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TRIBOLOGICAL PROPERTIES OF PM212: A HIGH-TEMPERATURE, SELF-LUBRICATING, POWDER METALLURGY COMPOSITE

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ABSTRACT

This paper describes a research program to develop and evaluate a new high temperature, self-lubricating powder metallurgy composite, PM212. PM212 has the same composition as the plasma-sprayed coating, PS212, which contains 70 wt % metal-bonded chromium carbide, 15 wt % silver and 15 wt % barium fluoride/calcium fluoride eutectic. The carbide acts as a wear resistant matrix and the silver and fluorides act as low and high temperature lubricants, respectively. The material is prepared by sequential cold press, cold isostatic pressing and sintering techniques. In this study, hemispherically tipped wear pins of PM212 were prepared and slid against superalloy disks at temperatures from 25 to 850 °C in air in a pin-on-disk tribometer. Friction coefficients range from 0.29 to 0.38 and the wear of both the composite pins and superalloy disks was moderate to low in the 10^{-5} to 10^{-6} mm^3/N-m range. Preliminary tests indicate that the material has a compressive strength of at least 130 MPa over the entire temperature range of 25 to 900 °C. This material has promise for use as seal inserts, bushings, small inside diameter parts and other applications where plasma-sprayed coatings are impractical or too costly.

INTRODUCTION

There is a great need for lubricating sliding components from below room temperature to high operating temperatures. Gas turbine seals, bearings and variable stator vane bushings are only a few examples. Other examples include cylinder wall/piston ring lubrication for Stirling engines and low heat rejection diesels as well as non-energy related applications such as high temperature process control valve stems and seats and various furnace components.

Traditionally, the approach to solve these difficult lubrication problems has been to lower the operating temperature with cooling systems so that oils, greases and common solid lubricants can be used. More recently, however, new materials have been developed that can provide low friction and wear over a wide temperature range. One material system in particular, is the PS200 composite coating system developed at NASA Lewis Research Center (Ref. 1).

PS200 is a plasma-sprayed composite coating which consists of a matrix of nickel-cobalt bonded chromium carbide combined with BaF_2/CaF_2 eutectic and silver. The metal bonded chromium carbide acts as a wear resistant matrix and the silver and fluorides function as low and high temperature solid lubricants, respectively. PS200 has been used successfully in a Stirling engine as a cylinder wall lubricant coating and also as a gas bearing journal back up lubricant (Ref. 2). PS200 type coatings are applied by plasma spraying. The coating technique is quite versatile for coating flat or outside diameter surfaces, but it is very difficult to coat inside diameters of small parts. The sprayed coating also requires diamond grind finishing. Thus, intricate parts are not practically coated.

One way to produce small, intricate components is by employing powder metallurgy (P/M) techniques instead of plasma-spraying. By making components by P/M, small parts with near net shape can be economically produced. Also, since P/M is a well developed process, quality control is relatively simple. For example, the final composition is the same as the starting powders, in contrast to the plasma spraying technique where some components may be lost in the deposition process. This paper, therefore, describes a preliminary research and development program to produce a powder metallurgy version of the PS200 materials, designated PM212, to complement the widespread application and potential use of the material system.

By making self-supporting, self-lubricating composite parts, many new potential applications are possible such as variable stator vane bushings, face seal inserts, and small diameter cylinder wall sleeves. Also, by incorporating appropriate powder metallurgy techniques, near net shape and finish can be achieved, dramatically reducing the manufacturing costs compared to plasma spray deposition.

This paper predominantly deals with one P/M product, made by low cost cold isostatic press (CIP) and sinter techniques. Triboproperties are determined on a pin-on-disk rig at temperatures from 25 to 850 °C.

MATERIALS

The PM212 is made from a powder blend of 70 wt % metal bonded chromium carbide, 15 wt % silver and 15 wt % BaF_2/CaF_2 eutectic. The exact starting powder composition and particle sizes are given in Table 1. The powders are simply blended together. No binder is added.

Silver, because of its low shear strength is a good low temperature lubricant (Ref. 3). Silver also has a high melting point, 961 °C, and good chemical stability making it an appropriate component of a high temperature composite. The fluoride eutectic is a good high temperature lubricant which undergoes a brittle to ductile transition at about 400 to 500 °C (Ref. 4).

The metal bonded chromium carbide acts as the wear resistant matrix. It is commercially available as a blended mixture of chromium carbide and nickel, cobalt and aluminum powders. The powder used is also suitable for plasma spray deposition techniques. To make the PM212 starting powder, the three components are blended in the appropriate proportions prior to compaction.

