N92-22516

SELF-LUBRICATING COATINGS FOR HIGH-TEMPERATURE APPLICATIONS

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SUMMARY

Solid lubricants with maximum temperature capabilities of about 1100 °C are known. Unfortunately, none of the solid lubricants with the highest temperature capabilities are effective below about 400 °C. However, research at Lewis shows that silver and stable fluorides such as calcium and barium fluorides act synergistically to provide lubrication from below room temperature to about 900 °C. This paper describes plasma-sprayed composite coatings that contain these solid lubricants in combination with a metal-bonded chromium carbide. The lubricants control friction, and the carbide matrix provides wear resistance. Successful tests of these coatings as backup lubricants for compliant gas bearings in turbomachinery and as self-lubricating cylinder liners in a four-cylinder Stirling engine are discussed.

INTRODUCTION

Some present-day aeropropulsion systems already impose severe demands on the thermal and oxidative stability of lubricant, bearing, and seal materials. These demands will be much more severe for systems planned to be operational around the turn of the century. The complex gas turbine engines in modern aircraft contain many variable geometry components with load-bearing surfaces that must be self-lubricating at high temperatures and gas pressures. In hypersonic aircraft of the future, the propulsion systems will also incorporate variable-angle air inlet ramps that will need seal surfaces with the ability to slide with low friction and wear at very high temperatures. In addition, the airframe control surface bearings may see high temperatures and certainly will need to be protected by sliding-contact control surface seals that will be the first line of defense against the temperatures generated by aerodynamic heating at hypersonic velocities.

Conventional solid lubricants such as graphite and molybdenum disulfide (MoS_2) are a class of materials with a layer lattice crystal structure which is ideal for providing the low shear strength associated with low friction. However, these lubricants have very limited high-temperature oxidation resistance. Both graphite and MoS_2 oxidize in air well below 500 °C. Therefore, it is necessary to creatively screen other classes of candidate materials for chemical and physical properties that are likely to afford the necessary combination of chemical stability and lubricity.

A class of materials that possess this combination of properties consists of the fluorides of the alkali metals, especially lithium fluoride (LiF), and the fluorides of the alkaline earth metals, especially barium fluoride (BaF_2)

and calcium fluoride (CaF_2). These compounds are lubricious above their brittle-to-ductile transition temperatures (typically about 500 °C) to just below their melting points, which are LiF, 870 °C; BaF_2, 1280 °C; and CaF_2, 1410 °C. Unfortunately, these compounds do not lubricate below their brittle-to-ductile transition temperatures. However, our research shows that a combination of silver (Ag), which is lubricious as a thin film below 500 °C, with the BaF_2/CaF_2 eutectic acts synergistically to provide lubrication from below room temperature to 900 °C (ref. 1).

This paper describes plasma-sprayed composite coatings that contain these solid lubricants in combination with a Nichrome matrix or with a metal-bonded chromium carbide. Successful tests of these coatings as seal material, as backup lubricants for compliant gas bearings in turbomachinery, and as self-lubricating cylinder liners in a four-cylinder Stirling engine are discussed.

MATERIAL PROPERTIES CONSIDERATIONS

There is clearly a need for high-temperature lubricants in many advanced terrestrial and aerospace applications where the high temperature often precludes the use of conventional liquid lubrication. Figure 1 lists examples of some of these application areas and the associated bearing and seal temperatures.

Conventional solid lubricants such as molybdenum disulfide (MoS_2) and graphite have limited high-temperature capability because they oxidize in air at temperatures below 500 °C. The effect of oxidation on the friction coefficient of MoS_2 is illustrated in figure 2. The sharp rise in the friction coefficient of molybdenum disulfide as the temperature is increased above about 350 °C is caused by oxidation of the solid lubricant to solid molybdenum trioxide and gaseous sulfur oxides. It is therefore clear that a primary criterion for the survivability of high-temperature materials is thermochemical stability. Some physical properties of importance involve the hardness and ductility or plasticity of the candidate material. Properties that effective solid lubricants have in common are the following: (1) they are soft, (2) they have a high degree of plasticity (the plasticity must be associated with a low yield strength in shear for lubricity), and (3) they must exhibit adequate adhesion to the lubricated surfaces. (Obviously, no matter how desirable the other properties of a solid are, that material cannot lubricate if it is not retained at the sliding interface.)

