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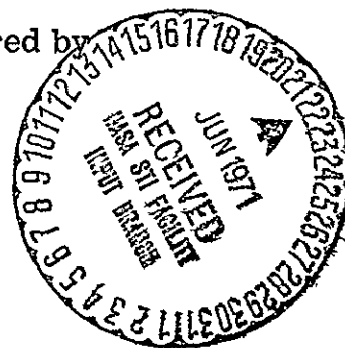
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**AN INVESTIGATION OF OXIDATION-RESISTANT  
SOLID LUBRICANT MATERIALS**

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TECHNICAL PAPER proposed for presentation at  
International Conference on Solid Lubricants sponsored by  
the American Society of Lubrication Engineers  
Denver, Colorado, August 24-27, 1971



FACILITY FORM 602

N71-27787 (ACCESSION NUMBER)	(THRU)
12 (PAGES)	33 (CODE)
Tmx-67845 (NASA CR OR TMX OR AD NUMBER)	15 (CATEGORY)

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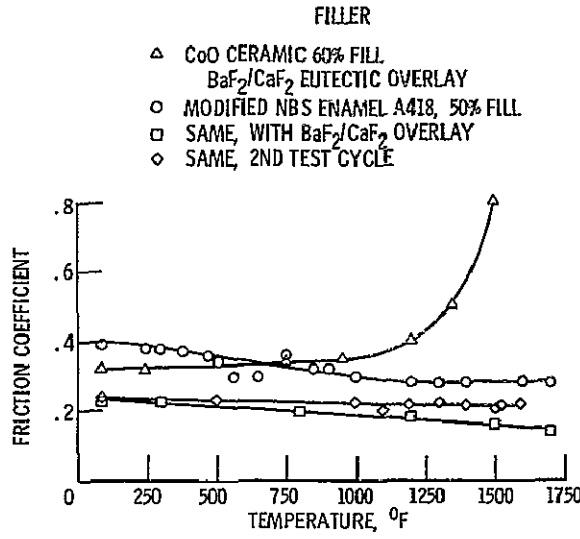


Figure 6. - Friction-temperature characteristics of oxidation-resistant self-lubricating composites, air atmosphere, 500 ft/min sliding velocity, 500 gm load, 3/16 in. hemispherical riders sliding on 0.060 inch thick self-lubricating composites backed with 1/2-inch-thick, dense nickel alloy.

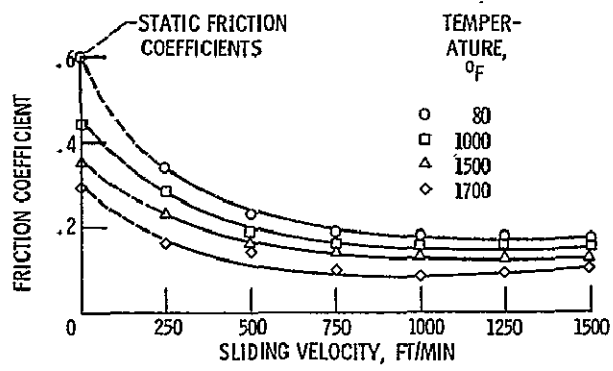


Figure 7. - Effect of sliding velocity on friction coefficients of self-lubricating composites with modified N. B. S. A418 enamel filler and BaF<sub>2</sub>/CaF<sub>2</sub> eutectic overlay, air atmosphere, 500 gm load.

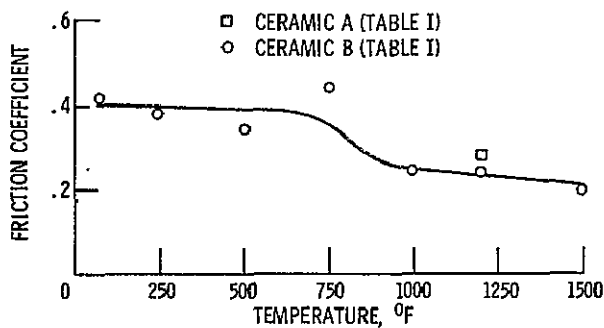


Figure 8. - Friction-temperature characteristics of cast ceramic riders sliding on nickel-chromium alloy disks, 500 ft/min sliding velocity, 1 kg load.

