1}{6} \text{Cr}_2\text{O}_3 + \frac{1}{2} \text{H}_2 = \frac{1}{3} \text{Cr} + \frac{1}{2} \text{H}_2\text{O}$	$(P_{\text{H}_2\text{O}})^{1/2} / (P_{\text{H}_2})^{1/2}$
	$\frac{1}{6} \text{Cr}_2\text{O}_3 + \text{Na} = \frac{1}{2} \text{Na}_2\text{O} + \frac{1}{3} \text{Cr}$	$(N_{\text{Na}_2\text{O}})^{1/2} / N_{\text{Na}}^b$

^aWhere P = partial pressure and N = mole fraction.

^bApplies only up to boiling point (1155° K) of sodium.

Table 3 - Standard free energies of reaction and equilibrium constants
for some fluorides and oxides

Com- pound	Melting point, °F	Reaction temperature		Environment					
				Oxygen		Hydrogen		Sodium	
		°K	°F	Standard free energy of reaction, ΔF° k cal g equiv O ₂ (a)	Equilibrium constant, K _{eq}	Standard free energy of reaction, ΔF° k cal g equiv H ₂ (a)	Equilibrium constant, K _{eq}	Standard free energy of reaction, ΔF° k cal g equiv Na (a)	Equilibrium constant, K _{eq}
CaF ₂	2480	500	440	+131	10 ⁻⁵⁷	+70	4.0×10 ⁻³¹	+11.0	1.7×10 ⁻⁵
		1000	1340	+123	2×10 ⁻²⁷	+60	9.6×10 ⁻¹⁴	+13.0	1.5×10 ⁻³
		1500	2240	+114	3×10 ⁻¹⁷	+49	7.9×10 ⁻⁸	+20.0	1.2×10 ⁻³
BaF ₂	2336	500	440	+144	3×10 ⁻⁶³	+68	3.2×10 ⁻³⁰	+10.0	4.5×10 ⁻⁵
		1000	1340	+135	5×10 ⁻³⁰	+58	3.2×10 ⁻¹³	+11.0	4.1×10 ⁻³
		1500	2240	+128	3×10 ⁻¹⁹	+48	1.1×10 ⁻⁷	+18.0	2.5×10 ⁻³
LiF	1598	500	440	+140	10 ⁻⁶⁰	+69	10 ⁻³⁰	+11.0	1.6×10 ⁻⁵
		1000	1340	+134	10 ⁻²⁹	+56	5.0×10 ⁻¹⁵	+11.0	3.9×10 ⁻³
		1500	2240	Molten	-----	Molten	-----	Molten	-----
NaF	1796	500	440	+162	2×10 ⁻⁷¹	+59	2.0×10 ⁻²⁶	No chemical reaction, but NaF dissolves in liq Na	-----
		1000	1340	+158	5×10 ⁻³⁵	+46	1×10 ⁻¹⁰		-----
		1500	2240	Molten	-----	Molten	-----		-----
NiO	3614	500	440	-----	-----	-2.5	12.2	-18	6.6×10 ⁻⁷
		1000	1340	-----	-----	-4.0	7.4	-15	1.8×10 ⁵
		1500	2240	-----	-----	-5.5	6.3	-11	3.9×10
Cr ₂ O ₃	3614	500	440	-----	-----	+14	1.4×10 ⁻⁶	-2.5	12.2
		1000	1340	-----	-----	+12	2.5×10 ⁻³	+1.0	6.1×10 ⁻¹
		1500	2240	-----	-----	+10	3.6×10 ⁻²	+10.0	3.6×10 ⁻²
Al ₂ O ₃	3722	500	440	-----	-----	+35	1×10 ⁻¹⁵	+19.0	5.4×10 ⁻⁹
		1000	1340	-----	-----	+32	1.1×10 ⁻⁷	+21.0	2.8×10 ⁻⁵
		1500	2240	-----	-----	+29	7.4×10 ⁻⁵	+29.0	5.0×10 ⁻⁵

^a Calculated from free energies of formation of reactants and products selected from refs. 6 to 8.

