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TRIBOLOGICAL PROPERTIES OF SELF-LUBRICATING FLUORIDE-METAL COMPOSITES TO 900° C (1650° F) - A REVIEW AND SOME NEW DEVELOPMENTS

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ABSTRACT

This paper summarizes the friction and wear behavior of some fluoride-metal, self-lubricating composites. Fluoride-infiltrated sintered nickel alloy composites and plasma-sprayed, co-deposited fluoride-nickel alloy composites are described. The importance of proper surface-conditioning of the composites is stressed. Performance of fluoride-metal composites in some machine application evaluation is discussed.

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INTRODUCTION

This paper reviews and summarizes the performance of some fluoride-metal composites as self-lubricating bearing materials at temperatures to 816° C (1500° F), and in a few examples to 900° C (1650° F). For the most part, the composites described are fluoride-infiltrated, sintered metals which were developed at Lewis Research Center NASA (1). A license has been granted by NASA to a manufacturer for the production and marketing of these materials (2, 3). The infiltrated composites are being evaluated in a number of machine applications, some of which will be discussed in this paper. A few relevant results with plasma-sprayed fluoride-metal composites are also reviewed.

In any lubricating material we want the usual tribological properties of low friction, low wear, and long wear life. However, an even more primary requirement is "survivability" - a material must be chemically and thermally stable in the service environment. Constituents of many environments in which high-temperature bearings are needed, most commonly atmospheric oxygen, are very chemically aggressive at high temperatures. Only a limited number of materials, which might have lubricating ability, are sufficiently stable to even be considered as candidates for use above 400° C (750° F). Among these are many oxides and some fluorides, specifically those of Group I metals (e.g., LiF) and Group II metals (e.g., CaF_2 and BaF_2). Fluorides of rare earth elements (e.g., LaF_2) are also chemically stable, but are not included in the scope of this paper. Stable fluorides are also of interest because they have thermal expansion characteristics that reasonably match those of a number of engineering alloys to which they can be bonded. Also they are relatively soft and non-abrasive to metals, especially at high temperatures. Initially, adherent fused coatings of BaF_2 and CaF_2 were developed for iron, cobalt, and nickel alloys. These coatings were found to have good lubricating properties at high temperatures (4). Subsequently, self-lubricating, fluoride-metal composites were developed (1).

Type of Composite Studied

Composites were prepared by vacuum impregnation of porous metals with molten BaF_2 - CaF_2 eutectic. Upon cooling below the eutectic melting point, 1022° C (1872° F), the composite consists of solid eutectic fluoride distributed uniformly through the pore structure of the metal. More recently, fluoride-metal composite coatings have also been prepared by plasma-spraying (5). The trends in friction and wear of the composites with variations in surface finishing operations (machining, grinding, etc.,) as well as with variation in sliding conditions such as sliding velocity and temperature have been studied. These trends have been found to be similar for infiltrated composites and plasma-sprayed composites and for a number of different nickel-chromium alloys in the composite matrices. Therefore the trends in friction and wear can be reasonably generalized for both preparation procedures and for the family of nickel-chromium alloys. Some of these trends are discussed in the following section.

DISCUSSION

Effect of Surface Finishing Procedures and Sliding Conditions

Figures 1, 2, and 3 are photomicrographs which illustrate the effect of various surface treatments on the fluoride distribution at the surface of an infiltrated composite. Figure 1(a) is a machined surface. Some pockets containing fluorides are evident but considerable metal smearing has covered over some of the fluoride areas. The machined surface can be enriched in fluorides by means of a light acid etch or electroetch which preferentially attacks the metal-chromium alloy (fig. 1(b)). Excessive etching must be avoided to prevent undercutting the fluoride pockets. Further fluoride surface enrichment can be achieved by heat treating the composite in argon or hydrogen for 4 hours at 870° C (1600° F) (fig. 1(c)). Alternatively, a smooth finish and a uniform fluoride-metal distributor can be achieved by wet-sanding the surface with progressively finer grades of waterproof sandpaper. The surface shown in figure 1(d) was finished with a final grade of 600 grit paper.

When the surface shown in figure 1(d) is heat treated for 4 hours at 1600° F, the fluorides migrate across the metallic phase until a fluoride film completely covers the surface of the composite, (fig. 2(a). This is the type of surface that provides the best run-in characteristics during sliding and which is most likely to result in long bearing life. The high fluoride content on the surface of the heat-treated part is easily demonstrated by lightly scraping the surface with a scalpel. In figure 2(b), a line of accumulated fluoride detritus can be seen at the edge of a scraped area.