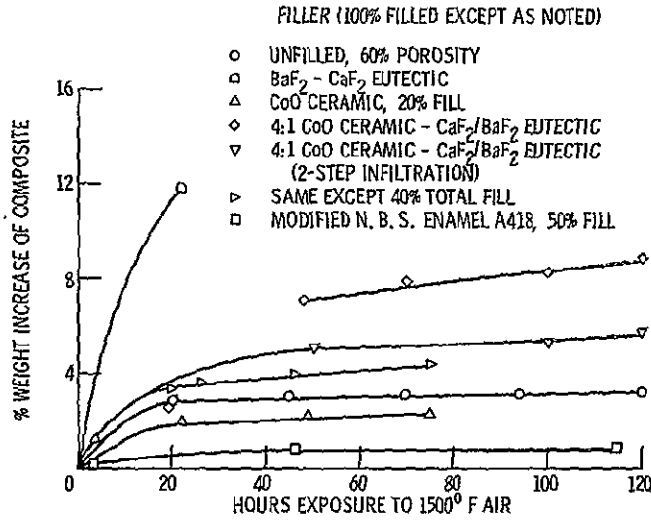


Figure 4. - Effect of lubricant fillers on oxidation kinetics of sintered nickel-chromium alloy B. Specimens: 0.60-inch thick sintered metal layer bonded on 0.065 inch thick dense nickel-chromium alloy backing.

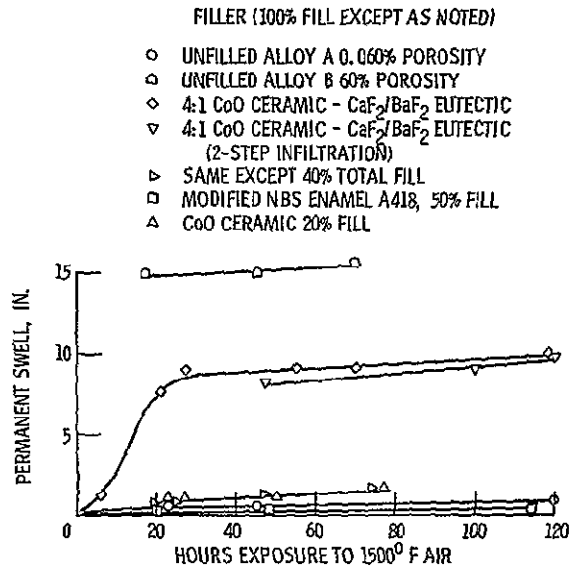


Figure 5. - Dimensional stabilities of some composites of sintered nickel-chromium alloy B in 1500° F air (unfilled alloys A and B for comparison). Specimens: 0.060-inch sintered metal layer bonded on 0.065 inch thick dense nickel alloy backing.

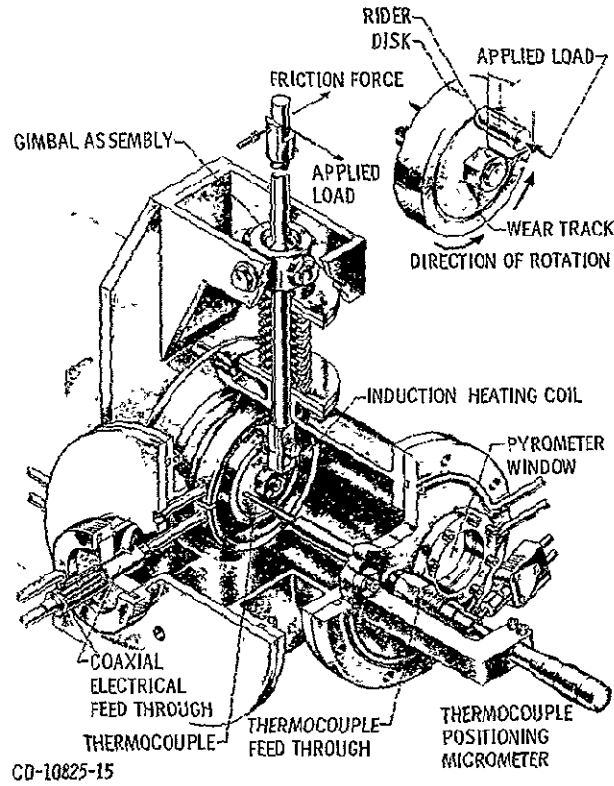


Figure 1. - Friction and wear testing device.

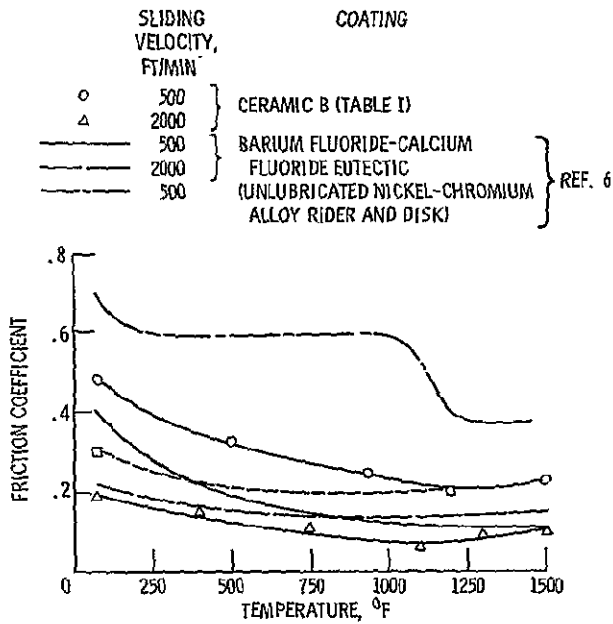


Figure 2. - Friction-temperature characteristics of fluoride coatings modified with silicate and oxide additions, air atmosphere, 1 kg load.