Table 4 - Friction and wear life for fluoride coating on nickel-chromium alloy in 10 percent hydrogen - 90 percent nitrogen atmosphere

[Sliding velocity, 2000 ft/min; riders, 3/16-in.-rad. hemispheres.]

Coating composition, weight percent	Coating thickness, mills ^a	Temperature, °F	Load, g	Coating wear life, cycles to failure	Friction coefficient	Rider wear rate, cu in./hr
80 CaF ₂ - 20 BaF ₂	2.0	1000	500	^b 229,000	0.16	8.4×10 ⁻⁶
38 CaF ₂ - 62 BaF ₂	1.5	75	500	^b 229,000	0.20	1.8×10 ⁻⁶
	1.0	1000	500	^b 229,000	.16	1.8
	1.2	1500	500	180,000	.15	1.8
	1.0	1500	500	80,000	.20	-----
	1.2	1500	1000	120,000	.20	-----
	1.3	1500	1000	120,000	.20	-----
77 CaF ₂ - 23 LiF	1.2	75	500	^b 229,000	0.16	5.0×10 ⁻⁶
	1.5	1000	500	229,000	.15	1.4
	1.2	1000	1000	80,000	.18	-----
	1.2	1200	1000	48,000	.15	-----
	1.2	500	1000	^c 10,000	^c .24	-----
	1.2	1000	1000	^c 20,000	^c .24	-----
100 LiF	1.3	1000	500	^b 229,000	0.15	6.3×10 ⁻⁶
	1.5	1500	500	229,000	.10	2.52×10 ⁻⁵
81.4 CaF - 18.6 NaF	1.5	1000	500	^b 229,000	0.07	2.4×10 ⁻⁷
54 CaF ₂ - 16 LiF - 30 Al ₂ O ₃	2.0	1000	500	^b 229,000	0.20	3.39×10 ⁻⁵
	1.5	1350	500	60,000	.25	-----
	2.2	1500	500	8,000	.15	-----
Uncoated	0	1000	500	-----	0.47	4.90×10 ⁻⁴
	0	1000	1000	-----	.47	9.90

^a1 mil = 0.001 in.

^bNo failure at end of run.

^c1000 ft/min.

