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FRICION AND WEAR OF PLASMA-SPRAYED
COATINGS CONTAINING COBALT ALLOYS
FROM 25⁰ TO 650⁰ C IN AIR

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PLASMA-SPRAYED COATINGS CONTAINING COBALT
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FRICITION AND WEAR OF PLASMA-SPRAYED COATINGS CONTAINING

COBALT ALLOYS FROM 25° to 650° IN AIR

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ABSTRACT

Four different compositions of self-lubricating, plasma-sprayed, composite coatings with calcium fluoride dispersed throughout cobalt alloy-silver matrices were evaluated on a friction and wear apparatus. In addition, coatings of the cobalt alloys alone and of one coating with a nickel alloy-silver matrix were evaluated for comparison. The wear specimens consisted of two, diametrically opposed, flat rub shoes sliding on the coated, cylindrical surface of a rotating disk. Two of the cobalt composite coatings gave a friction coefficient of about 0.25 and low wear at room temperature, 400° and 650° C. Wear rates were lower than those of the cobalt alloys alone or the nickel alloy composite coating. However, oxidation limited the maximum useful temperature of the cobalt composite coating to about 650° C compared to about 900° C for the nickel composite coating.

INTRODUCTION

The plasma spray process is convenient for applying relatively thick coatings. Coating thickness is typically in the range of 0.005 to 0.050 cm, but can be thicker if desired. The process is therefore attractive for making self-lubricating composites in the form of bonded coatings. Plasma sprayed composite coatings of molybdenum disulfide and copper have been reported; these coatings exhibited a moderately low friction coefficient of about 0.3 to 370° C, but rapidly deteriorated due to oxidation at higher temperatures (1). Plasma sprayed

compositions containing nickel oxide (NiO) and calcium fluoride (CaF₂) were shown to be self lubricating from 260° to 750° C (2). Other coatings of CaF₂, nichrome (NiCr), and glass were self-lubricating from about 500° to 900° C (3).

More recently, progress has been made in developing plasma spray coatings that are self-lubricating at both low and high temperatures (4,5,6). These "wide-temperature-spectrum" coatings have typically contained CaF₂ for high temperature lubrication, silver (Ag) to reduce friction at low temperatures, and NiCr to promote bonding to superalloys. In some cases, glass is also incorporated to harden the coatings and to act as a diffusion barrier to inhibit oxidation of NiCr. These coatings typically gave friction coefficients of 0.25 ± 0.05 from cryogenic temperatures to about 900° C. Wear rates were low enough for some slow speed applications such as oscillating plane bearings but would probably be excessive where high-speed and long-life are required.

In this program, therefore, cobalt alloys are substituted for NiCr in an attempt to reduce the wear coefficient of the coatings. Cobalt (Co) in its hexagonal crystalline form is known to be wear resistant (7). The hexagonal structure can be stabilized by alloying; molybdenum (Mo) is a particularly good stabilizing element (8). A composite of sintered 75 percent Co-25 percent Mo infiltrated with calcium fluoride-barium fluoride eutectic has shown some promise as a high-temperature bearing material (9). In this program, the CoMo alloy and two commercial cobalt alloys with a laves phase microstructure, described in (10), were plasma-sprayed alone and as matrix alloys in multicomponent coatings.

A double rub shoe friction and wear machine was used to evaluate the coatings. Experiments were performed from room temperatures to 650° C in an air atmosphere at a sliding velocity of 27.4 cm/sec.

APPARATUS

A schematic of the wear test specimen configuration and a cross section of the test head are shown in figures 1 and 2. The specimens are two flat rub shoes and a rotating disk. The rub shoes are diametrically opposed. They are loaded against the outer rim of the rotating disk by pressurizing a calibrated pneumatic belows which transmits force through a mechanical lever system to the shoes. In most cases the lubricant coatings were bonded to the rim of the disk and the shoes were uncoated.

The specimens were induction-heated. The induction coil arrangement is shown in figure 2. The specimens were heated by direct induction and by conduction from the heating sleeves indicated in the drawing.

Specimen temperatures was monitored with an infra red pyrometer sighted on the rim of the rotating disk about 90° away from the sliding contacts. The pyrometer was calibrated for the emissivity of the coating material. In addition, thermocouples were inserted into small holes in the sides of the rub shoes about 1.5 mm below the sliding contact. After a few minutes of sliding contact, the pyrometer and thermocouple indications agreed within about 5 percent although the temperature in the contact itself could not be directly measured.

MATERIALS

The disks and shoes were made of precipitation hardenable nickel-chromium superalloy. The disks were Inconel 750 and the shoes were Rene 41. The disks were hardened to about R_c 35 and the shoes to R_c 40.