PROCESSING TECHNIQUES

The material studied in this program was prepared by a cold press (CP), cold isostatic press (CIP) and sinter technique. First the powders are poured into a steel die and cold pressed at 54.2 MPa. The resulting compact is then carefully placed in a rubber bag and cold isostatically pressed at 406 MPa. The green compact, which is about 70 percent dense, is weighed and measured and then sintered in a hydrogen atmosphere at 1100 °C for 20 min. Heating and cooling rates are constant at 10 °C/min.

The sintered slug has a measured bulk density of about 80 percent. Liquid porosimetry was done on some samples which indicated that approximately one-third of the remaining porosity is open. Accurate values for the pore size was unavailable because chemical amalgamation between the silver in the P/M product and the mercury, the porosimetry liquid, occurred.

Figure 1 shows some cross sections of the material after sintering. X-ray energy dispersive spectroscopy (EDS) analysis is used to obtain elemental analyses of the phases present. In general, the sintering results in densification but little or no chemical reactions between phases. This is inferred from the EDS analyses which identifies each phase without significant impurities.

Other processing techniques were also evaluated. They included: (1) cold press and sintering which resulted in a low density product with poor tribological and mechanical properties, (2) hot pressing at 1100 °C, and (3) hot isostatic pressing at 900 and 1100 °C. In general, hot consolidation techniques produce products which have densities in the range of 80 to 90 percent and triboproperties similar to the CIP and sinter materials but are more expensive to produce. Therefore, only the CIP/sinter processing route is considered in detail here.

SPECIMEN PREPARATION

The sintered slugs are approximately 10 mm in diameter and 25 mm long. To make the wear pin specimens, the slugs are rough machined to an outside diameter of 9.5 mm with a tungsten carbide tool bit. Water was used as grinding lubricant/coolant to prevent contamination of the parts. The ends of the pin were then diamond ground to a radius of 4.76 mm.

Following the machining, the pins are heat treated in H_2 at 750 °C for 30 min to help bring more lubricants (silver and fluoride) to the machined surface. The lubricants have a tendency to migrate to the surface at elevated temperatures because their thermal expansion coefficients are greater than the metal-bonded ceramic matrix (Table 1). Thus when the specimens are heated the lubricants get squeezed to the surface.

The wear specimens could be made to net or near net size and shape. However, our current equipment and dies were limited to cylindrical rods. Therefore post sinter machining was required. The material is also machinable by wire electrodischarge machining.

WEAR TEST PROCEDURES

The specimens were tested in a pin-on-disk tribometer (Fig. 2). With this configuration, a hemispherically tipped pin made from PM212 was slid against disks made from a precipitation hardenable nickel cobalt chromium superalloy, R41. R41 has a hardness of RC 38 to 40 at room temperature. Its composition is given in Table 2.

The pin generates a 51 mm diameter wear track on the disk. Sliding was unidirectional at 0.27 to 5 m/sec and loads of 0.5 to 3.0 kg were applied with deadweights. Most of the tests were done at 2.7 m/sec sliding velocity and 0.5 kg load so that direct comparisons of the data could be made to previous work with the PS212 coating. The disk was heated with a low frequency induction heater. Temperature was measured with an infrared pyrometer capable of measuring surface temperatures from 100 to 1400 °C ±5 percent. The test atmosphere was air with a relative humidity of 35 percent at 25 °C. In general, tests were run for 30 min then the specimens were removed from the rig and wear measurements were made. A relocation dowel on the specimen holder allowed for accurate replacement of the specimens.

RESULTS

The friction and wear results are given in Table 3 and graphed in Figs. 3 to 5. The friction and wear of the composite/metal couple are similar to results obtained previously with the PS200 coating on a metal disk slid against a metal pin (Ref. 5) (Fig. 6).

The friction for the PM212 pins sliding against R41 disks ranges from 0.29±0.03 at 850 °C to 0.35±0.05 at 25 °C. Wear factors for the composite pins are lower at 760 to 850 °C than at 25 and 350 °C but are well within the moderate to low range (see Appendix). Disk wear factors show no trends with temperature but range between $3.5 \pm 1.0 \times 10^{-6}$ $mm^3/N\text{-}m$ at 350 °C to $7.0 \pm 2.0 \times 10^{-5}$ $mm^3/N\text{-}m$ at 25 °C.