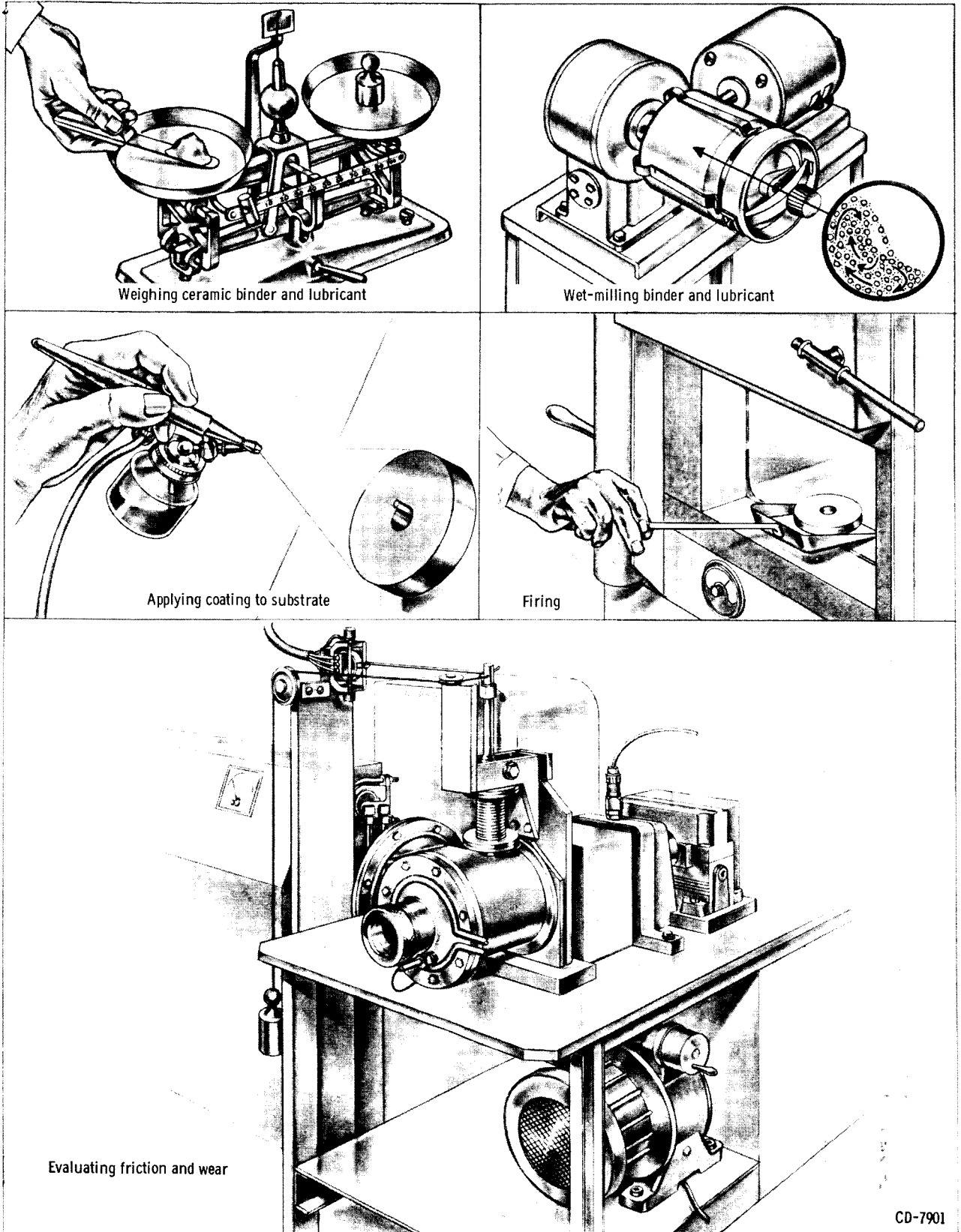