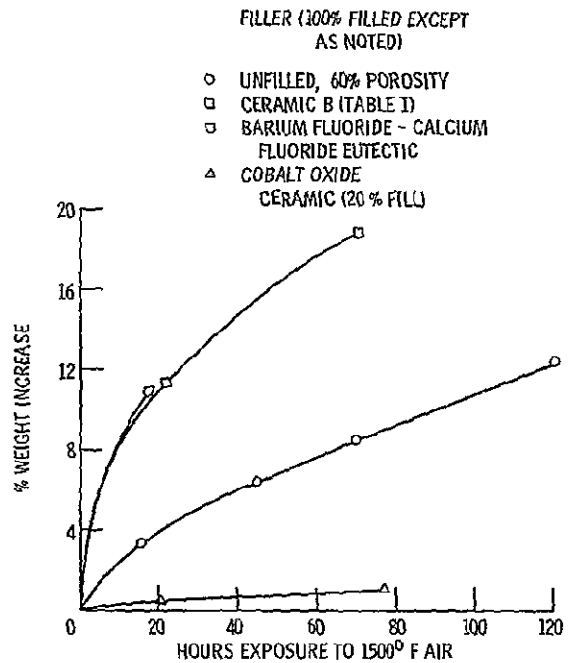


Figure 3. - Effect of lubricant fillers on oxidation kinetics of sintered nickel-chromium alloy A. Specimens: 0.060-inch sintered metal bonded on 0.065-inch thick dense nickel alloy backing.

TABLE V

WEAR OF RIDERS<sup>1</sup> AND COMPOSITE DISKS

500 gm load, 500 ft/min sliding velocity

Disks: Backed, self-lubricating composites; composite layer, 0.060-inch thick; sintered, nickel base alloy B; porosity of sintered layer, 60%; lubricating fillers, as specified below.

Lubricating Filler and Overlay	Test History Hours at Temp. (°F)	Average Rider Wear Rate (in <sup>3</sup> /hour)	Disk Appearance
CoO ceramic, 60% fill of porosity BaF <sub>2</sub> -CaF <sub>2</sub> eutectic	6 hrs. temp. cycled 80° F to 1300° F and back to 80° F	$5.3 \times 10^{-6}$	smooth, glazed
	1/2 hour at 1500° F	none: much transfer of disk material to rider	deeply grooved, plastically deformed wear track
Modified NBS A418 enamel 50% fill	4 hours at 1300° F	$4.2 \times 10^{-6}$	deep plastic deformation but smooth, glazed track
	1 1/3 hours 80° F to 1700° F	$6.0 \times 10^{-6}$	glazed, deep plastically deformed track
	2/3 hour at 1700° F		
Modified NBS A418 enamel 50% fill + sintered overlay of BaF <sub>2</sub> -CaF <sub>2</sub> eutectic	1 hour 80° F to 1700° F	$5.2 \times 10^{-7}$	relatively slight plastic deformation of track
	1 1/2 hours at 1700° F		
	1 hour 80° F to 1600° F	$7.6 \times 10^{-7}$	relatively slight plastic deformation of track
Control: Unlubricated wrought nickel base alloy B	6 hours at 1600° F		
	1 hour 80° F to 1500° F	$5.0 \times 10^{-6}$	moderate deformation of wear track
	4 hours at 1500° F		
	1 hour at 80° F	$1.0 \times 10^{-3}$	
	1 hour at 1500° F		

<sup>1</sup>Nickel alloy (composition in Table I)

TABLE III

## EFFECT OF 1500° F AIR EXPOSURE ON FLUORIDE COATINGS

Coating	Time at 1500° F (hours)	Appearance of Coatings
60 w/o CaF <sub>2</sub> - 40 w/o BaF <sub>2</sub>	0	Smooth, white coating
	7	White with many minute spalled areas
	24	Greenish-yellow, loose and powdery
Ceramic A (Table I)	0	Smooth, white coating
	7	Rough, dark green, but well-bonded
	24	Rough and powdery
Ceramic B (Table I)	0	Smooth, cream-colored coating
	7	No change
	24	Very slight edge spalling otherwise smooth and adherent