We have used calcium fluoride, barium fluoride, and silver as solid lubricants in our high-temperature coatings. They satisfy all of the above criteria over specific ranges of temperatures. Thermochemical calculations indicate that these materials should be chemically stable to high temperatures in air or in hydrogen, and this has been experimentally verified. The hardness-temperature characteristics of these two fluorides and of metallic silver are given in figure 3(a) from reference 2. Silver is very soft at room temperature with a hardness of about 30 kg/mm^2, and this continuously decreases to about 4 kg/mm^2 at 800 °C. Thin films of silver lubricate quite well at temperatures up to about 500 °C, but appear to have inadequate film strength to support a load at higher temperatures. The fluorides, on the other hand, are considerably harder than silver at the lower temperatures, but their hardness drops off rapidly with temperature, and at about 400 °C, their hardness is 30 kg/mm^2 or less. Also, brittle-to-ductile transition temperatures, at high strain rates, of 300 to 400 °C have been reported for these fluorides (refs. 3 to 5). Since fluoride coatings have been shown to become lubricious at about 400 °C, but ineffective as lubricants at lower temperatures (ref. 1), there is an apparent correlation of hardness-temperature characteristics and of the brittle-to-ductile transition temperature with the friction-temperature characteristics.

Because silver films are lubricative at the lower temperatures and the fluorides discussed are lubricative at higher temperatures than silver, it is reasonable that a composite coating containing silver and the fluorides might be lubricious over a wide temperature range, and this has been demonstrated repeatedly in our research (refs. 1 and 6). Figure 3(b) from reference 1 illustrates this point. The friction-temperature characteristics of 0.02-mm-thick, fused fluoride coatings with and without silver, which were prepared by a process similar to porcelain enameling, are compared. The all-fluoride coatings were lubricous only above about 400 °C, while the coatings that also contained silver lubricated from room temperature to 900 °C. These results with relatively thin coatings led to research with plasma-sprayed coatings.

PLASMA-SPRAYED COATINGS

Researchers at Lewis have reported two series of plasma-sprayed coatings containing fluoride solid lubricant: the PS100 and the PS200 series (refs. 6 and 7). The first series contains stable fluorides and silver with a Nichrome binder; the second series contains the same lubricants and chromium carbide with a nickel-cobalt alloy binder. The proportions of the components can be varied to optimize the coatings for various uses. In general, the PS100 series, which is softer, has been useful in applications where a slightly compliant, but nongalling coating is needed. The friction and wear properties of PS100 and PS101 are illustrated in figure 4. The PS100 composition, which contained calcium fluoride as the only lubricant, lubricated above about 400 °C, but not at lower temperatures. The transition from high to low friction and wear corresponded to the brittle-to-ductile transition temperature of calcium fluoride at high shear rates. The addition of silver as the second lubricant in PS101 resulted in a coating with good lubricating properties from -60 to 900 °C. The Nichrome-based coatings exhibited moderate ductility. This property and their good lubricating properties have led to their application in high-temperature, lightly loaded shaft seals. An example of this type of application is the shaft seal shown in figure 5 from reference 8. Wear coefficients k for the PS100 series of coatings are on the order of 10^{-5} mm^3/Nm, and the friction coefficient is typically 0.2.

When more wear-resistant coatings are needed, the PS200 series is preferable. The PS200 concept is summarized in figure 6. As the sketch indicates, the coating is a composite material with the lubricating solids distributed throughout a very wear-resistant chromium carbide/nickel alloy matrix. The solid lubricant content can be optimized for a particular set of operating conditions. A typical composition consists of 10 wt % each of silver and calcium fluoride/barium fluoride eutectic in the metal-bonded chromium carbide matrix. Results of friction and wear tests and applications of this coating are given in the following section. Wear coefficients are about one-tenth those of PS100.

APPLICATION TESTS OF PS200 GAS BEARINGS

Figure 7 is a gas bearing journal coated with PS200 and finished by diamond grinding. Start-stop tests of this journal in a foil bearing were conducted by using the test apparatus shown in figure 8 and reported in references 9 and 10. Torque profiles during start-stop cycles show that the highest torque occurs at the beginning and end of each cycle when the surface velocity is below the critical lift-off velocity for the bearing and the journal is in sliding contact with the bearing foils. Foil bearings with PS200 coated journals have routinely survived durability tests consisting of 9000 starts and stops (18 000 rubs) at preprogrammed bearing temperatures from 25 to 650 °C, and have not failed in long duration life tests of up to 30 000 start/stop cycles. Therefore, the bearing life is determined by the number of start/stop cycles it can survive before the lubricant coating fails or excessive foil wear occurs.

Typical wear data for Inconel X-750 bearing foils are given in figure 9. Data are compared for foils run against a journal coated with PS200 and one coated with metal-bonded chromium carbide with no solid lubricant additions. The foils run against the unmodified coating were worn excessively after 3000 start/stop cycles, while those run against PS200 easily survived a specified 9000 start/stops. The initial run-in wear rate against PS200 levels off to a very low steady-state value, thus providing much longer bearing life than could be predicted by a linear extrapolation of the wear rate during run-in.