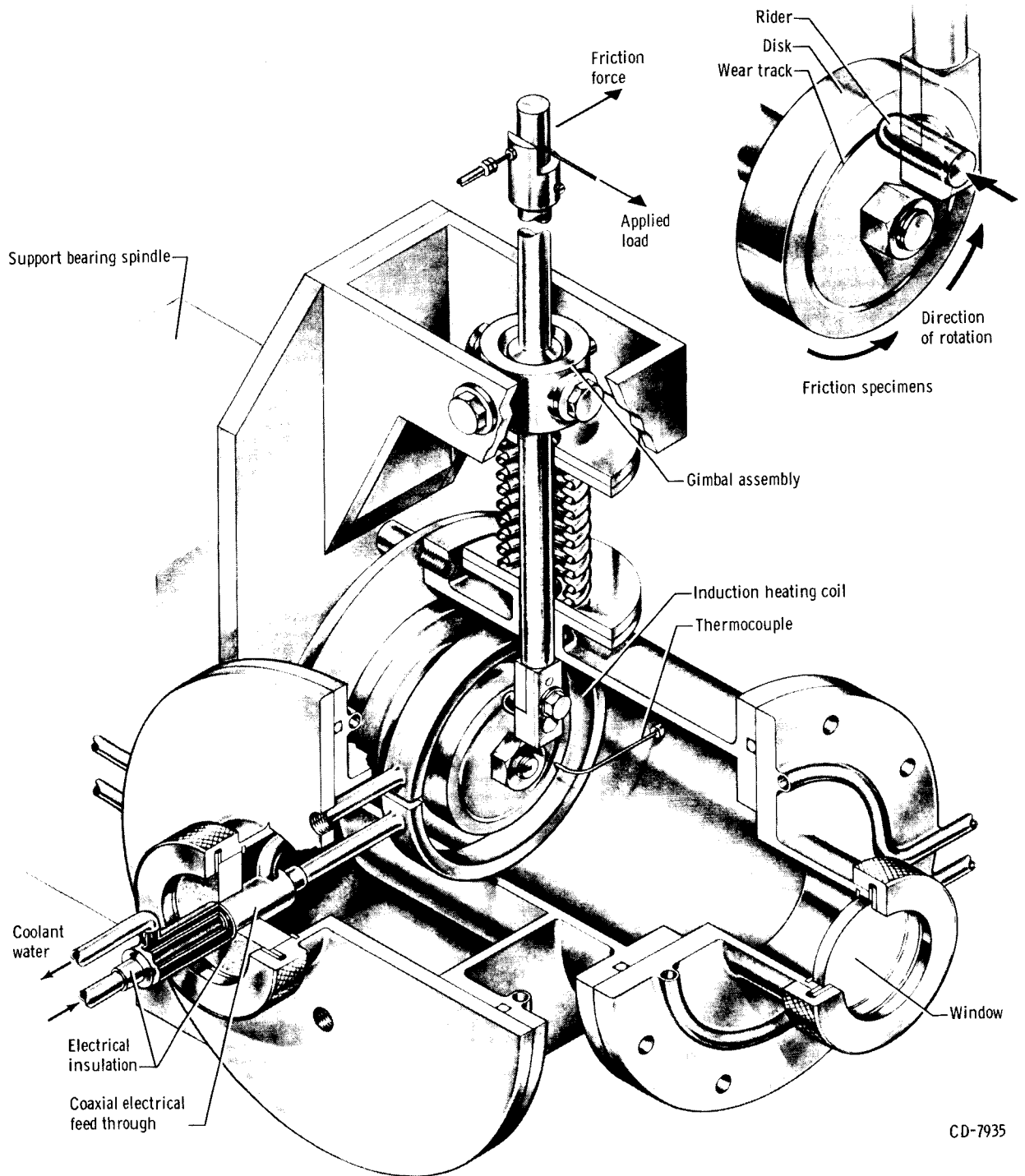


