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A NEW CHROMIUM CARBIDE-BASED TRIBOLOGICAL COATINGS FOR USE TO 900 °C WITH PARTICULAR REFERENCE TO THE STIRLING ENGINE

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ABSTRACT

A new chromium carbide-based coating (PS 200) is described. This coating is shown to have good friction and wear properties over a wide temperature range. A nickel alloy-bonded chromium carbide coating was used as a baseline material for comparison with experimental formulated coatings. Coatings were plasma sprayed onto metal disks, then diamond ground to a thickness of 0.025 cm. Friction and wear were determined using a pin on disk tribometer at temperatures from 25 to 900 °C in hydrogen, helium, and air. Pin materials included several metallic alloys and silicon carbide.

It was found that appropriate additions of metallic silver and of barium fluoride/calcium fluoride eutectic to the baseline carbide composition significantly reduced friction coefficients while preserving, and in some cases, even enhancing wear resistance. The results of this study demonstrate that PS 200 is a promising coating composition to consider for high temperature aerospace and advanced heat engine applications. The excellent results in hydrogen make this coating of particular interest for use in the Stirling engine.

INTRODUCTION

The lubrication of the piston ring/cylinder contacts in the Stirling engine is a challenging, high temperature tribological problem. Metal temperatures as high as 600 to 1000 °C are anticipated near the top dead center area of the cylinder walls. The working gas in the thermodynamic cycle under consideration is either helium or hydrogen. The lubricant coating therefore, must not only provide low friction and wear, but must also be thermochemically stable at high temperatures, especially in the strongly reducing hydrogen atmosphere.

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 top of the piston ring. This gap is known as the "appendix gap" and it is the source of parasitic energy losses that are caused by: 1) shuttling heat from the hot end of the cylinder to the cold end by the motion of the piston; and 2) pumping losses associated with repeated compression and expansion of the gas in the appendix gap.[1] It would therefore be advantageous to minimize the volume of the appendix gap by locating the piston ring in a groove near the top of the piston. Thus, an objective of this program was to provide a piston ring/cylinder coating combination that would be self lubricating in hot hydrogen. A specially-designed piston using a "hot ring" is shown in Fig. 1 from Ref. 1.

Previous research had demonstrated the lubricating properties of plasma sprayed coatings consisting of a nichrome matrix with additives of silver and calcium fluoride.[2] These coatings are self lubricating from cryogenic temperatures to 900 °C with friction coefficients of 0.20±0.05. Wear rates are acceptable for low speed applications, but would be too high for high speed applications with the long life requirements of engine components. Therefore a goal of this program was to formulate self lubricating, high temperature coatings with superior wear resistance. Certain hard materials such as chromium oxide, silicon carbide, cubic boron nitride, and chromium carbide can be considered for wear control at high temperature, but they are not self lubricating because of their usually high friction coefficients and because they can be abrasive. However, it is possible to add solid lubricants to bonded carbide coating compositions to achieve truly self lubricating materials. In Ref. 3 we reported preliminary data that disclosed the composition of a new chromium carbide-based coating, PS 200, which contains the solid lubricant additives: metallic silver and barium fluoride/calcium fluoride eutectic. The effectiveness of this coating as a back-up lubricant for high temperature gas bearings operating at high temperature in an air atmosphere was reported in Ref. 4.

Chromium carbide was selected as the wear control component of this coating because it has an excellent combination of high hardness and good chemical stability in chemically reactive environments. It was demonstrated in Ref. 3 that the additives were effective in reducing friction coefficients from 25 to 900 °C in air without sacrificing wear resistance. In the present research, PS 200 was evaluated for its suitability as a cylinder liner coating for the Stirling engine. A number of candidate ring materials were tested in sliding contact with this coating. Helium and hydrogen atmospheres were employed at temperatures from 25 to 760 °C to simulate the Stirling engine environment. Also, more detailed data were obtained on the friction and wear properties of PS 200 in air to 900 °C.