The PM212 composite generally exhibited stable friction and wear properties during long tests (e.g., 8 hr at 850 °C); however, at 350 °C, the material exhibited a repeatable peculiarity in its tribological behavior. After ≈8 km of sliding at 350 °C, the friction increased from about 0.35 to about 0.5 and pin material transferred (namely Ni, Co) to the disk surface. If the specimens were either heated to above 400 °C or cooled to below 300 °C and run for a few minutes and then returned to 350 °C, the good triboproperties were restored until the 8 km point was reached again. Therefore, the friction of the PM212 composite sliding against R41 was stable for only a limited period between 300 and 400 °C. This behavior was not observed during previous testing of the plasma-sprayed PS200 coating and may not occur for geometries different than pin-on disk.

The effect of load on the friction and wear of PM212 was also ascertained. Under loads of 0.5 to 3 kg the wear factors are constant (i.e., if the load was doubled the wear rate was doubled). Since the tribometer used was limited to 3 kg loads or less, the ultimate load capacity could not be determined. From the data, however, it can be inferred that the dynamic load capacity for the material is at least 20 MPa (≈3000 psi).

Preliminary compression strength data is given in Table 4. The strength averages 180 MPa (≈20 000 psi) and shows a maximum of 356 MPa (≈40 000 psi) at 400 °C, almost the same temperature that displays the unstable friction properties. Therefore, there may be a connection between the peak in the compressive strength and friction behavior at 350 °C.

The effect of velocity on the friction coefficient is given for one pin and disk specimen pair in Fig. 7. In general, as the velocity increases the friction decreases. At high speeds, friction coefficients are usually between 0.30 and 0.20. At elevated temperatures, there is less of a friction dependence on speed. This indicates that frictional heating and surface temperatures may be playing a role.

DISCUSSION

The friction and wear properties of PM212 sliding against R41 are comparable to the plasma-sprayed coatings, PS212, as indicated in Fig. 6. This behavior is encouraging because it indicates that for applications in which PS212 have been successful, such as gas bearing journals, Stirling engine cylinder walls and high temperature process control valves, components made by powder metallurgy techniques may also be successful. In addition, geometries which are not practical or conducive to using plasma spray techniques, such as small inside diameters, bushings, ball bearing cages, etc., can easily be satisfied via powder metallurgy processing techniques.

During processing development, it was determined that the sintering temperature must be high enough to melt both the fluorides and the silver. This provides for approximately 40 vol % liquid phase during sintering. Specimens made by sintering at lower temperatures exhibited poor triboproperties.

The reason for this behavior seems to be the development of an interconnected lubricant structure which allows lubricants to exude to the rubbing surface at elevated temperatures. When the sintering is predominantly solid state (e.g., at 900 °C) the resulting product cannot resupply lubricants to the sliding surfaces because the lubricant network is generally not continuous and the lubricants are trapped by the matrix.

The processing atmosphere also plays an important role in the processing of the material. Specimens produced in air at 1100 °C are oxidized and do not perform well. Also, specimens produced in argon display variable tribological behavior, perhaps due to differences in the humidity content of the furnace. Therefore, dry hydrogen was chosen as the preferred sintering atmosphere for this material.

Following the diamond grinding, a heat treatment in hydrogen at 750 °C is performed to help develop a lubricant film at the ground surface. While this step is not critical it probably reduces initial run-in wear as the lubricants, which are depleted by the grinding process, are replenished by the heat treatment. Parts made to net shape without diamond grinding would not need the post sinter heat treatment.

The evidence for the existence of a continuous lubrication network can be inferred from two sources. First, photomicrographs of polished cross sections indicated long chains of interconnected lubricant areas (Fig. 8). Second, short heat treatments at 750 °C cause a large increase in Ag, Ca, and Ba concentrations at the surface. This is detected with EDS analysis before and after heat treatment. Since the lubricants have higher thermal expansion coefficients than the metal bonded chromium carbide matrix, they are forced out at elevated temperatures. If the lubricant network were not interconnected this exuding behavior would be inhibited.

The time dependent behavior of PM212 material at 350 °C is very interesting. EDS analysis performed on the disk wear tracks before and after the friction increases, indicated that during sliding a thin, smooth lubricant film of silver and fluorides (detected by Ca, Ba presence) is present up to 8 km. After 8 km of sliding, pin material including the metal-bonded carbide matrix transfers to the disk. This leads to a rough wear track and increased friction and pin wear.

It is likely that the beneficial lubricant film that is built up on the wear track during sliding at elevated temperatures (above 350 °C) is worn off over ≈8 km of sliding exposing clean R41 to the pin. Since both the pins and disk contain Ni and Co, there is a tendency to transfer pin material to the disk as in cold welding. Surface profilometery, of the disk wear track indicate a build up of 2 to 5 μm of transfer material.