Fig. 1. - Application and evaluation of ceramic-bonded calcium fluoride coating.



CD-7935

Fig. 2. - High-temperature friction apparatus.

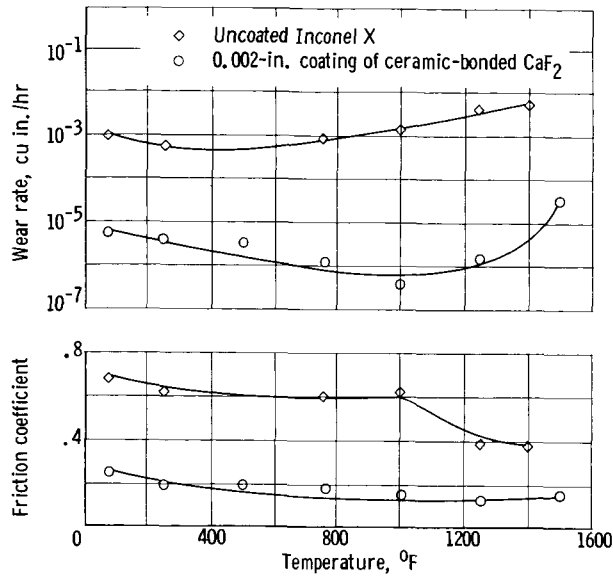


Fig. 3 - Effect of temperature on lubricating properties of ceramic-bonded calcium fluoride coatings on Inconel X. Coating thickness, 0.001 to 0.002 inch; sliding velocity, 430 feet per minute; load, 1 kilogram.