Figure 3 gives a cross-section through a wear surface on a properly prepared, heat-treated composite. The fluorides and metal are uniformly distributed through the bulk, but the surface is completely covered with a fluoride film about 2×10^{-4} cm thick.

Some recommended, machining, etching, and heat-treatment procedures are given in table I. As indicated in this table, diamond grinding may also be used as an alternative to machining and sanding or to remove tool marks after machining.

Figure 4 gives the friction and wear of an infiltrated composite in air from room temperature to 816° C (1500° F). It is clear that composite wear and the friction coefficient decrease with increasing temperature. Also somewhat lower composite wear and much lower friction coefficients were observed with composites which had a thin overlay of fluoride eutectic compared to those which had not been tested to enrich the surface with fluoride. The data of figure 4 were obtained at a sliding velocity of 10 m/sec (2000 ft/min). The high sliding velocity is favorable to the frictional behavior of the composites. The data of figure 5 from (5), gives friction coefficients as a function of temperature for plasma-sprayed composite coatings at a low average sliding velocity of 1.6 m/sec (320 ft/min). The room temperature value is 0.4 for a correctly prepared surface, but may be as high as 0.55 for the as-machined surface.

Figure 6 shows the highly-glazed surfaces that are characteristic of fluoride composites sliding under favorable conditions. The glaze is entirely non-metallic and consists of fluorides contaminated with varying amounts of metal oxides from the matrix metal. Within limits, oxide contamination has not been found to significantly influence the self-lubricating characteristics of these composites. Oxidation is a problem only when it is severe enough to cause excessive surface roughening, spalling of the fluoride glaze, or unacceptable distortion of the part.

Composition Variables

Most of the early laboratory work with fluoride-metal composites employed nickel-base alloys or the metal matrix. However, some work has been done with stainless steels (6) and cobalt alloys (7). Both have some favorable features. The stainless steels are less expensive than nickel alloys but will probably have lower maximum temperature limitation due to oxidation. Cobalt-molybdenum alloys have been investigated because friction and wear studies of cast cobalt molybdenum alloys demonstrated their superior friction and wear properties in vacuum when compared to nickel alloys or steel. The favorable friction and wear characteristics were attributed to the hexagonal crystal structure of these alloys (8).

Friction and wear studies of sintered cobalt-molybdenum infiltrated with CaF_2 - BaF_2 eutectic indicated the possibility of reduced wear compared to nickel alloy metal matrices (7). Oxidation characteristics at high-temperatures are generally speaking not as good as nickel chromium alloys, but the addition of chromium to the cobalt-molybdenum composition has improved oxidation resistance without changing the desirable hexagonal structure to the less wear-resistant face-centered carbon structure.

Considerations Relevant to the Wear of Fluoride Infiltrated Porous Metals

It is important to understand that self-lubricating properties of a composite are primarily surface-related. It is the condition and the composition of the surface that is the prime determining factor in friction and wear phenomena. The bulk composition is important in regard to deformation characteristics and in acting as a lubricant reservoir, but the most carefully formulated and engineered composite bearing material is only as good as its surface.

In a self-lubricating composite with a metallic component, the metal generally serves some function other than providing the desirable tribological properties of low wear and low friction. Most generally the function of the metal is to provide desirable mechanical and physical properties such as mechanical strength, a suitable thermal expansion coefficient and thermal conductivity. The non-metallic filler provides the lubricating function and at times oxidation-protection. The implication here is that the metal constituent is needed throughout the bulk of the composite in order to serve its function but is not desirable at the sliding surface. The lubricating material is needed at the surface and within the bulk only as a reserve supply of lubricant which resupplies the surface as wear takes place.

From these considerations and from experimental evidence, it is clear that the finishing operations on composite materials are very important. Every effort should be made to avoid smearing the metal over the surface (metal surface enrichment). On the other hand, operations which enrich the surface with the non-metallic components of the composite, are highly desirable.

Manufacturing and Applications

Fluoride-metal composites have been produced in many shapes and sizes. They can be produced by sintering and infiltration in bulk form or in parts close to their final dimensions. Parts are finished by machining and surface conditioning treatments. Some parts are shown in figure 7. The very thin rings are especially illustrative of the non-brittle, elastic nature of these composites. (They can be flexed considerably without damage - an unusual characteristic in self-lubricating, high-temperature composites.