Two methods to avoid this problem are to (1) chose a different counterface material, a nickel-chromium alloy for example, or (2) when sliding under these load and speed conditions, limit sliding at 350 °C to less than 8 km.

CONCLUSIONS

In this study the process development and triboproperties of powder metallurgy PM212 have been ascertained. From this work the following conclusions can be drawn:

1. The composite material PM212, fabricated by powder metallurgy techniques, has triboproperties similar to plasma sprayed PS212.

2. Based upon its tribological properties and compressive strength, the powder metallurgy composite, PM212, may be successful as self-lubricating bushings, valve guides and seal inserts and in other applications.

3. The PM212 composites function by providing a wear resistant matrix with an interconnected lubricant structure. During heating or sliding, lubricants are supplied to the sliding contact reducing friction and wear.

4. During processing, liquid phase sintering at 1100 °C is necessary to provide the interconnected lubricant network and good tribological properties. Specimens processed at lower temperatures have adequate mechanical strength but poor tribological properties.

5. The PM212 pins show increased friction and wear after sliding at 2.7 m/sec velocity, 0.5 kg load at 350 °C for over 8 km of sliding. This can be avoided by sliding for brief periods at other temperatures to inhibit pin matrix transfer and foster lubricant film development on the counterface or by operating at different loads and speeds.

APPENDIX - EXPLANATION OF WEAR FACTORS

The wear factor (K) used in this paper is a coefficient which relates the volume of material worn from a surface to the distance slid and the normal load at the contact. Mathematically, K is defined as:

$$K = \frac{V}{S \times W}$$

where

W the normal load at the sliding contract, kg

S the total distance slid, mm

V the volume of material worn away, mm^3

The physical interpretation of the numeric value of the K factor is as follows:

$K = 10^{-4}$ $mm^3/N\text{-}m$ high wear

$K = 10^{-5}$ to 10^{-6} $mm^3/N\text{-}m$ moderate to low wear

$K = 10^{-7}$ $mm^3/N\text{-}m$ very low wear

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TABLE 1. - COMPOSITION OF THE THREE MAJOR COMPONENTS

Component	Composition, wt %	Particle size	Coefficient of thermal expansion
Bonded chromium carbide			
Ni	28	-200 + 400 Mesh	$\approx 13\times10^{-6}$/°C
Al	2		
Cr_3C_2	58		
Co	12		
Silver metal			
Ag	100	-100 + 325	$\approx 25\times10^{-6}$/°C
Prefused eutectic			
BaF_2	62	-200 + 325	$\approx 30\times10^{-6}$/°C
CaF_2	38		

TABLE 2. - MECHANICAL PROPERTIES AND COMPOSITION OF DISK MATERIAL

[Data taken from manufacturers' literature.]

Material	R41
Elemental weight percent	
Ni	Balance
Cr	19
Co	11
Mo	10
Ti	3.1
Al	1.5
Fe	0.3
Ultimate tensile strength, MPa	
25 °C	1400
650 °C	1314
Yield strength 0.2 percent offset, MPa	
25 °C	1043
650 °C	982
Hardness at 25 °C	RC 38 to 40

TABLE 3. - DATA SUMMARY

Temperature, °C	Load, kg	Friction coefficient, µm	K_{PM212}, mm^3/Nm	$K_{René\ 41}$, mm^3/Nm	Number of tests
850	0.5	0.29±0.03	$4.1\pm2.0\times10^{-6}$	$5.0\pm1.0\times10^{-6}$	2
760	↓	.35±0.06	$3.6\pm0.9\times10^{-6}$	$1.0\pm6\times10^{-5}$	4
[a]350		.38±0.02	$3.9\pm1.8\times10^{-5}$	$3.5\pm1.0\times10^{-6}$	3
25		.35±0.05	$3.2\pm1.5\times10^{-5}$	$7.0\pm2.0\times10^{-5}$	2

[a] Friction and wear increase after ≈8 km of sliding at 350 °C. Friction increases to ≈0.5 and the pin material transfers to surface of disk.

TABLE 4. - PRELIMINARY COMPRESSIVE STRENGTH DATA

[Preliminary data on two specimens at each temperature.]