STIRLING ENGINE CYLINDER LINER

PS200 was evaluated as a cylinder liner coating for an automobile Stirling engine. This was part of the DOE/NASA Automotive Stirling Engine Project. The lubrication of the piston ring/cylinder contacts in the Stirling engine is a challenging high-temperature tribological problem. Metal temperatures are as high as 600 to 1000 °C near the top of the cylinder walls. The working fluid in the engine thermodynamic cycle is hydrogen. The lubricant coating, therefore, must not only provide low friction and wear, but also must be thermochemically stable in a strongly reducing hydrogen atmosphere. Friction measurement, employing a pin-on-disk wear test machine, showed that a cobalt alloy, Stellite 6B, is a good counterface material in sliding contact with PS200. The friction coefficients for 6B on PS200 in helium and in hydrogen are summarized in figure 10. Friction coefficients were typically 0.2 in hydrogen from room temperature to 760 °C and considerably lower than measured for a baseline chromium carbide coating with no solid lubricant additions.

In current designs of the Stirling engine, the piston rings are made of reinforced polytetrafluoroethylene (PTFE). They are located in ring grooves near the bottom of the piston where the temperatures are relatively low and do not degrade the PTFE. This arrangement results in a long, annular gap from the top of the piston to the piston ring. This gap, known as the appendix gap, is the source of parasitic energy losses (ref. 11). It therefore would be desirable to minimize the appendix gap by locating the top ring in a groove near the top of the piston. A schematic of the ring locations in the baseline piston and in a piston with an added Stellite 6B hot ring are shown in figure 11.

A four-cylinder automotive Stirling engine was used in an engine test reported in reference 12 (fig. 12). The cylinders were bored out to allow for a PS200 coating thickness of 0.25 mm (0.010 in), and the pistons were modified to accept the hot piston rings. The coatings were sprayed on the cylinder walls to a thickness of about 0.35 mm (0.015 in), then were diamond ground to a final thickness of 0.25 mm. Engine tests were run at 700 °C heater head temperature and 5, 10, and 15 MPa mean operating pressures over a range of operating speeds. Tests were run both with the hot rings in place and without them to provide a baseline for comparison. At some operating conditions, efficiency as indicated by specific fuel consumption increased up to 7 percent compared to the baseline engine. Under other conditions, no significant differences in efficiency were measured. The overall average indicated about a 3-percent increase in efficiency with the hot rings over the baseline configuration. This increase was over and above the friction loss introduced by the hot rings. Seal leakage measurements showed a significant reduction in leakage with the hot ring in place. In addition, cylinder wall temperature measurements indicated less cylinder heating in the appendix gap area between the lower piston rings and the hot ring. Approximately 22 hr of ring-on-coating operation was recorded. After the initial break-in period, ring and coating wear were low. Although this application test involved an automobile engine, the results of this program are relevant to sliding contact seals and bearings in aeropropulsion systems. The results are especially relevant to the hydrogen-fueled engine being considered for hypersonic aircraft of the future.

CONCLUDING REMARKS

This paper reviews some of the tribological research at NASA Lewis Research Center that is relevant to the lubrication of high-temperature aeropropulsion sliding contact bearings and seals with solid lubricants. The most significant conclusions are

1. Certain materials properties can be used to establish a qualitative model for predicting whether or not a chemical element or compound is likely to have solid lubrication capability within a given temperature range. The required properties are plasticity, low yield strength in shear, low hardness, and thermochemical stability at the temperatures and in the environment of interest.

2. For solid materials that lubricate only at elevated temperatures, the onset of lubrication appears to correlate with their brittle-to-ductile transition temperatures.

3. Some combinations of two or more solid lubricants, each with different temperature capabilities, can be incorporated into composites with a broader temperature capability than that of any single solid lubricant.

A recently developed coating employing this concept is PS200. This is a plasma-sprayed composite coating in which silver and barium fluoride/calcium fluoride eutectic are dispersed throughout a matrix of metal-bonded chromium carbide. Silver alone is lubricative to about 500 °C, while the fluorides are lubricative from 400 to 900 °C. The combination in this coating lubricates from room temperature to 900 °C.

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CURRENT AND FUTURE NEEDS FOR HIGH-TEMPERATURE SOLID LUBRICANTS	TEMPERATURE, °C
• AIRCRAFT GAS TURBINE ENGINES	
VARIABLE STATOR-VANE BUSHINGS	
COMPRESSORS—CURRENT	350
TURBINES—NEAR FUTURE	1000
THRUST-REVERSAL BEARINGS	800
• SUPERSONIC AIRCRAFT (MACH 3-5)	
CONTROL-SURFACE BEARINGS	350
CONTROL-SURFACE RUB SEALS	650
• HYPERSONIC AIRCRAFT	
CONTROL-SURFACE RUB SEALS	500-2000
• ROTARY ENGINES FOR GENERAL AVIATION	
APEX SEALS	300-650
• ADIABATIC DIESEL CYLINDER LINERS	600-1100
• STIRLING ENGINES	760-1100
• AUTOMOTIVE GAS TURBINE ENGINES	
REGENERATOR WEAR FACE SEALS	260-1100
FOIL BEARINGS (MAIN SHAFT)	650

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Figure 1. - Applications for high-temperature solid lubricants.