Some applications for which fluoride-metal composites are being evaluated are:

(1) Vuilleumier Helium Refrigerator, Displacer positioning rings (9, 10)

The Vuilleumier (VM) machine is based upon a modified Sterling cycle and is used to cool helium gas to as low as 11° K. The machine is used in cooling systems on board aircraft and space vehicles. A piston-like displacer at the hot end of the machine operates in helium at 650° C (1200° F). This displacer is positioned by "hot rider rings." The BaF_2 - CaF_2/nichrome composites are in an advanced stage of testing as the material for these rings.

Some early failures with these rings led to an investigation at Hughes Aircraft that verified the importance of proper surface treatments to achieve the necessary fluoride enrichment (10). Suitably, treated rings have now accumulated over 2000 hours of succesful operation in the VM refrigerator. The tests have involved repeated room temperature starts and brief periods of room temperature operation followed by heating and long duration sliding at 650° C (1200° F) in a cryogenic refrigerator designed to operate for long durations in space.

(2) Regenerator Seals for Automotive Turbines

Major automobile manufacturers are evaluating fluoride-metal composites for possible use as sliding contact seals on porous-ceramic and on metal-honeycomb rotating heat exchangers. The wear rates of the composites have been excessive when sliding against porous ceramics, but results have been quite promising for sliding against metal honeycomb at temperatures to 816° C (1500° F). In some cases, special glasses were incorporated into the composites. It is known that some glasses can be used for oxidation protective coating for metals (5, 11, 12). In this application, the use of sintered cobalt-molybdenum or cobalt-molybdenum-chromium alloys as the matrix material for the composites has resulted in composites that are more wear-resistant than those employing nichrome.

(3) Apex Seals for Rotary Engines

A major automobile manufacturer is evaluating fluoride-nichrome composites as the apex seal material for rotary engines. Preliminary testing in a state-of-the-art engine is encouraging. However, the most interesting consideration is the potential usefulness of this composite in advanced engines in which the seal will operate at higher temperatures - temperatures which are too high for some of the currently-used apex seal materials.

CONCLUDING REMARKS

The fluoride-metal composites, which have been described in this presentation, were developed in a basic materials research program. They are now being evaluated for a number of applications.

The laboratory evaluations included friction and wear studies to 900° C (1650° F) with a pin-on disk wear test machine. While numerical data are not generally available for results in machine applications, the materials have performed well or poorly in application in a manner quite predictable from the results of laboratory studies. This is especially true in regard to the effects of proper surface conditioning and of temperature on friction and wear. However, wear was sensitive to details of component design. For example, wear rates in sliding contact bearings and seals are influenced by wear debris and clearances in a manner that must be evaluated for the particular machine component under consideration.

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TABLE I. - FINISHING PROCEDURES FOR COMPOSITES OF

NICKEL-CHROMIUM ALLOYS AND CaF_2 - BaF_2

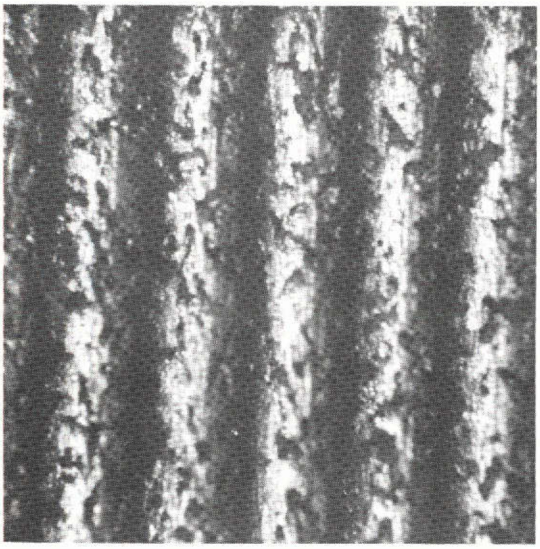
A. Recommended Machining Practice
   (1) Machine dry
   (2) Use a single-point carbide tool
   (3) Machine at a low speed of 9-12 m/min (30-40 fpm)
   (4) Remove no more than 0.010 cm (0.004 in.) per cut