Temperature, °C	Proportional limit, MPa	0.2 Percent offset, MPa	Maximum strength, MPa
25	187	185	191
350	221	271	356
760	80	104	119
900	24	34	42

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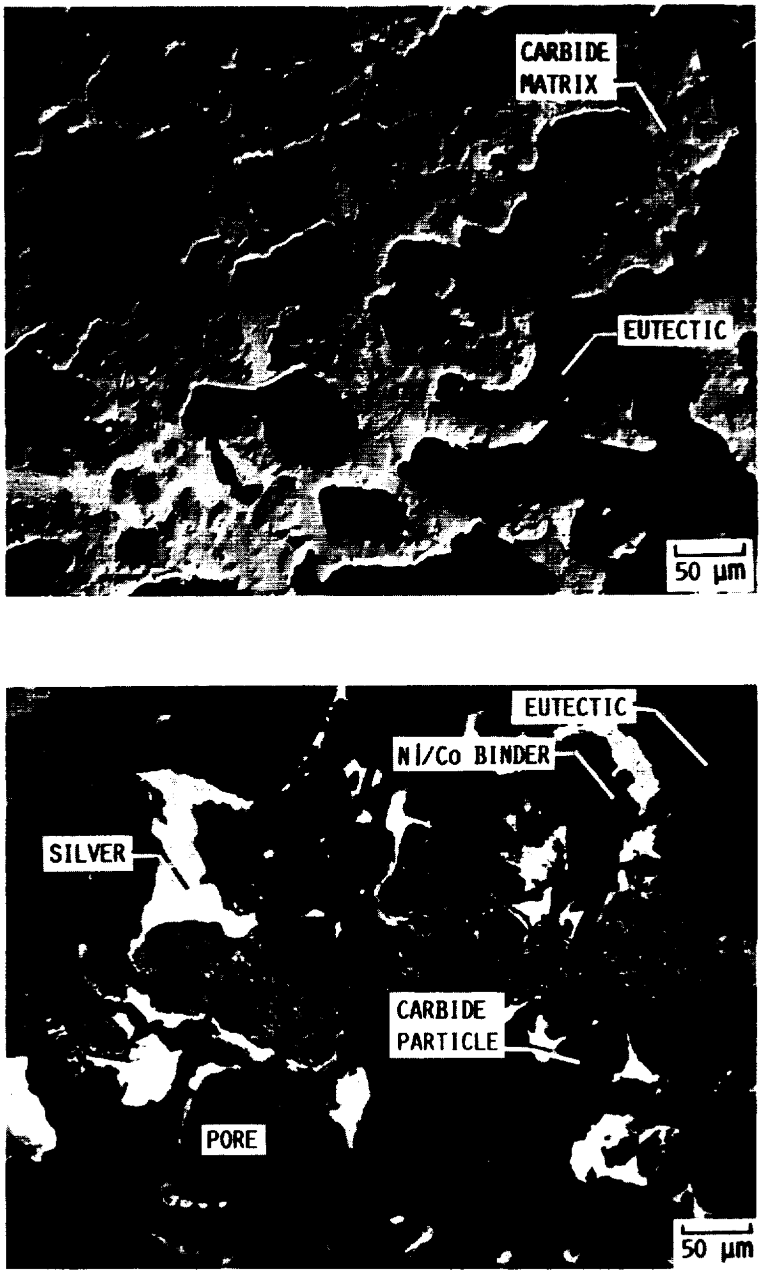

FIGURE 1. - OPTICAL (FIG. 1A) AND BACKSCATTERED SEM (FIG. 1B) MICROGRAPHS OF PM212.