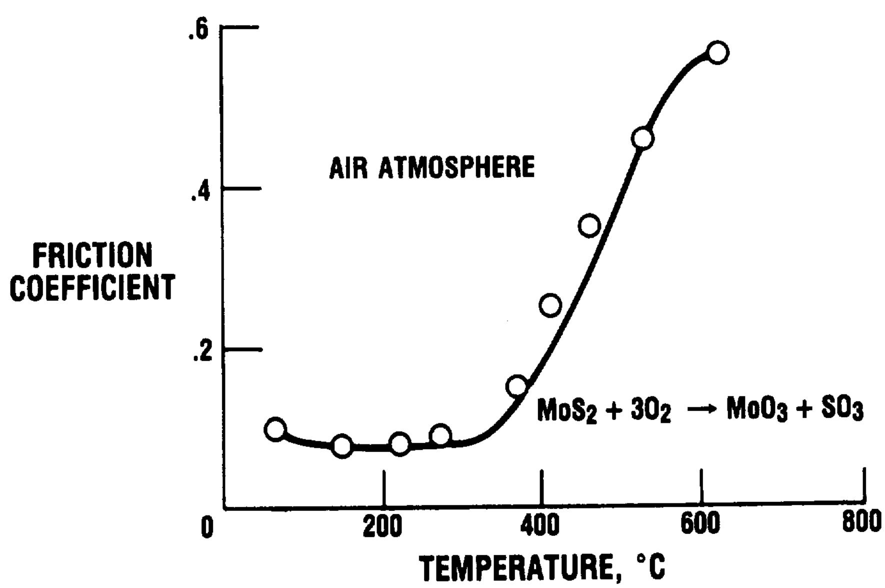

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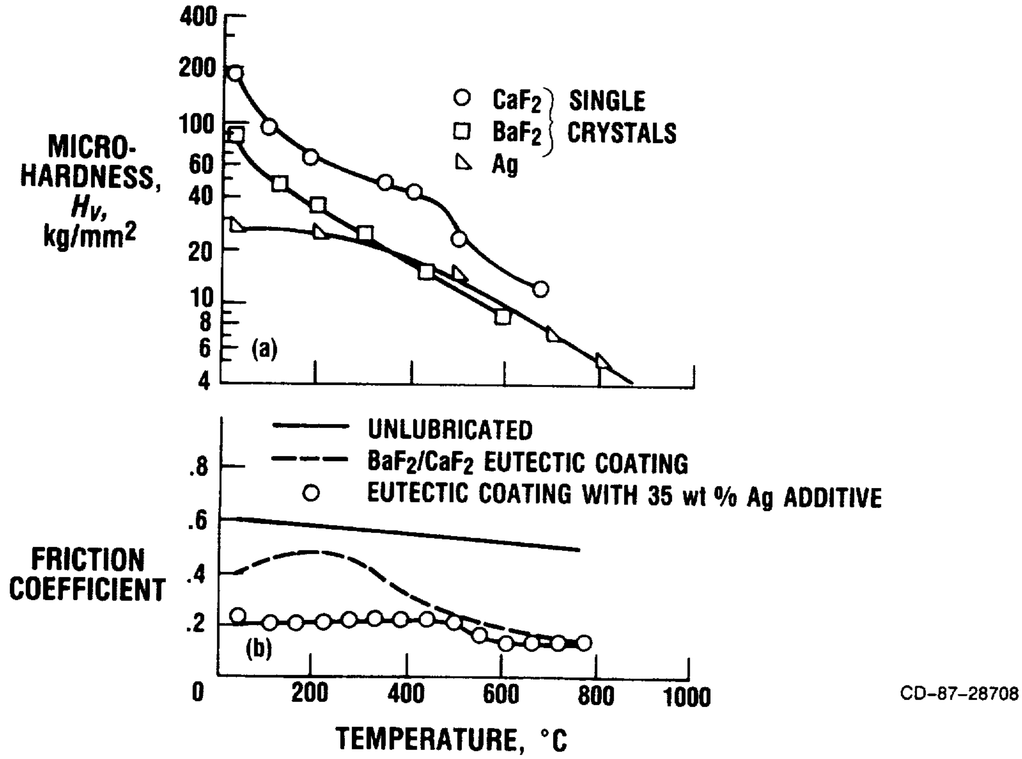
Figure 2. - Effect of oxidation on lubrication with molybdenum disulfide.



(a) Microhardness.
(b) Friction coefficient.

Figure 3. - Effect of temperature on microhardness and friction coefficients of coating materials.