Substrate: Nickel-chromium alloy (Table I)

Coating Thickness: 0.001 inch

TABLE IV

## WEAR OF RIDERS AFTER SLIDING ON COATED DISKS\*

Lubricating Coating	Temp. (°F)	Wear Rate (in <sup>3</sup> /hr)
Ceramic A (Table I)	80	0.8 x 10 <sup>-6</sup>
	1200	0.3 "
Ceramic B (Table I)	80	3.2 x 10 <sup>-6</sup>
	500	0.5 "
	930	1.2 "
	1200	3.3 "
	1500	1.0 "
Unlubricated	80	1.0 x 10 <sup>-3</sup>
	1500	8.0 "

Load, 1 kg

Sliding velocity, 500 ft/min.

Coating thickness, 0.001 inch

\*Nickel alloy (composition in Table I)

TABLE I

NOMINAL COMPOSITIONS OF SUBSTRATE AND COATING MATERIALS, W/O

<u>Rider and Substrate Alloy</u>	
49.8 Ni, 19.0 Cr, 11.0 Co, 5.0 Fe, 0.1 C, 0.5 Si, 10.0 Mo, 1.5 Al, 0.1 Mn, 3.0 Ti	
<u>Coating Compositions</u>	
<u>Ceramic A:</u>	60.8 CaF <sub>2</sub> , 13.1 LiF, 17.4 Ca <sub>2</sub> SiO <sub>4</sub> , 8.7 CaO
<u>Ceramic B:</u>	48.3 BaF <sub>2</sub> , 21.7 CaF <sub>2</sub> , (70 fluorides), 20 Ca <sub>2</sub> SiO <sub>4</sub> 10 CaO

TABLE II

NOMINAL COMPOSITIONS OF MATERIALS USED  
IN SELF-LUBRICATING COMPOSITES

POROUS MEDIA	
<u>Sintered Alloy A</u>	46.9 Ni, 22 Cr, 1.5 Co, 9 Mo, 0.5 W, 18 Fe, 0.1 C, 1.0 Si, 1.0 Mn
<u>Sintered Alloy B</u>	72 Ni, 17 Cr, 9.85 Fe, 0.15 C, 1.0 Mn
LUBRICATING FILLERS	
<u>CoO Ceramic</u>	60 CoO, 20 BaO, 20 B <sub>2</sub> O <sub>3</sub>
<u>BaF<sub>2</sub>/CaF<sub>2</sub> Eutectic</u>	69 BaF <sub>2</sub> , 31 CaF <sub>2</sub>
<u>Ceramic B (Table I)</u>	
<u>Modified NBS Enamel A418</u>	Solids content of unmodified A418 before firing is: 20.8 SiO <sub>2</sub> , 31.4 BaCO <sub>3</sub> , 2.7 ZnO, 3.5 CaCO <sub>3</sub> , 0.8 Al(OH) <sub>3</sub> , 6.4 B <sub>2</sub> O <sub>3</sub> , 1.4 ZrO, 4.7 clay, 28.3 Cr <sub>2</sub> O <sub>3</sub>

ing on coatings of the two compositions.

Although the data is preliminary, it supports the concept that fluoride-silicate ceramics may have possibilities for use as cast self-lubricating materials, especially for high-temperature applications.

#### Concluding Remarks

1. The compatibility of  $BaF_2$ - $CaF_2$  coatings with 1500 F air was improved significantly by the addition of calcium silicate and calcium oxide to the coating formulations.

2. Self-lubricating composites were developed which have good oxidation resistance during long duration exposure in air to at least 1500 F. The composites are a porous sinter of nickel alloy powder infiltrated with a high-temperature enamel and an overlay of  $BaF_2$ - $CaF_2$  eutectic. At a sliding velocity of 500 feet per minute, the friction coefficients were  $0.20 \pm 0.05$  from 80 to 1700 F.

3. Cast ceramics containing calcium fluoride and calcium silicate has good mechanical strength and were self-lubricating to at least 1500 F. They formed excellent transfer films when sliding against metal surfaces.

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protection were obtained with a filler which is a modification of an enamel composition developed by the National Bureau of Standards.<sup>(10)</sup> The original coating composition was designated A418 by the NBS and is given in Table II. The modifications were made to improve the wettability of the molten enamel for infiltration into sintered metals. With a 50 percent fill of modified A418, the weight increase was less than one percent after 100 hours at 1500 F.

Figure 5 gives the effect of exposure to 1500 F air in terms of the permanent swell of filled and unfilled sintered alloys. The swell is the increase in thickness of an originally 0.060-inch thick composite layer on a dense metal backing. Unfilled alloy A swelled 0.015 inch after only 10 hours exposure. Unfilled alloy B is much better with about 0.0007 inch swell after 120 hours. A 0.0002-inch swell occurred for alloy B with a modified A418 enamel filler. Swell with a CoO ceramic filler either alone or after a second infiltration with BaF<sub>2</sub>-CaF<sub>2</sub> eutectic was about 0.002 inch in 100 hours.