EXPERIMENTAL PROCEDURE

Friction and wear experiments were performed using the tribometer shown in Fig. 2. A standard pin on disk specimen configuration is used. The pins are 0.48 cm radius cylinders with a 0.48 cm radius hemispherical tip ground on one end. During sliding experiments the pins are placed in sliding contact with a flat, coated surface of the rotating disk. The wear track is 5.0 cm in diameter. The controlled atmospheres are dry hydrogen, dry helium, and air with a relative humidity at 25 °C of 50 percent. Specimens are induction heated, and temperature is measured with an infra red pyrometer at a spot of about 1.0 mm diameter on the wear track.

Wear Factor, k

Wear is expressed in this paper as a wear factor which relates volumetric wear to sliding distance (or sliding duration at a given sliding velocity) and to load. Use of this factor assumes that wear volume is directly proportional to the product of the sliding distance and the load. Although this assumption is an oversimplification, it has been found to be a reasonable one for steady state wear after the initial run in stage of wear is completed. Comparison of wear factors then allows one to estimate the relative wear resistance of various sliding combinations. The wear factor equation and units are:

$$\text{Wear factor } (k) = \text{volumetric wear } (cm^3)/\text{sliding distance } (cm) \times \text{load } (kg)$$

The units then simplify to:

$$k = cm^2/kg.$$

Wear factors typically vary from 10^{-7} to 10^{-11} cm^2/kg, with 10^{-7} indicating unacceptably high wear for any application (usually accompanied by galling with severe surface damage), and 10^{-10} or lower indicating the wear rates needed for long life sliding components. Intermediate rates may or may not be acceptable depending upon the requirements of the specific application.

MATERIALS

Pin and Substrate (disk) Materials

The pin materials chosen were considered as candidate piston ring materials for the Stirling engine. They are two ferrous alloys, Nitronic-60 and XF818; a precipitation hardenable nickel base super alloy, Inconel X-750; and a hardenable cobalt alloy, Stellite 6B. All alloy nominal compositions are given on Table I.

The coatings tested in helium and hydrogen were applied to disks of XF818, which is the alloy for the Stirling engine cast cylinder block. The coatings tested in air to 900 °C were applied to Inconel X-750 because of its superior oxidation resistance.

Coatings

The baseline coating composition is a nickel alloy bonded chromium carbide with no solid lubricant additions. X-ray diffraction analysis of this material identified a face centered cubic nickel solid solution and orthorhombis chromium carbide with the formula, Cr_3C_2. PS 200 was formulated by adding silver and the fluoride eutectic to this baseline composition. The chemical compositions are given in Table II. The disks to be coated were pretreated by sand blasting then they were plasma spray coated with a 0.008 cm thick bond coat of nichrome. The carbide base coatings were then sprayed onto the bond coat to a total coating thickness in excess of 0.035 cm. The coatings were then diamond ground to a thickness of 0.025 and a surface finish of about 0.2 μm (excluding microporosity effects on surface roughness). Plasma spray parameters for PS 200 are the following:

Power: 400 amps at 32 V

Arc gas: Argon (1.4 m^3/hr flow rate)

Powder carrier gas: Argon (0.4 m^3/hr)

Powder flow rate: 1kg/hr

Gun to specimen distance: 15 cm

RESULTS AND DISCUSSION

Screening of Candidate Piston Ring Materials in Helium

Candidate high temperature piston ring materials were chosen from among iron, cobalt, and nickel base alloys that were judged to have adequate mechanical strength and are reputed to have reasonable resistance to adhesive wear to at least 760 °C. Friction coefficients for these alloys sliding against PS 200 are summarized in Fig. 3, and the results are discussed below.

Inconel X-750. - This alloy has a high chromium content, it is age hardenable to Rockwell C-40, and has been a successful counterface material sliding against previously-reported coatings containing fluoride solid lubricants.[2,3,4]

Wear factors for this alloy sliding on PS 200 were in the 10E-9 cm^2/kg range at 25 and 350 °C and in the 10^{-10} cm^2/kg range only at 760 °C. The wear factors at the lower temperatures would probably be too high for piston rings with a long life requirement. Friction coefficients were about 0.4; too high for high energy efficiency.

Nitronic-60, (N-60) ferrous alloy. - This alloy is an austenitic stainless steel, a class of alloys generally associated with very bad galling and adhesive wear characteristics. N-60, however, is formulated for wear resistance by means of an exceptionally high silicon content of 3.5 to 4.5 percent compared to about 0.15 percent normally present in austenitic stainless steels. N-60 did have reasonably good wear factors in the 10^{-10} cm^2/kg range at all test temperatures. PS 200 wear against this alloy was in the same desirable range. However, friction coefficients were again higher than desired, about 0.4.