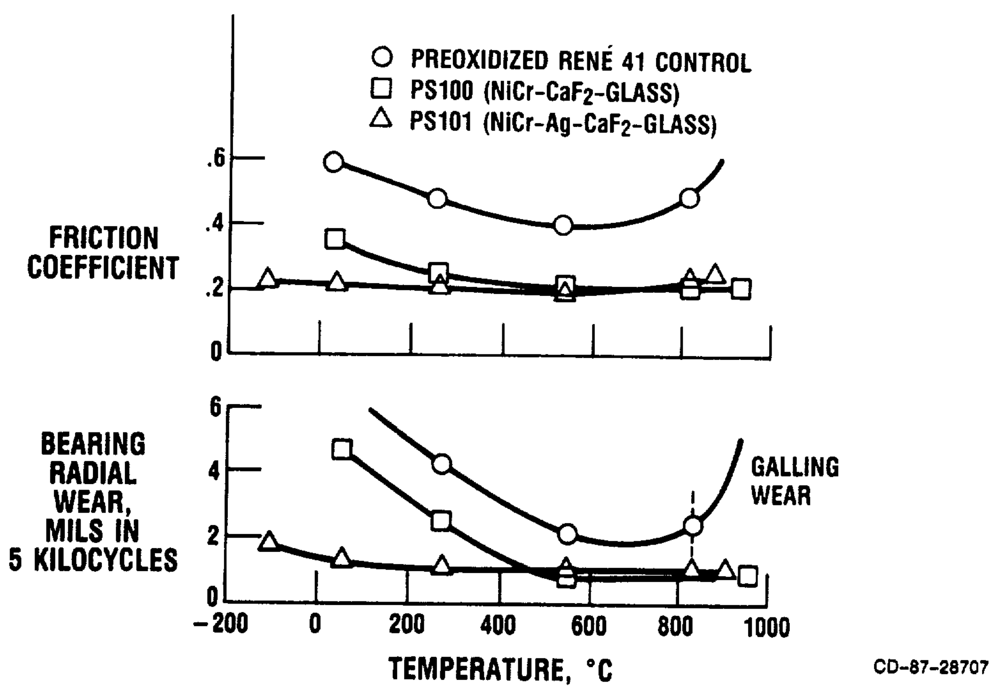


Figure 4. - Plasma-sprayed coatings for self-aligning oscillating bearings (34-MPa radial load).

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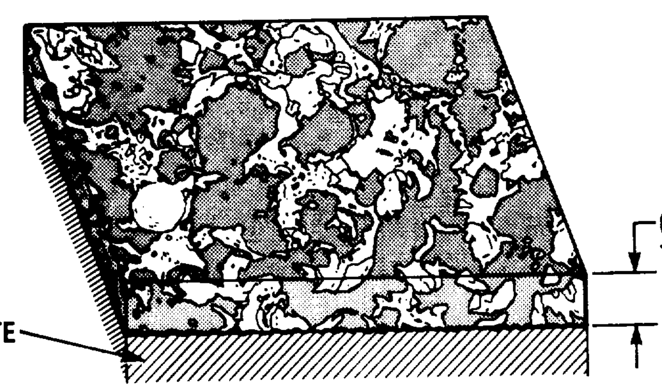
Figure 5. - Compressor/turbine shaft seal operates at 650 °C.



COMPOSITION	FUNCTION
32% Ni ALLOY 48% Cr_3C_2	WEAR AND OXIDATION RESISTANCE
10% Ag	LOW-TEMPERATURE LUBRICATION
10% BaF_2/CaF_2 EUTECTIC	HIGH-TEMPERATURE LUBRICATION

• LUBRICATES IN AIR, HELIUM, OR HYDROGEN TO −900 °C

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Figure 6. - The concept of PS200 - a plasma-sprayed composite solid lubricant coating.

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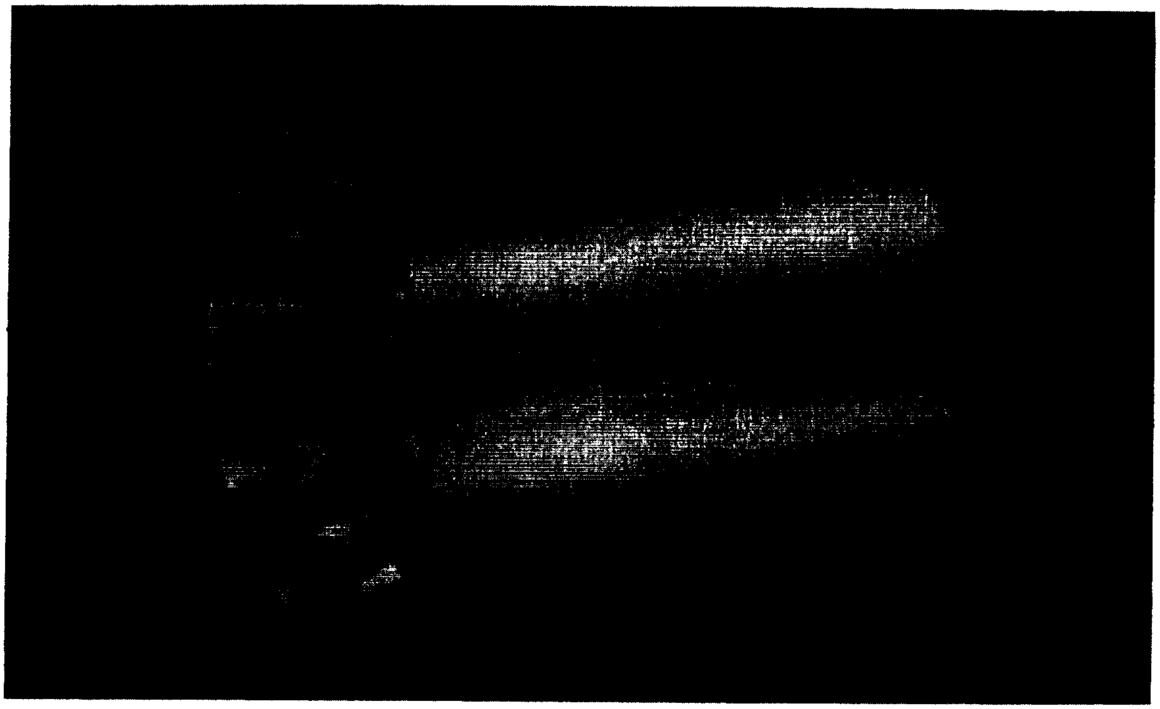