After the favorable experience with coatings of ceramic B (silicate-modified BaF<sub>2</sub>-CaF<sub>2</sub>) in 1500 F air, it was surprising that this same composition provided no oxidation protection when used as a filler for sintered metals. The good resistance of coatings of ceramic B to spalling or powdering during prolonged exposure to 1500 F air may be attributable to the improved cohesion and mechanical strength of this material compared to BaF<sub>2</sub>-CaF<sub>2</sub> coatings and may not be related to oxidation protection of the substrate alloy.

Figure 6 gives the friction coefficients of some self-lubricating composites from 80 to 1700 F and at a sliding velocity of 500 feet per minute; Table V gives the corresponding wear observations. A composite with a CoO ceramic filler and a BaF<sub>2</sub>-CaF<sub>2</sub> lubricating overlay gave friction coefficients from 0.32 at 80 F to 0.40 at 1200 F. Friction increased markedly at higher temperatures. Rider wear rates were moderate, but the wear tracks on the disks deformed plastically above 1300 F. The CoO ceramic was very soft at 1300 F thus accounting for the severe plastic deformation.

Composites with modified A418 enamel

filler gave a friction coefficient of 0.39 at 80 F and this very gradually decreased with temperature to 0.28 at 1200 F and remained at that value to 1700 F. Rider wear was again moderate and the wear tracks were plastically deformed. Substantial further benefits were derived by applying a sintered overlay of BaF<sub>2</sub>-CaF<sub>2</sub> on the composites filled with modified A418 enamel. Friction coefficients were 0.24 and 80 F and in the range of 0.14 to 0.22 at 1700 F. Rider wear was very low and there was very little plastic deformation of the wear track.

The effects of sliding velocity on the friction coefficients of this composite material are given in Fig. 7. Friction coefficients tended to decrease with increasing sliding velocity and temperature. At 80 F the friction coefficients were 0.34 at 250 feet per minute and 0.18 at 1500 feet per minute. At 1700 F the friction coefficients were 0.16 at 250 ft/min and 0.10 at 1500 feet per minute. Static friction coefficients were considerably higher (0.6 at 80 F and 0.30 at 1700 F).

#### Cast Ceramic Self-Lubricating Materials

The fluoride-silicate compositions were much stronger mechanically than the all-fluoride materials. This suggested that fluoride-silicate ceramics might be strong enough to be useful as cast self-lubricating parts. Ceramics A and B were cast into riders for sliding friction studies. For comparison, castings of the BaF<sub>2</sub>-CaF<sub>2</sub> eutectic composition were also made; they were, however, too weak and brittle to be useful slider materials.

The friction-temperature characteristics for cast ceramic riders sliding on nickel alloy disks are given in Fig. 8. At 1200 F, the friction coefficient of ceramic A was higher than that of ceramic B. The friction coefficients of ceramic B were a little higher than they were for thin coatings of the same compositions bonded to a substrate alloy. However, no disk wear occurred at all. The self-lubricating ceramic materials formed a transfer film on metal disks and after only a few disk revolutions, the ceramics were actually sliding on their own transfer film. These films were, of course, formed at a sacrifice of rider material; and rider wear was higher than the wear of metal riders slid-

all-fluoride coating became loose and powdery during an exposure of 24 hours duration. No molten phase was visible on ceramic A, which theoretically has a small percentage of molten phase at 1500 F, but the coating also became rough after only 7 hours and was loose and powdery after 24 hours. Ceramic B remained well-bonded and smooth after 24 hours in air at 1500 F.

### Friction and Wear Experiments

The results of sliding friction experiments with the experimental coatings are summarized in Fig. 2 (friction) and in Table IV (wear). The friction coefficients are compared to data from (6) for  $BaF_2$ - $CaF_2$  coatings without silicate additions. At a sliding velocity of 500 feet per minute, nickel-chromium alloy specimens, which were lubricated with ceramic B, had friction coefficients of 0.48 at room temperature and less than 0.25 from 900 to 1500 F. At a higher speed of 2000 feet per minute the friction coefficients were below 0.2 from 80 to 1500 F with a minimum of 0.06 at 1100 F. Therefore, the friction coefficients with this composition were higher than they were with the reference all-fluoride coatings at 500 feet per minute, but lower than they were with the reference coatings at 2000 feet per minute. Friction coefficients for lubrication with coatings of ceramic A at 500 feet per minute were 0.3 at 80 F and 0.2 at 1200 F.