XF818, cast ferrous alloy. - This is also an austenitic steel, but it has a dual microstructure of austenite dendrites with an extensive interdendritic phase consisting of a lamellar austenite/metal boride eutectic. This alloy differs from standard stainless steels in having twice their nickel content and 0.7 percent boron. It also contains at least twice as much carbon as most other austenitic stainless steels.

Pin and coating wear factors were both in the 10^{-10} cm^2/kg range and friction coefficients were lower than with the previous alloys; they were 0.3 at 25 and 350 °C, and 0.4 at 760 °C.

PS 200 versus PS 200. - The coating was applied to pins with a large radius tip (4.45 cm) to insure that the coating would not wear out in a reasonable test duration. Coating wear turned out to be low enough that this precaution may not have been necessary. All pin wear factors were in the 10^{-10} cm^2/kg range and coating wear on the disks was too small to measure by profilometry (wear depth was less than the original surface roughness). Friction coefficients were all about 0.3.

Stellite 6B. - This is a known wear resistant alloy. It is heat treatable to a hardness of Rockwell C-42, and retains good hot hardness at 760 °C. Results with this alloy were easily the best from among the uncoated pin materials. Pin wear factors were in the 10^{-10} cm^2/kg range and coating wear was also very low. Friction coefficients were 0.25 to 0.38 in helium.

Equally promising results were obtained with PS 200 coated pins and 6B pins. The concept of an uncoated piston ring is of course simpler and therefore 6B was chosen for further evaluation in hydrogen.

Stellite 6B/PS 200 in Hydrogen

The friction coefficients for this combination in helium and in hydrogen are compared in Fig. 4. Even better results were obtained in hydrogen than in helium. Friction coefficients were 0.18 to 0.25. Wear factors were all in the 10^{-11} to 10^{-10} cm^2/kg ranges, and somewhat lower than in helium at any given test condition.

Control Experiments with Stellite 6B versus the Baseline Carbide Coating

Figure 4 shows the benefit derived by the solid lubricant additives in PS 200. Friction coefficients with the baseline coating were high and erratic both in helium and in hydrogen. Typical values of friction coefficient for the baseline coating were 0.5 to 0.6. Therefore, a significant accomplishment achieved by formulating PS 200 was to reduce friction while retaining the inherent wear resistance of bonded chromium carbide.

Tribological Performancence of PS 200 in Air

In order to determine the effect of an oxidizing atmosphere on the tribological properties of PS 200, friction and wear experiments were performed using an air atmosphere at temperatures to 900 °C. The friction coefficients of Stellite 6B and of several other pin materials sliding on PS 200 are given in Fig. 5, and compared to results with the baseline carbide coating. In all cases, the solid lubricant additions were responsible for lower friction compared to the baseline coating. Friction coefficients at any given temperature were about the same as in helium. Wear factors tended to be higher in air than in helium, especially at the higher temperatures, probably due to the contribution of oxidative wear. Wear nevertheless was still in the low to moderate regimes. However, very low pin and coating wear factors were obtained with one combination, alpha silicon carbide/PS 200. Pin and coating wear were in the 10^{-11} cm^2/kg range at all temperatures to 900 °C.

CONCLUDING REMARKS

A specific objective of this research was to invent a self lubricating cylinder coating composition with good tribological and chemical stability properties in Stirling engine working fluids (helium and hydrogen) to 760 °C. The purpose was to discover a piston ring/cylinder coating materials combination that would enable the use of "hot piston rings" in the Stirling engine. Therefore, a number of candidate piston ring materials were evaluated in sliding contact with the experimental coating.

Experiments were also performed in air to 900 °C to accomplish a more generic objective of comparing tribological behavior in an oxidizing atmosphere with performance in inert and reducing atmospheres.

Some of the more significant results of this program are the following:

1. The friction coefficients of plasma sprayed chromium carbide coatings were markedly reduced by the addition of silver and of barium fluoride/calcium

fluoride eutectic to the coating composition. This occurred with no sacrifice to the inherent wear resistance of the bonded carbide baseline coating.