B. Abrasive Finishing
   (1) Wet sand through four progressively finer papers 150 grit to 600 grit

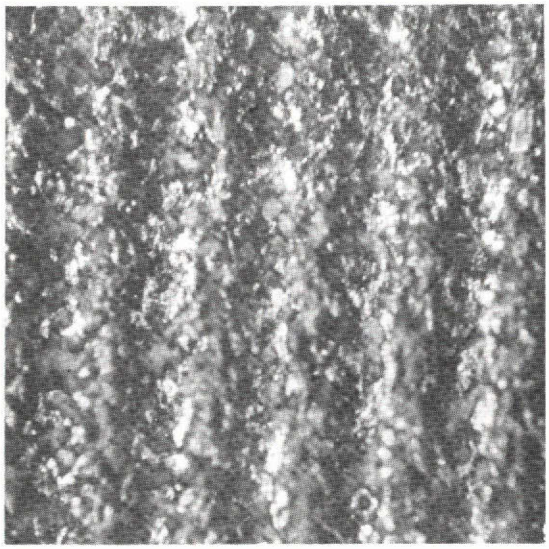
C. Alternate to A and B or following A
   (1) Grind with a diamond wheel. (Use light cuts to avoid metal smearing.)

D. Etching (optional)
   (1) 30 sec, 60° C in 92 v/oHCl - 5 v/oH_2SO_4 - 3 v/oHNO_3

E. Heat Treatments (optional but recommended)
   (1) 30 min. 816° C (1500° F) in air for air applications to 650° C (1200° F) max.
   (2) 4 hours 870° C (1600° F) in argon for applications in non-oxidizing atmospheres to 816° C (1500° F) max.



(a) Machined.



(b) Surface (a). Acid etched to remove smeared metal.

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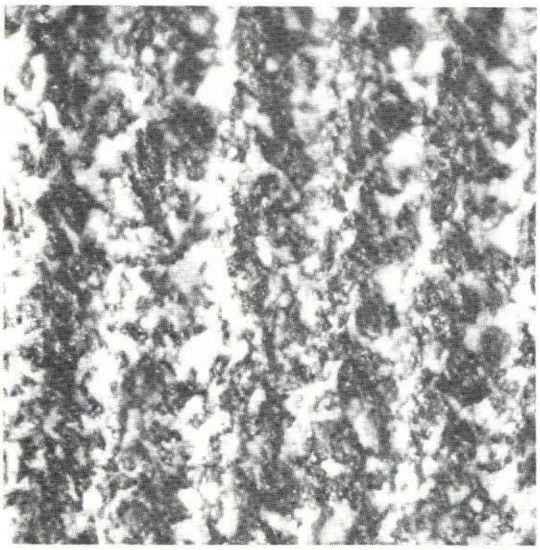
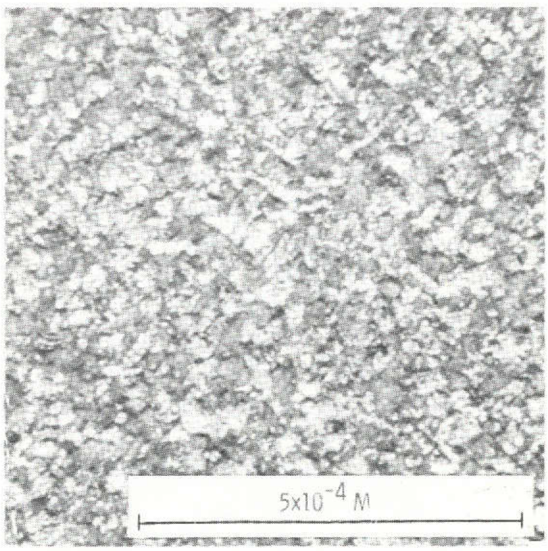


(c) Surface (b). Heat-treated 4 hours at 870° C (1600° F) in Argon.



(d) Surface (a). Wet-sanded to remove machining marks (uniform fluoride-metal distribution).

Figure 1. - Effect of surface treatments on topography of composites. Oblique illumination; X100.