Lubrication with either coating reduced rider wear rates by a factor of about 1000 compared to the wear of unlubricated specimens (Table IV).

### Composite Developments

The compatibility of fluoride coatings with 1500 F air was improved by additions of calcium silicate and calcium oxide. This suggested that similar additions might be beneficial in lubricating fillers for composites. Self-lubricating composites consisting of sintered metals infiltrated with  $BaF_2$ - $CaF_2$  eutectic have been reported. (8) These composites have been successfully used as the material for self-lubricating cages in ball bearing experiments at temperatures to 1500 F. Bearing life at 1500 F was limited, however, by oxidation of the sintered metal in the composite structure. Oxidation causes the sintered structure to swell, which eventually causes

a loss of cage clearances in the bearing. Good lubrication is obtained up to the time at which distortions cause the cage to jam. Self-lubricating composites are, therefore, a class of materials for which improved oxidation resistance can result in a substantial gain in the usefulness of the material.

The compositions of the sintered metals and of the filler components used in this study are given in Table II.

### Oxidation Rate Determinations

Thermogravimetric (TGA) curves for sintered nickel alloy A and for the same material with various fillers are given in Fig. 3. The specimens were exposed to air at 1500 F. The sintered metal filled with  $BaF_2$ - $CaF_2$  eutectic or with ceramic B oxidized at about twice the rate of the unfilled sintered metal. A partial fill (20 percent of the pore volume) with a cobalt oxide ceramic (Table II) reduced the oxidation rate to about one-tenth that of the unfilled sintered metal.

The fluorides are not in themselves chemically reactive with either air or the metal. However, they do appear to act as a diffusion medium for the metal oxides which normally form protective surface films on nickel base alloys. Because these oxides diffuse into the fluoride filler, they do not provide the tight oxide film which normally inhibits further oxidation.

In Fig. 4 oxidation data for filled and unfilled alloy B are given. This alloy oxidizes at about 1/3 the rate of alloy A and was therefore used in most subsequent experiments. Again, a relatively high oxidation rate occurred when the fluoride eutectic filler was used. Oxidation rates were lower when a 4:1 mixture of CoO ceramic and  $BaF_2$ - $CaF_2$  eutectic were used. Further improvement was obtained by means of a two step infiltration in which the CoO ceramic was first infiltrated into the porous sintered metal structure, then the fluoride eutectic was infiltrated at a lower temperature. This procedure presumably reduced the amount of direct metal to fluoride contact. A filler of CoO ceramic with no fluoride reduced metal oxidation rates below those of the unfilled metal.

By far the best results in oxidation

filtration into the pore structure. The percent fill of the pore structure was controlled by the weight of filler used. Ceramic B was infiltrated by heating in argon to 2100 F for 20 minutes.

#### Cast Ceramic Materials

Cast riders of ceramic A and B were made by pouring the molten ceramic into 3/8-inch diameter holes drilled into a high density carbon block. Hemispherical tips were ground on the ends of the resulting cylindrical castings. Ceramic A was cast at a melt temperature of 2000 F. Ceramic B was cast at a melt temperature of 2150 F; in this case it was necessary to preheat the molds to about 500 F in order to obtain sound castings.

#### Results and Discussion

Research to develop improved high-temperature solid lubricants included the development of (1) new coating formulations, (2) new self-lubricating composites, and (3) cast ceramic self-lubricating materials. These three areas will be discussed separately. A major unifying factor in all three areas is that calcium fluoride ( $\text{CaF}_2$ ) and barium fluoride ( $\text{BaF}_2$ ) are the primary lubricating components. For coatings and composites, oxide ceramics or glasses were incorporated in an attempt to improve oxidation protection to the metal at the metal fluoride interfaces. For cast, non-metallic, self-lubricating materials, oxides were added to improve mechanical strength of the cast material.

#### Coating Developments

Calcium fluoride coatings containing calcium silicates and calcium oxide ( $\text{CaO}$ ) were prepared. The silicates and the oxide were added to give the  $\text{CaF}_2$  coating some of the characteristics of porcelain enamels which provide oxidation protection to the metal substrate. However, the silicate content was kept at a lower level than is usual for porcelain enamels in order to keep the coating from becoming too brittle.

#### Phase Considerations

A ternary phase diagram for the  $\text{CaF}_2$ - $\text{SiO}_2$ - $\text{CaO}$  system is given.<sup>(9)</sup> Some important features of this system are: (1) the

existence of a  $\text{Ca}_2\text{SiO}_4$ - $\text{CaF}_2$  binary eutectic at 43 w/o  $\text{Ca}_2\text{SiO}_4$  with a melting point of 2285 F, (2) a  $\text{CaO}$ - $\text{CaF}_2$  binary eutectic at 82 w/o  $\text{CaF}_2$  with a melting point of 2484 F, (3) a ternary eutectic of 47 w/o  $\text{CaF}_2$ -45 w/o  $\text{Ca}_2\text{SiO}_4$ -8 w/o  $\text{CaO}$  with a melting point of 2246 F, and (4) no solid solubility is indicated. Compositions were selected from this ternary system for evaluation as solid lubricants.