2. The new coating composition, PS 200, consists of a nickel alloy bonded chromium carbide base with the addition of 10 wt % silver and an equal amount of barium fluoride/calcium fluoride eutectic. These additives reduced the friction coefficients in hydrogen from a typical value 0.6 for the baseline carbide coating to about 0.2 for PS 200.

3. The most suitable candidate piston ring material identified for sliding contact against PS 200 is a hardenable cobalt-chromium alloy, Stellite 6B. PS 200 sliding against itself also provided low friction and wear.

4. Additional experiments in an air atmosphere showed that Stellite 6B and alpha silicon carbide on PS 200 provide moderate friction coefficients and low wear to 900 °C.

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2. H.E. Sliney, Thin Solid Films, 64, 211 (1979).
3. H.E. Sliney, "The Role of Silver in Self Lubricating Coatings for Use at Extreme Temperatures," NASA TM-86943, 1985.
4. R.C. Wagner, and H.E. Sliney, "Effects of Silver and Group II Fluorides Addition to Plasma Sprayed Chromium Carbide High Temperature Solid Lubricant for Foil Gas Bearings to 650 °C," NASA TM-86985, 1985.

TABLE I. - NOMINAL COMPOSITION AND ROCKWELL HARDNESS OF CANDIDATE PISTON RINGS MATERIALS.

Pin material	Element wt %														Rockwell hardness
	Ni	Cr	Co	C	Fe	Al	Si	Ti	Mo	Mn	B	W	N	Cb	
Inconel X-750	70	16	1	0.1	7.5	1	---	2.5	----	1	---	-	----	---	R_c40
XF818	18	18	--	.2	54.6	-	.3	---	7.5	.15	.7	-	.12	0.4	R_c18
Stellite 6B	2	30	59	1	1	-	.75	---	.75	1.25	---	4	----	---	R_c42
Nitronic 60	8	18	--	.1	61.8	-	4.0	---	----	.8	---	-	.12	---	R_c28

*NOTE: Compositions taken from manufacturer's data. Hardness values taken at room temperature.

TABLE II. - COMPOSITIONS AND PARTICLE SIZES OF PLASMA SPRAY POWDERS

Component	Composition wt %	Particle size
Bonded chromium carbide		
Cr_3C_2 Ni Co Al	58 28 12 2	-200 + 400 mesh
Silver metal		
Ag	100	-100 + 125
Eutectic		
BaF_2 CaF_2	62 38	-200 + 325

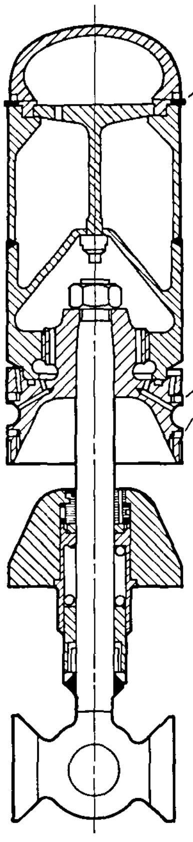

Figure 1. - Stirling engine piston with "hot ring" (ref. 1).