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Figure 7. - Gas bearing journal coated with PS200 and finished by diamond grinding.

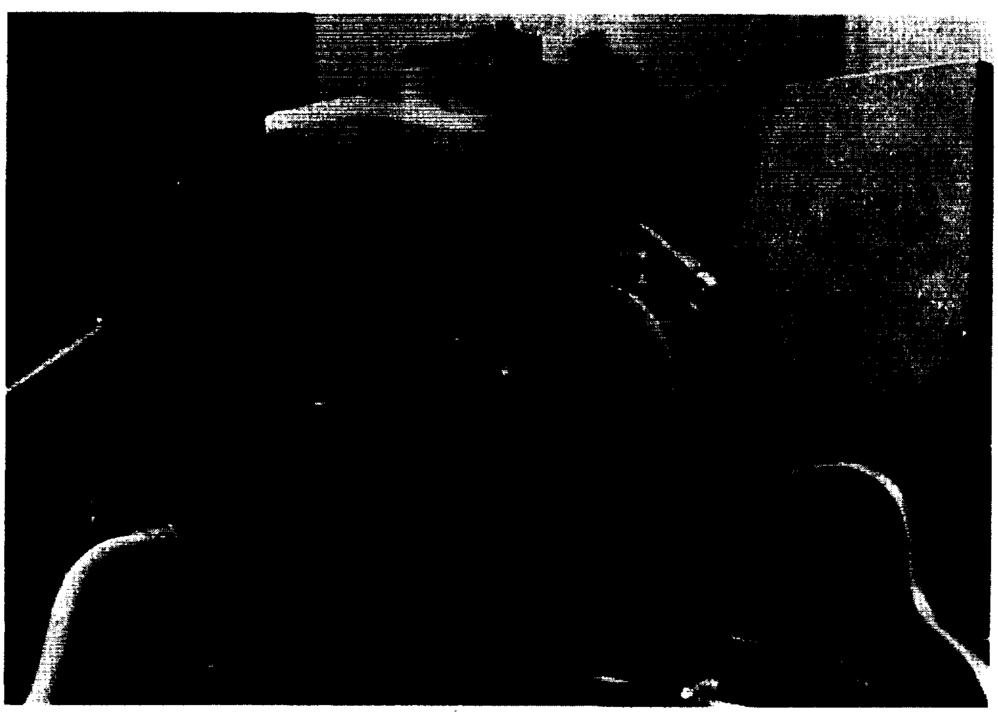

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Figure 8. - Foil bearing under test at 700 °C.