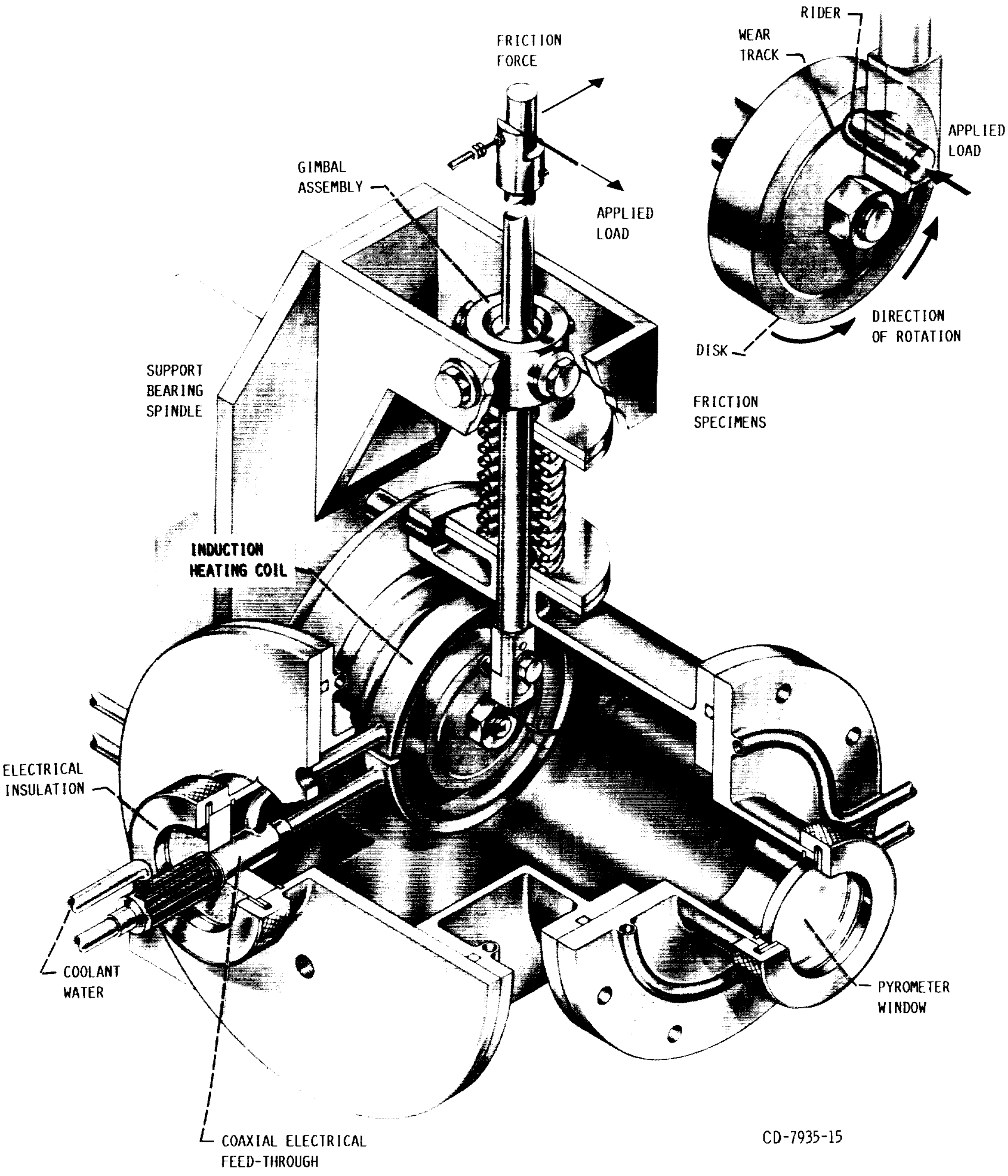

FIGURE 2. - HIGH-TEMPERATURE FRICTION APPARATUS.

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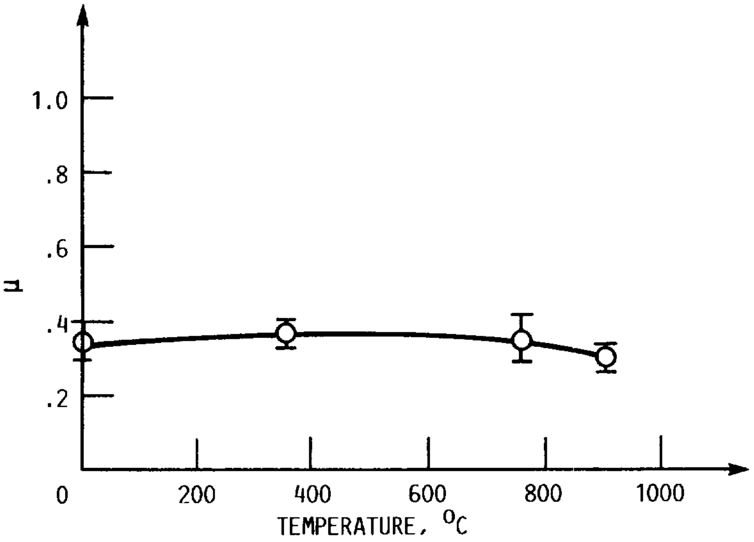

FIGURE 3. - FRICTION COEFFICIENT VERSUS TEMPERATURE FOR PM212.