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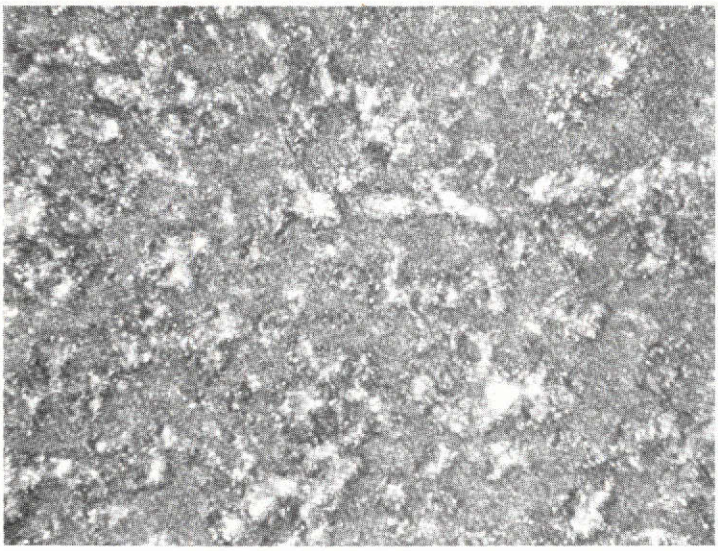
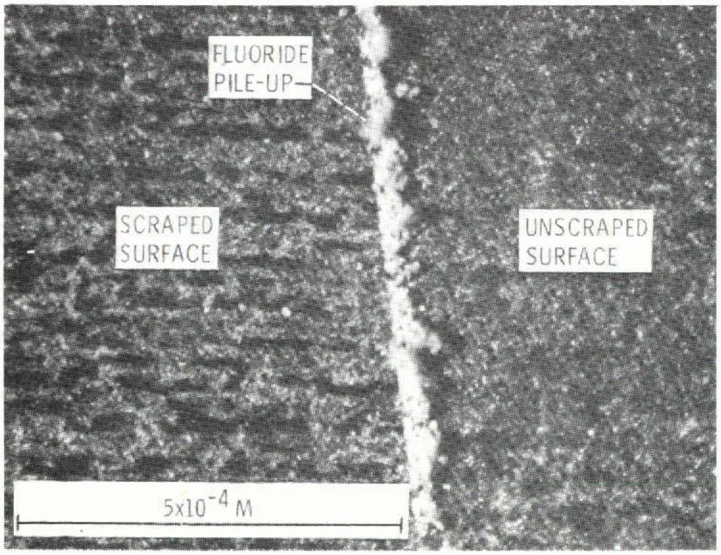


(a) HEAT TREATED 4 HOURS AT 870° C (1600° F).



(b) HEAT TREATED SURFACE SCRAPED (LEFT TO RIGHT) TO SHOW HIGH FLUORIDE CONTENT OF SURFACE.

Figure 2. - Heat-treated composite surfaces. Oblique illumination; X100.

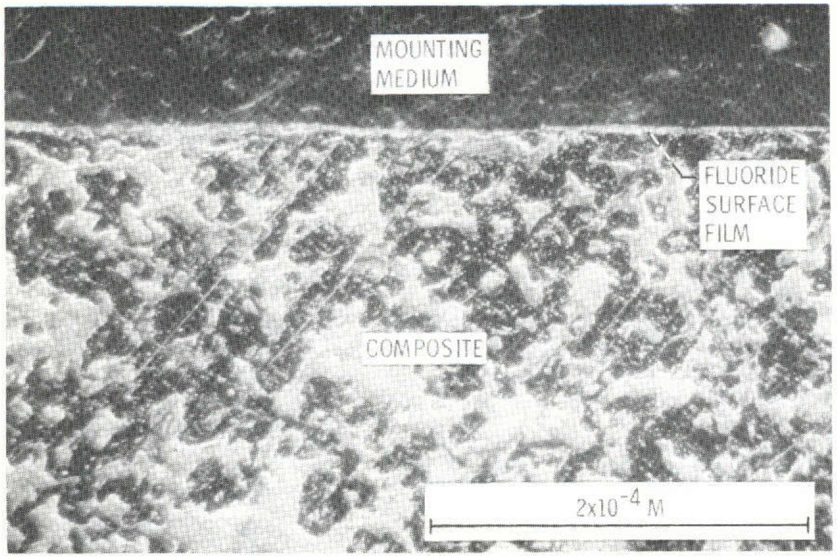


Figure 3. - Cross section of composite with fluoride surface-enrichment. White area: BaF_2 - CaF_2 eutectic; dark areas: Nichrome; oblique illumination; X250.