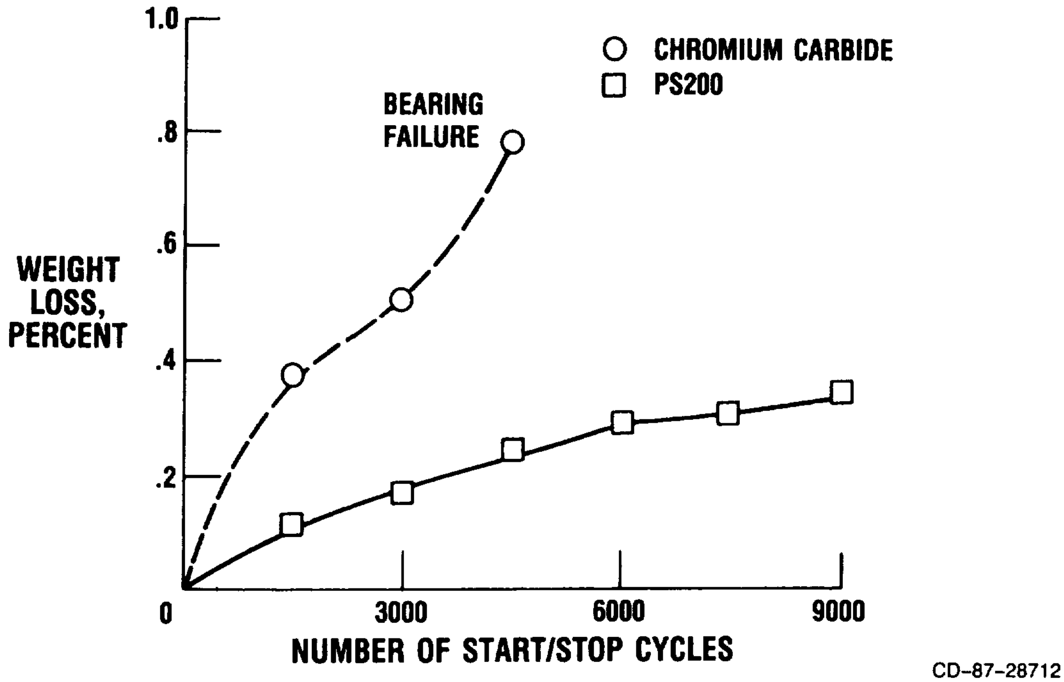

Figure 9. - Wear profiles of preoxidized Inconel X-750 foil bearings run against journals lubricated with plasma-sprayed chromium carbide or PS200.

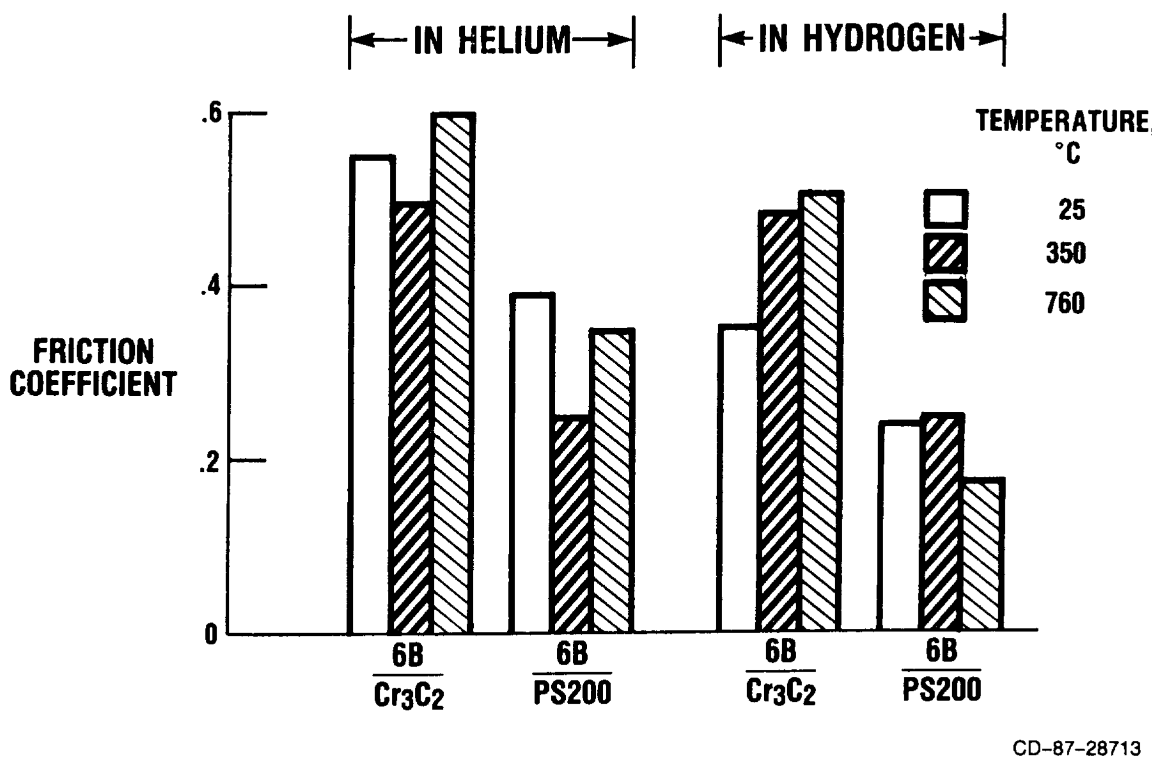

Figure 10. - Bonded chromium carbide and PS200 in Stirling engine atmospheres.