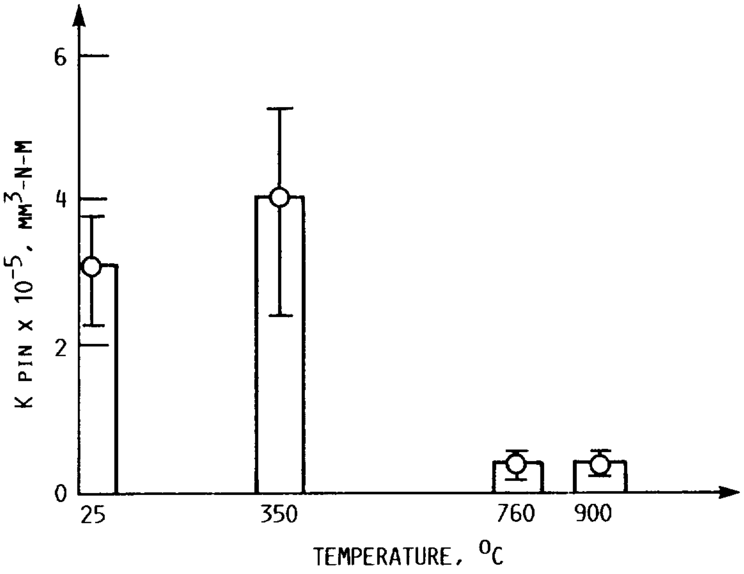

FIGURE 4. - PM212 PIN WEAR COEFFICIENT.

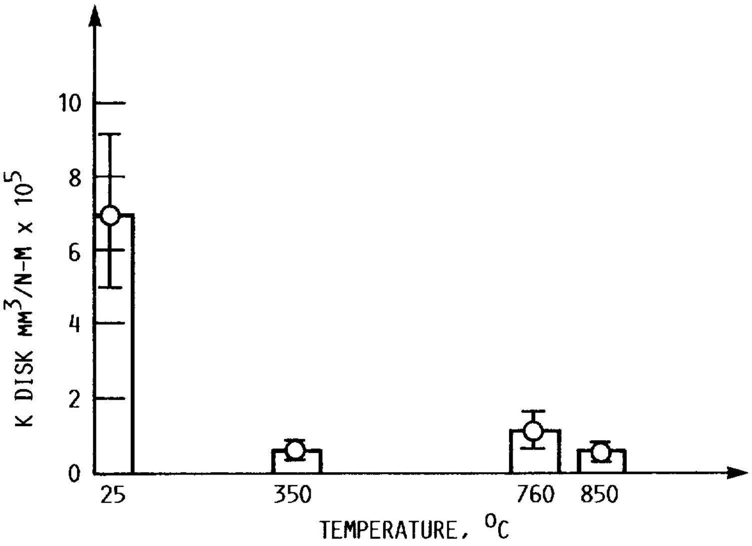

FIGURE 5. - DISK WEAR COEFFICIENT FOR RENE' 41 DISK SLIDING AGAINST PM212 PIN.

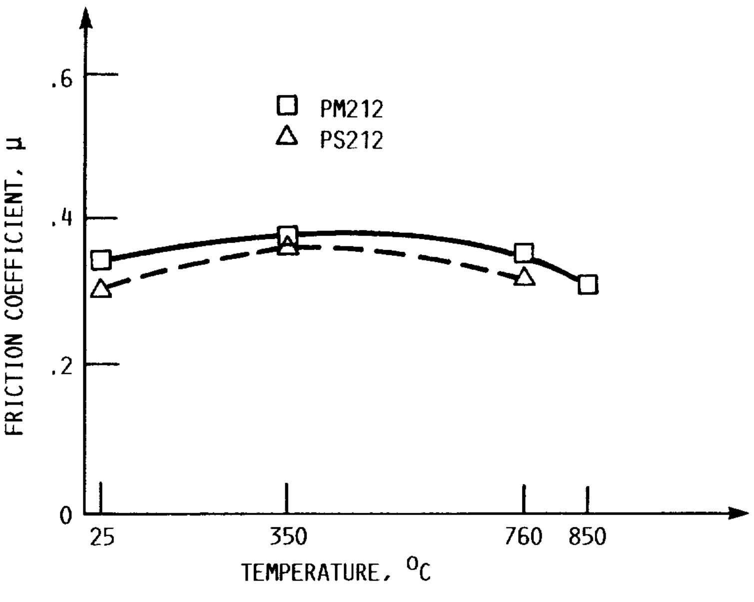

FIGURE 6. - FRICTION COEFFICIENT COMPARISON OF PM212 AND PS212 (PLASMA SPRAYED COATING) IN AIR, 35 PERCENT R.M. AT 25 °C. 0.5 kg LOAD, 2.7 M/s SLIDING VELOCITY.