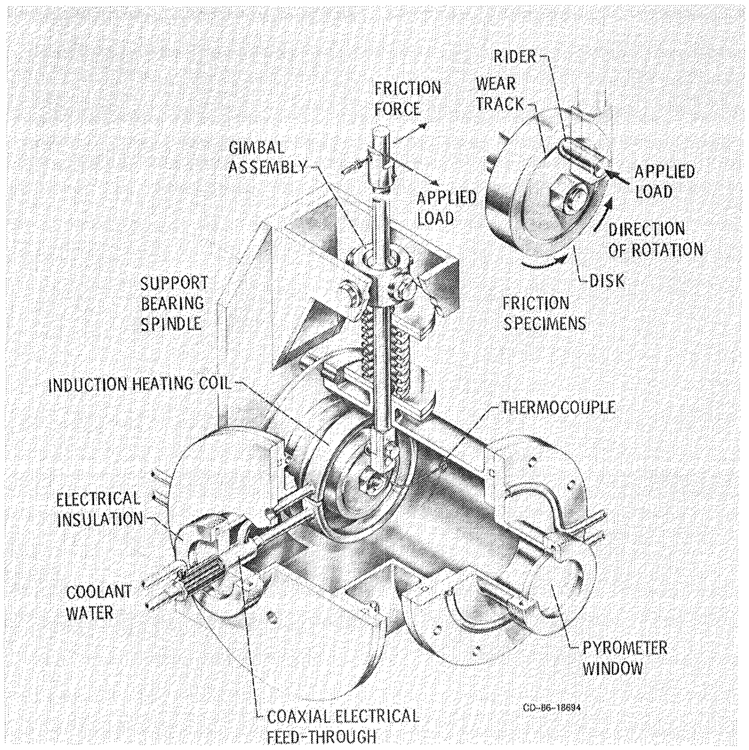

Figure 2. - Friction and wear testing device.

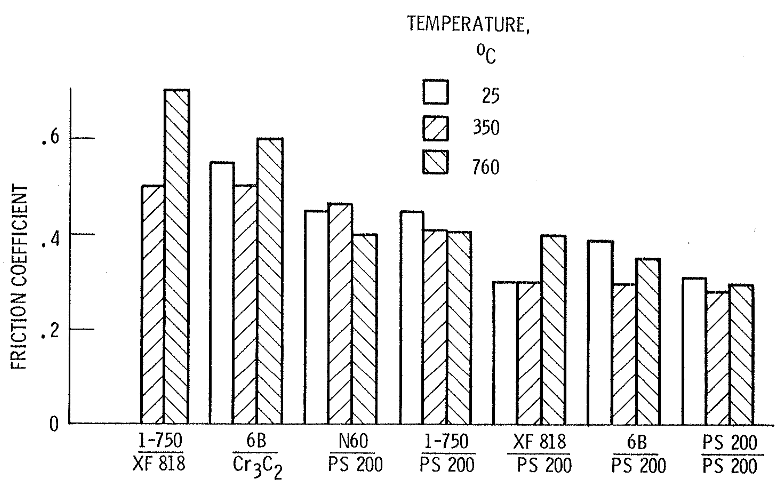

Figure 3. - Friction coefficients in helium of candidate piston ring materials sliding on PS 200 compared to unlubricated contacts.

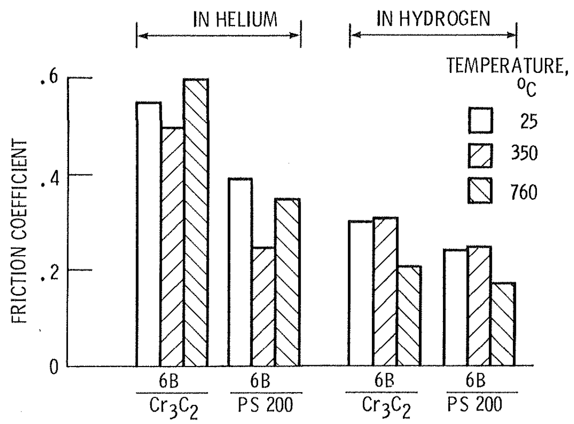

Figure 4. - Friction coefficients in helium and in hydrogen for Stellite 6B sliding on bonded chromium carbide and on PS 200.

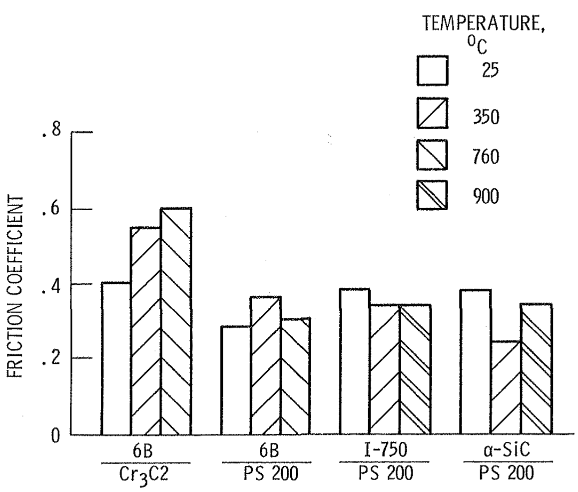

Figure 5. - Friction coefficients in air for sliding on bonded chromium carbide and on PS 200.

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