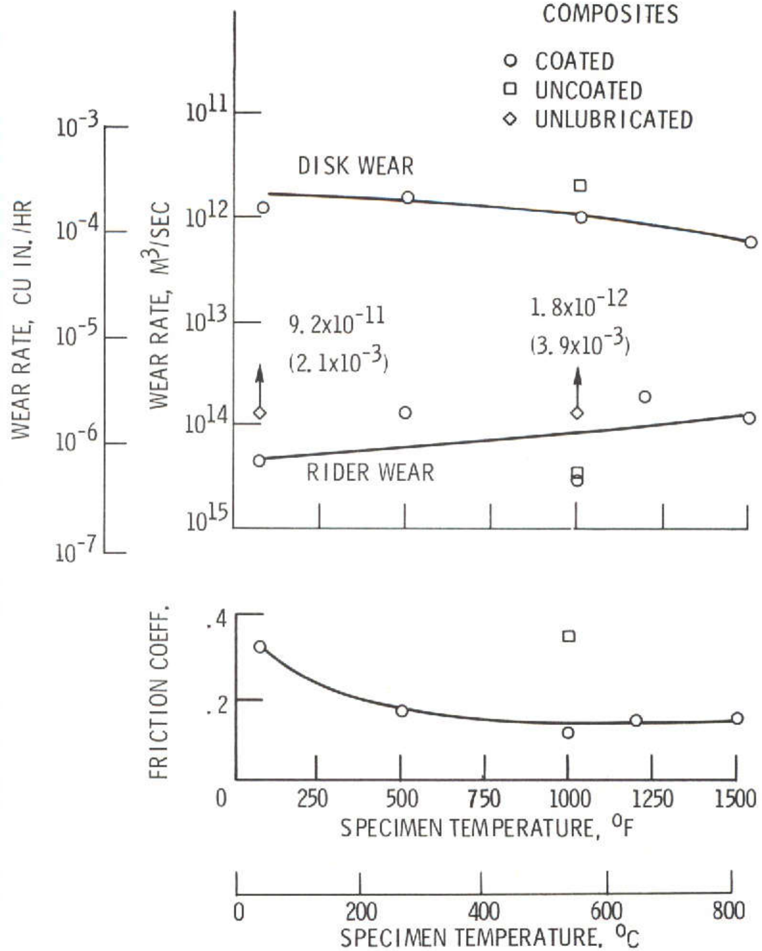


Figure 4. - Friction and wear of fluoride-infiltrated sintered Inconel composites and cast Inconel pins. 500-gm load, 10 m/sec.

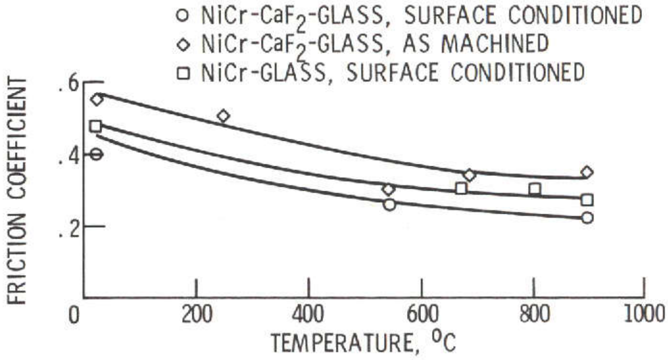


Figure 5. - Friction of some plasma-sprayed composites in pin on disk experiments. 1 kg load; 1.6 m/sec.

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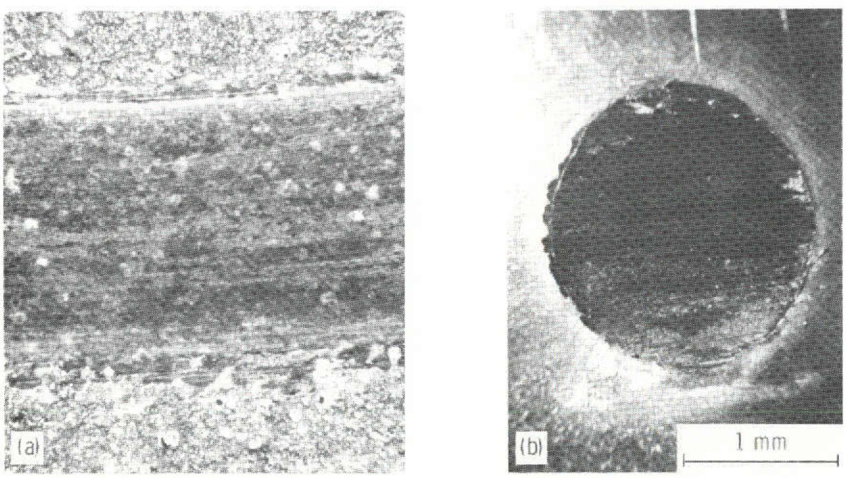

Figure 6. - Photomicrographs of sliding surfaces on (a) plasma-sprayed composite, (b) René 41 pin. Load, 1 Kg; 1.6 M/sec; room temperature to 900° C.

Figure 7. - Some parts that can be made from fluoride-metal composites.

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