Lithium fluoride ( $\text{LiF}$ ) or  $\text{BaF}_2$ - $\text{CaF}_2$  eutectic (instead of  $\text{CaF}_2$  above) were added to some of the compositions in order to further reduce the melting points and thereby reduce the firing temperature required to obtain well-bonded coatings.

After experimentation with a number of compositions, two of them, which formed uniform well-bonded coatings on a nickel chromium alloy were chosen for friction and wear studies. The compositions are given in Table I.

Cooling curves were experimentally obtained for these compositions. One composition designated ceramic A in Table I contained  $\text{LiF}$ . When cooled from the molten state, thermal arrests occurred at 1900 F and 1300 F indicating solidification began at 1900 F but some liquid phase remained down to 1300 F (possibly the quaternary eutectic melting point). The other composition designated ceramic B, solidified over a much narrower temperature range of 1650 to 1700 F.

#### Effect of Oxidation

Sprayed-on films of ceramic A and ceramic B were fusion-bonded to a nickel-chromium substrate alloy in a furnace with an air atmosphere. Well-bonded, smooth coatings were obtained. When a furnace atmosphere of argon was used, the coatings were even more uniform in texture and appearance than those fired in air. Therefore, it is preferable, but not essential, to fire these compositions in a non-oxidizing atmosphere. Compositions consisting entirely of fluorides, on the other hand, must be fired in an inert atmosphere; those fired in air were very rough, scaly, and poorly adherent.

The effects of prolonged exposure to air at 1500 F on coatings of ceramics A and B and on a  $\text{BaF}_2$ - $\text{CaF}_2$  coating with no silicate addition are given in Table III. The

It was, therefore, the objective of the research described in this paper to develop high-temperature solid lubricants which provide oxidation protection as well as a lubricating function. The scope of this study encompassed the development of solid lubricant coatings, self-lubricating sintered metal composites, and cast ceramic self-lubricating materials. Oxidation rates were measured by TGA and as a function of composite swell at 1500 F in air. Friction and wear studies were performed over a range of sliding velocities from 250 to 2000 feet per minute and at temperatures from room temperature to 1750 F. Static friction coefficients were also measured in some cases.

### Apparatus

The friction apparatus is shown in Fig. 1. The specimens consist of a rotating disk in sliding contact with a rider having a hemispherical tip with a 3/16-inch radius. The rider slides on a 2-inch diameter track on the flat surface of the disk. Three methods of lubrication were used: (1) solid lubricant coatings were bonded to the disk, (2) a 0.060-inch thick self-lubricating composite layer was bonded to the disks, or (3) the riders were made of cast self-lubricating ceramic compositions.

### Materials and Procedure

#### Coatings

The riders and disks used in the coating studies were made of a nickel-chromium alloy with the composition given in Table I; The compositions of the solid lubricant coatings are also given in Table I.

The ceramic compositions given in Table I were based on the  $\text{CaF}_2$ ,  $\text{Ca}_2\text{SiO}_4$ ,  $\text{CaO}$  ternary system. After a consideration of the phase diagram for this system,<sup>(9)</sup> the composition 70 w/o  $\text{CaF}_2$ , 20 w/o  $\text{Ca}_2\text{SiO}_4$ , 10 w/o  $\text{CaO}$  was chosen as a reasonable starting point for the formulation of silicate-modified fluoride coatings. This composition contains enough  $\text{CaF}_2$  for lubrication and is close enough to the ternary eutectic composition to have about 100 F lower melting point than  $\text{CaF}_2$ . Ceramics A and B of Table I are modifications of the starting composition that were made to further lower the melting point.

In ceramic A,  $\text{LiF}$  was added to give the composition shown in Table I. In ceramic B,  $\text{BaF}_2$ - $\text{CaF}_2$  eutectic was substituted for  $\text{CaF}_2$ .

The ceramic frits used for the coatings were prepared in the following manner: Reagent grade powders were mixed in the proper proportion, melted in nickel crucibles, quenched by pouring onto a stainless steel strip, then ground into a ceramic frit with a -100 mesh (less than 150  $\mu\text{m}$ ) powder particle size.