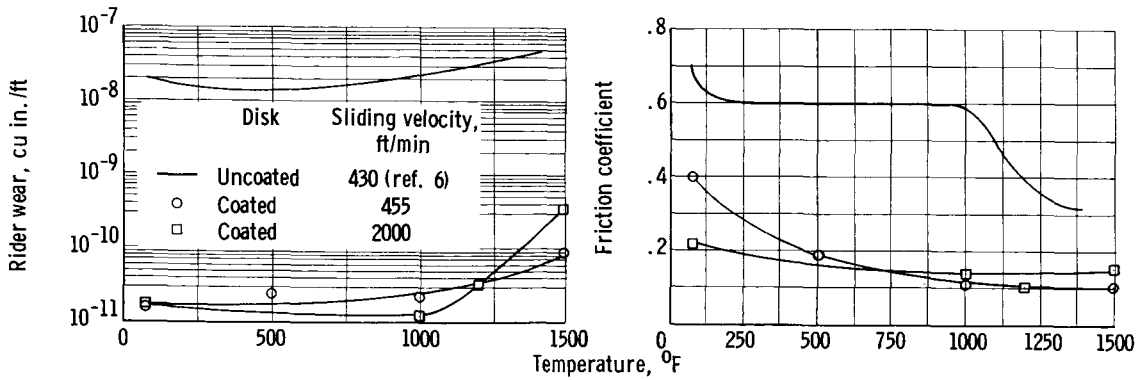


Fig. 4 - Lubricating properties of fused fluoride coating composition in air at two sliding velocities. Coating, 38 percent calcium fluoride - 62 percent barium fluoride; coating thickness, 0.001 to 0.002 inch; duration of run, 1 hour; load, 500 grams; specimens, 3/16-inch-radius riders sliding against coated disks; separate experiments with different specimen for each data point.

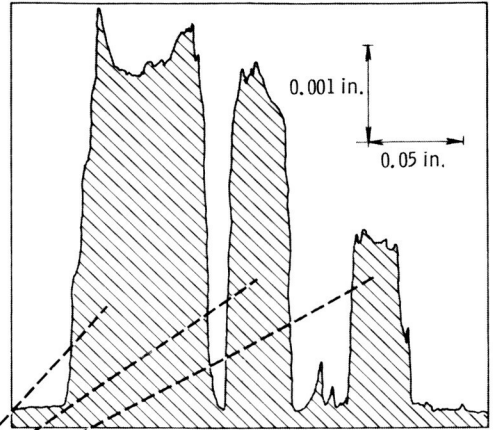


Wear scar on rider; friction coefficient, 0.45



0.05 in.

Wear tracks in disk in area of severe metal transfer



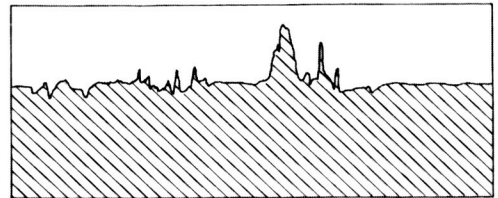
Welded metal from disk

Surface profile across wear track in area of severe metal transfer



0.05 in.

Wear track in disk in area of severe metal transfer



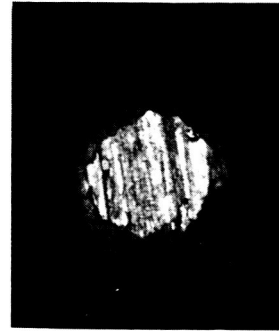
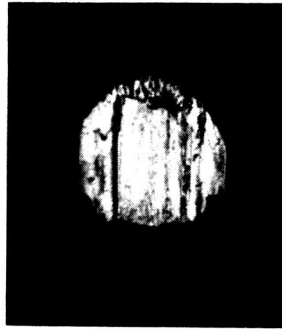
Surface profile across wear track in area of mild metal transfer

C-68689

Fig. 5. - Wear of uncoated nickel-chromium specimens in 10 percent hydrogen - 90 percent nitrogen atmosphere. Temperature, 1000^o F; duration of run, 40,000 cycles; sliding velocity, 2000 feet per minute at 3820 rpm; load, 1000 grams.