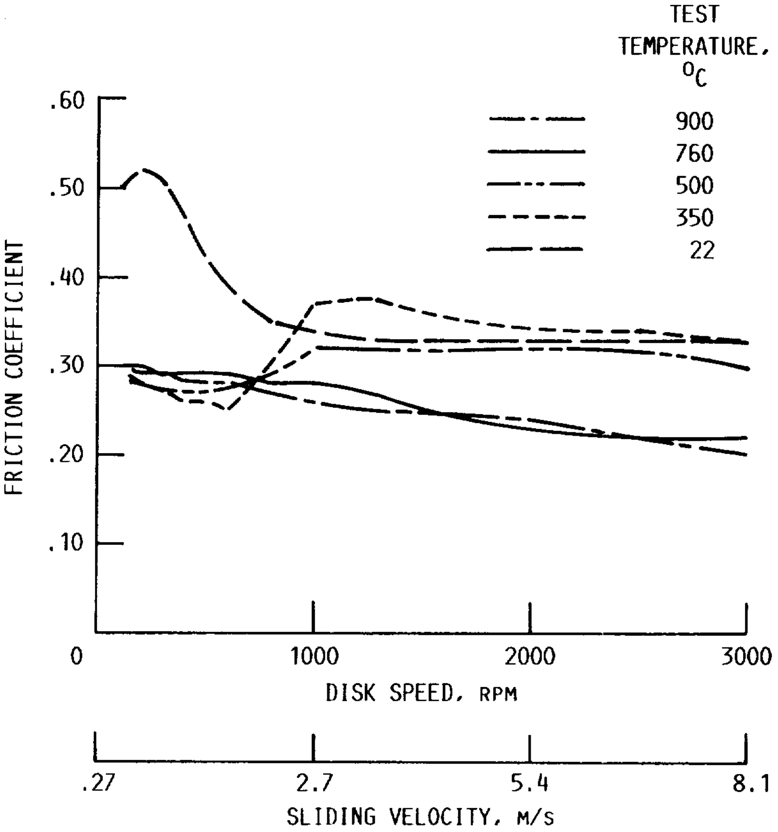

FIGURE 7. - FRICTION COEFFICIENT VERSUS SLIDING VELOCITY, 0.5 kg LOAD, IN AIR.

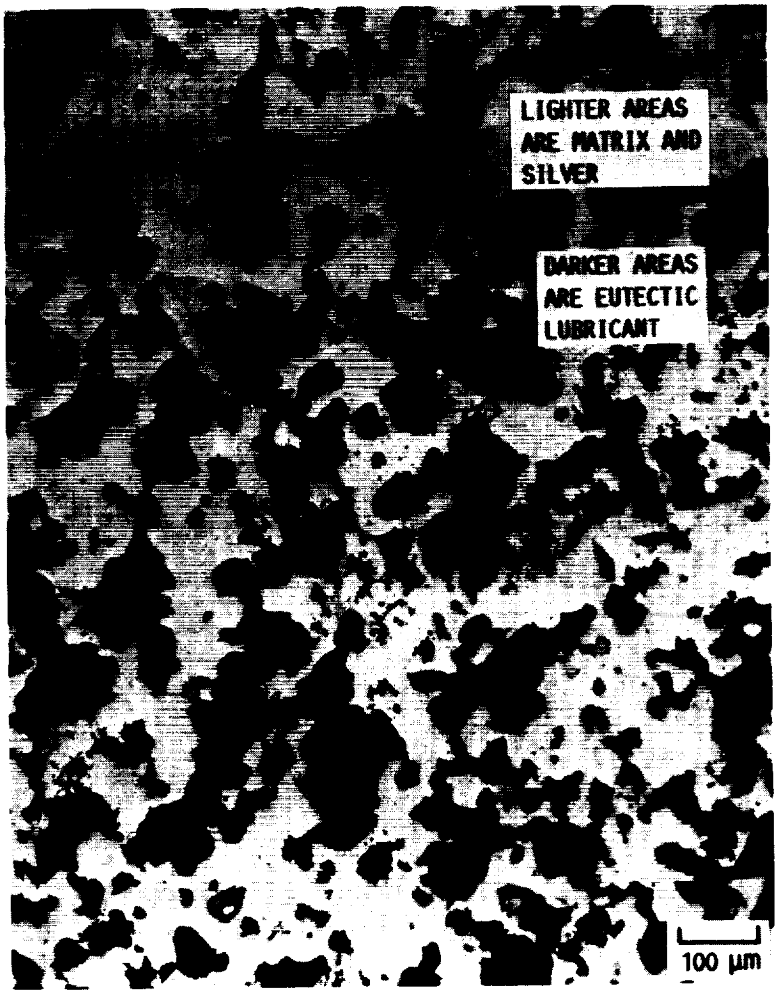

FIGURE 8. - PHOTOMICROGRAPHIC CROSS-SECTION OF PM212 SHOWING INTERCONNECTED LUBRICANT (FLUORIDES ARE DARK AREAS) STRUCTURE.

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16. Abstract

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