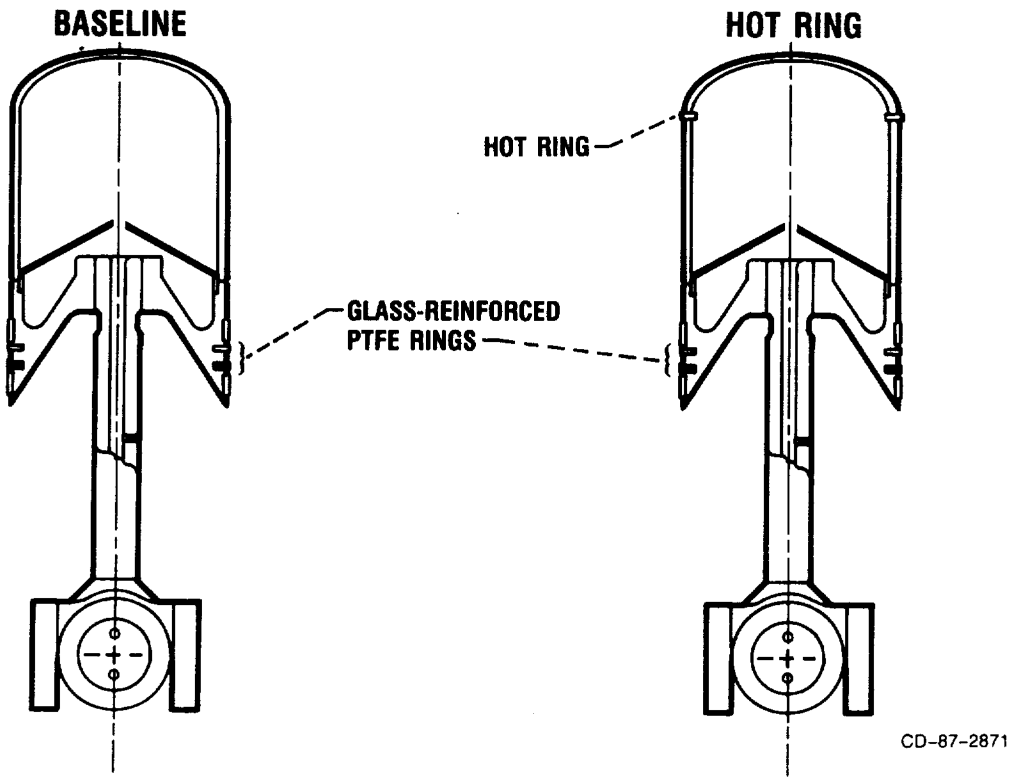

Figure 11. - Application example: Stirling engine hot piston ring tests.

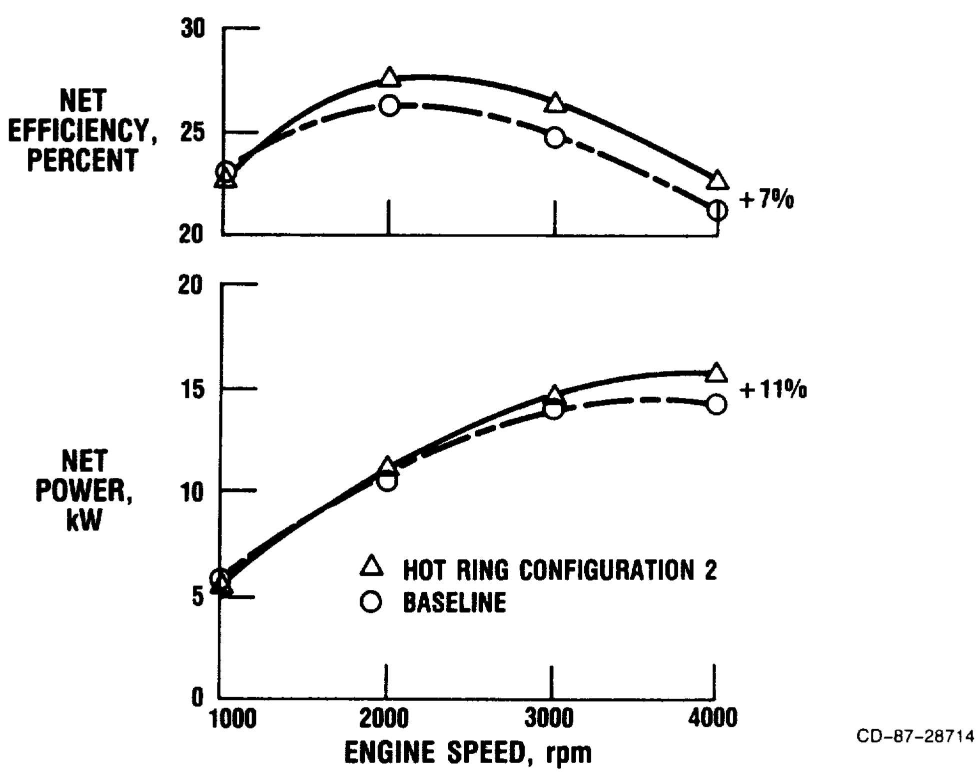

Figure 12. - Results of hot piston ring tests.