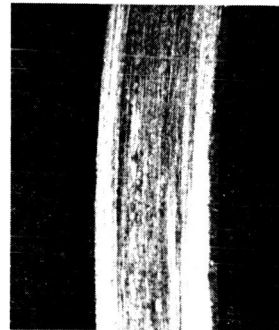
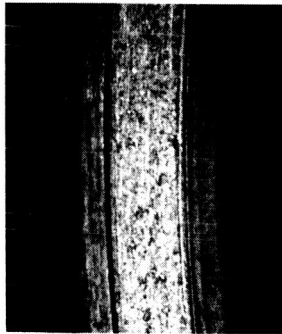
0.0015 Inch coating of 80 calcium fluoride - 20 barium fluoride;
friction coefficient, 0.16

0.0015 Inch coating of 77 calcium fluoride - 23 lithium fluoride;
friction coefficient, 0.15



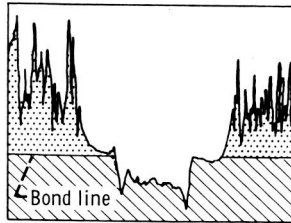
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Wear scars on riders



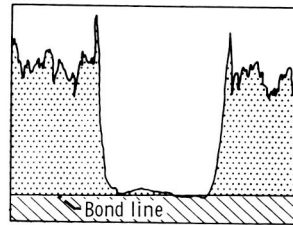
0.05 in.

Wear tracks on disks



0.001 in.
0.05 in.

Coating
Substrate metal



C-68690

Surface profiles across wear tracks

Fig. 6. - Wear in 10 percent hydrogen - 90 percent nitrogen atmosphere when disks were coated with fused fluorides. Temperature, 1000^o F; duration of run, 229,200 cycles; sliding velocity, 2000 feet per minute at 3820 rpm; load, 500 grams.

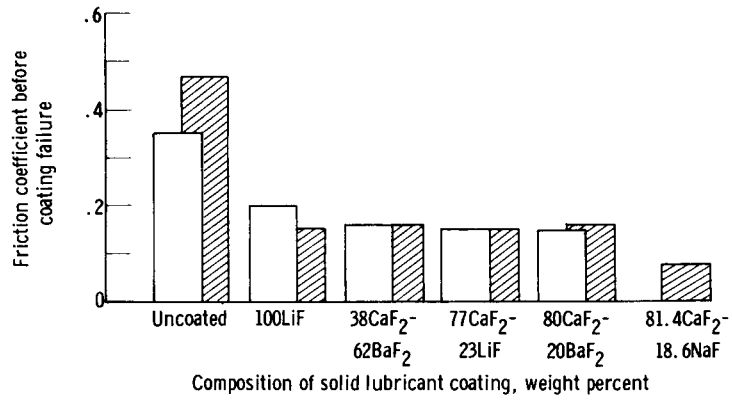
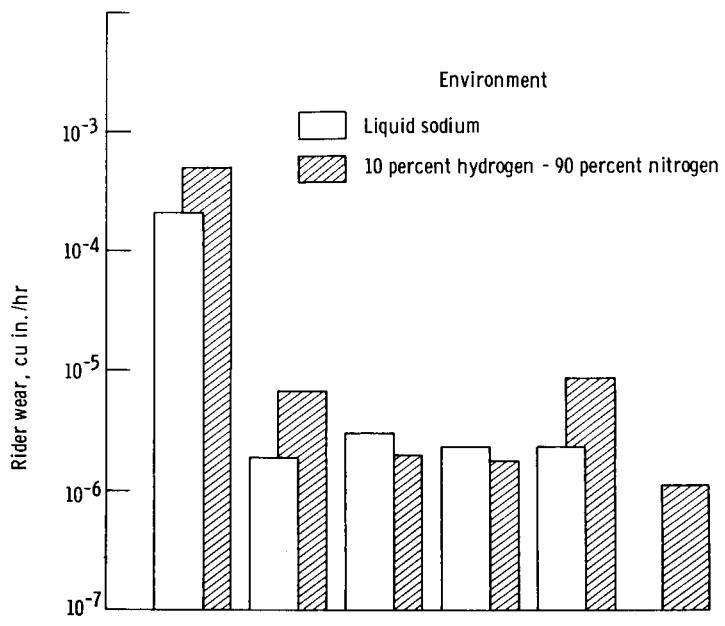
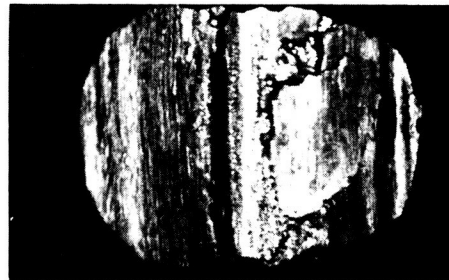
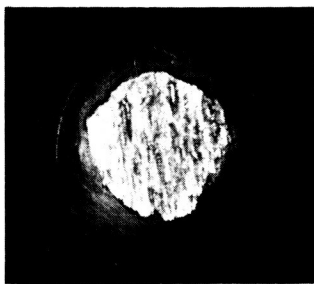