The powdered ceramic was mixed with water to form a slurry that was sprayed on the metal disks with an air brush. The disks were lightly sandblasted before spraying. The disks were heated to about 160 F before and during spraying to hasten evaporation of the water carrier. The coating material was sprayed to a thickness of  $0.0015 \pm 0.0005$  inch. Coating bond was then achieved by firing the specimens in an air or argon atmosphere to a temperature just above the melting point of the ceramic. Satisfactory firing procedures were 5 minutes at 1750 F for ceramic A and 10 minutes at 1800 F for ceramic B. These times and temperatures are guides. Optimum firing times and temperatures vary with the size of the specimens and the type of furnaces used.

#### Composites

Composites were made by infiltrating sintered nickel-chromium alloys with molten ceramics. The compositions of the porous sintered alloys and the infiltrants or fillers are given in Table II. The sintered metal was of 40 percent theoretical density and was prepared from metal powders in a -150+250 mesh (60 - 100  $\mu\text{m}$ ) particle size range. The sintered material was a 0.060-inch thick powder layer which was bonded during sintering to a 0.060 or 0.50 inch thick dense nickel-chromium alloy backing. The dense metal backing has several advantages: (1) it economizes on the amount of composite material in the part, (2) it provides very superior mechanical strength compared to a part made entirely of porous sintered material, and (3) it provides an easy means of attachment to other parts.

The steps in the infiltration procedure: prepare cold pressed compacts of the filler, place weighed compacts on the sintered surface, then heat the parts in argon to melt the filler material and permit in-

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### Abstract

Recent research at NASA-Lewis on solid lubricants for use at high temperatures in air and other gaseous environments is presented. The characteristics of oxide and fluoride lubricants at temperatures to 1700 F are described. Data is presented for fluoride coatings with silicate and other additives incorporated to give improved wear life and better oxidation protection to the substrate metal. Experience is described for fluoride-metal self-lubricating composites with improved metal oxidation resistance to 1700 F. The concept of cast, self-lubricating ceramics is also explored.

### Introduction

The maximum temperature at which a solid lubricant can be used in an air atmosphere is usually limited by oxidation. Oxidation of the lubricated metal can be beneficial in some cases.<sup>(1,2)</sup> However, oxidation of the solid lubricant is almost always undesirable, especially if the oxidation products are hard and abrasive. The air oxidation of MoS<sub>2</sub> and related materials (dichalcogenides of tungsten, molybdenum, and tantalum) have been measured by thermogravimetric (TGA) techniques.<sup>(3,4)</sup> The oxidation rates of MoS<sub>2</sub> and tungsten disulfide (WS<sub>2</sub>) have also been measured by high-temperature dynamic X-ray diffraction techniques.<sup>(5)</sup> In air, MoS<sub>2</sub> oxidizes rapidly at 750 F and appreciable oxidation can occur with moderate air flow rates across the lubricated surfaces at temperatures as low as 600 F.

In a search for solid lubricants with a higher temperature capability, the chemically stable fluorides of the alkaline earth metals were studied; two of these, calcium fluoride (CaF<sub>2</sub>) and barium fluoride (BaF<sub>2</sub>) appear to be the most promising.<sup>(6)</sup> Conventionally-sprayed coatings of these fluorides were bonded to nickel base alloys by fusing in a controlled atmosphere furn-

ace. Researchers in France have shown that CaF<sub>2</sub> coatings can also be applied to stainless steel by a plasma spray technique.<sup>(7)</sup>

It has been observed that a ceramic, which is used to bond some fluoride coatings to metal substrates, may also provide oxidation-protection to the metal surface. For example, CaF<sub>2</sub> coatings with a cobalt oxide ceramic binder can be bonded to the metal substrate by firing the coatings at 2000 F in an air atmosphere, these coatings are adherent and metal oxidation is not excessive during the firing procedure. Coatings composed only of fluorides, on the other hand, must be fired in a non-oxidizing atmosphere in order to achieve good coating adhesion and to avoid excessive oxidation at the coating/metal interface.<sup>(6)</sup>

Similar considerations may apply to self-lubricating composite materials. The oxidation rate of the metallic components in fluoride-metal composites is a critical factor in their performance. Calcium and barium fluorides themselves are stable but afford no oxidation protection to the powdered metal. The sintered metal, because of its large surface area, oxidizes rapidly at much lower temperatures than the same alloys in the dense wrought or cast forms. For example, some nickel-chromium alloys in the dense form have adequate oxidation resistance to over 1800 F but in the sintered form they have unacceptable high oxidation rates above 1200 F.

Oxidation of sintered metal parts causes swelling and other undesirable distortions. These distortions sooner or later cause a loss of working clearances in bearings. Therefore, although self-lubricating composites have the potential for longer wear life than solid lubricant coatings, they are seriously limited by oxidation to about 1200 F for long durations (1000 hr or more) and to about 1500 F for short durations (100 hr or less).<sup>(8)</sup>