Fig. 7 - Lubrication of nickel-chromium alloy with fused fluoride coatings in liquid sodium and in 10 percent hydrogen - 90 percent nitrogen atmosphere. Temperature, 1000^o F; coating thickness, 0.001 to 0.002 inch; sliding velocity, 2000 feet per minute; load, 500 grams; specimens, 3/16-inch-radius hemispherical riders sliding against disks coated as indicated.

Coated disk after 44,000 cycles;
friction coefficient, 0.15

Uncoated disk after 229,200 cycles;
friction coefficient, 0.35



0.05 in.

Wear scars on riders



0.05 in.

Wear tracks on disks

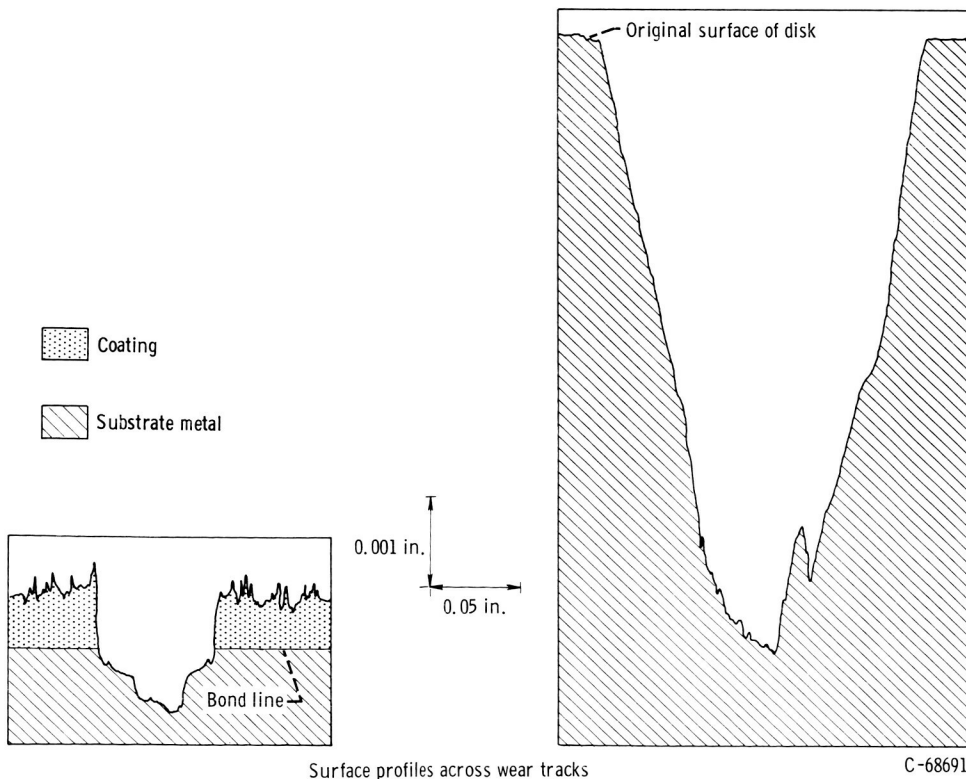


Fig. 8. - Comparative wear of coated and uncoated nickel-chromium alloy in liquid sodium. Temperature, 1000° F; coating, 38 percent calcium fluoride - 62 percent barium fluoride; coating thickness, 0.001 inch; sliding velocity, 2000 feet per minute at 3820 rpm; load, 500 grams.

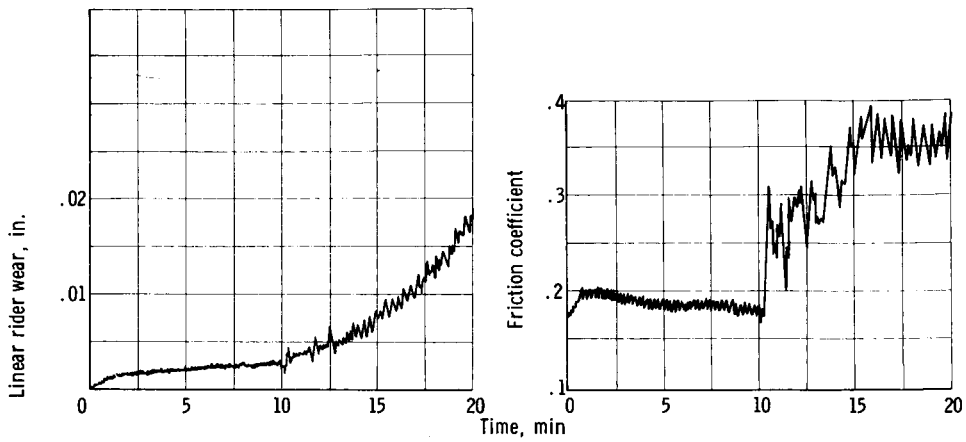


Fig. 9 - Wear and friction recorder traces showing failure of lithium fluoride coating after $10\frac{1}{2}$ minutes in liquid sodium at 3820 rpm and 1000° F.

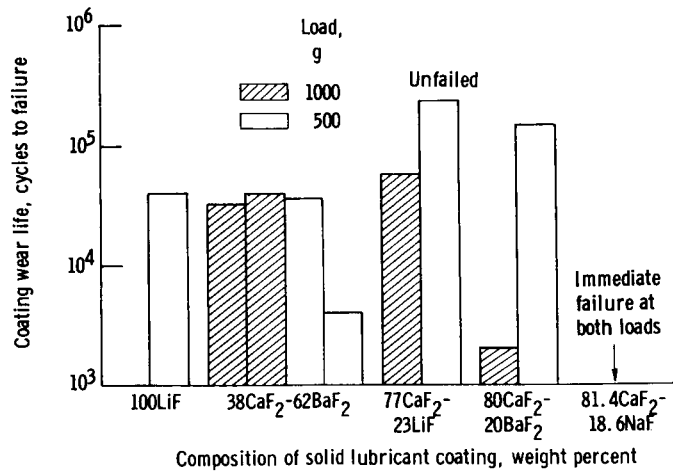


Fig. 10 - Wear life of fluoride solid lubricant coatings in liquid sodium. Temperature, 1000° F; coating thickness, 0.001 to 0.002 inch; sliding velocity, 2000 feet per minute at 3820 rpm; specimens, $3/16$ -inch-radius hemispherical riders sliding against disks coated as indicated.