The surface to be coated was sand blasted, then plasma sprayed with about 0.008 cm thick bond coat of 80 nickel-20 chromium (nichrome). The lubricating coating was then applied until a total coating thickness (bond and top coat) of about 0.040 cm was achieved. The coating was then ground and finish lapped to a final thickness of 0.025 cm (0.008 cm bond coat and 0.017 cm lubricant coat).

After finishing, the coatings had a reflective, polished appearance and were smooth to the touch. However, profilometer measurements indicated a roughness of 1.0 to 1.5 μm (40 to 60 in.) RMS. This roughness was primarily due to microporosity in the coatings. The surface profile in figure 3 shows that between the pores the surface is flat and smooth; there are few asperities or projections on the surface, but there are numerous pores. If the signals for the pores would have been filtered from the stylus output, it is estimated the surface finish would be about 0.10 to 0.15 μm RMS or about one-tenth of the indication when the pores are included in the measurements.

The code numbers and the nominal chemical compositions of the coatings are given in table I. For example: PS-T400 is a plasma-sprayed cobalt alloy coating of the following composition by weight: 62Co-28Mo-8Cr-2Si. PS106T is a formulated, multicomponent coating: 35T400-35Ag-30CaF₂. This coating was derived from a previously reported (4) coating, PS106 which contains nichrome instead of T400. This coating was included in the present program to compare the behavior of cobalt alloys to nichrome as matrix metal in self-lubricating coatings. The plasma spray parameters used for the various coatings are given in table II.

An example of coating microstructure and composition is given in figure 4 which is composed of a scanning electron micrograph and three X-ray dot maps of the lapped and polished surface of PS106. The X-ray maps show that all three components of the coating are well distributed throughout the field of view. It is important that the nichrome areas, which are identified by the NiK α dot map, were not smeared over the surface by the final surface finishing operation. Nichrome alone has severe galling or cold welding tendencies, but finish-lapped PS106 coatings had no cold welding tendencies. The cobalt alloys in general have less galling tendency than nichrome, but careful surface finishing procedures are desirable for all coatings in order to avoid uncontrolled surface smearing.

WEAR MEASUREMENTS

Wear was measured by specimen weight loss and by dimensional measurements of the worn surfaces. Weight loss was divided by the density of the worn material to obtain the wear volume. (A coating's density was assumed to be the average of the densities of its components weighted according to their volume fraction in the composition.) This method was reasonably accurate and correlated with dimensional measurements for room temperature tests. However, errors were introduced in high temperature tests due to specimen weight gain caused by oxidation. Therefore most of the wear volumes were calculated from dimensional measurements.

Shoe wear, for example, was calculated from the width length, and contour of the wear scars. In most cases the contour was to a good approximation the segment of a circle with the radius of the disk. Disk wear introduced only an insignificant error because the depth of disk wear was a small fraction of the disk radius.

Disk or coating wear volume was determined by multiplying the disk circumference by the cross sectional area of the wear track. Profilometer traces from several locations of each track were used to determine an average cross sectional area of the wear track.

Wear volumes were divided by the load and sliding distance to give the volumetric wear coefficients. Strictly speaking, these coefficients are merely averaged wear rates for the experimental conditions used in this program which were 20 minutes at 27.4 cm/sec and a load of 222 N (50 lb) per rub shoe. However, past experience with similar coatings indicated that (within wear data repeatability), wear was linear with time and load at least for running times of 20 to 120 minutes and loads of 111 and 222 N (25 and 50 lb) per rub shoe. Nonlinearity can be expected if the unit load exceeds the yield stress of the coating or if oxidation significantly changes the chemical composition of the surfaces over the duration of the wear experiment.

RESULTS AND DISCUSSION

Friction at Room Temperature

The friction and wear of unformulated cobalt alloy coatings were measured. This provided base line data to compare with the formulated coatings. Figure 5 gives the friction characteristics at room temperature of all coatings studied. The traces are hand-drawn representations of the continuously-recorded friction coefficients. They show any changes in friction and widths of the traces indicate whether smooth or rough sliding occurred.

Figure 5(a) gives the friction characteristics of the laves phase alloy T400 and of two formulated coatings PS106T and PS120 which contain T400. PS106 which contains nichrome instead of T400 is included for comparison. This coating was previously described in (4). The friction coefficients for T400 were between 0.3 and 0.4 during the first ten minutes, but sliding became rough and friction rose to 0.6 by the end of the 20 minute test. The friction coefficient of PS106, on the other hand, remained at about 0.3 during the entire test. The friction coefficient of PS106T was between 0.15 to 0.2 for a while but increased to 0.28 after twenty minutes. PS120 had a stable friction coefficient of 0.24 after the first few minutes of sliding.

Figures 5(b) and (c) are for T800 (which has more chromium and less molybdenum than T400), for CoMo (75Co-25Mo), and for formulated coatings containing these alloys. Sliding became very unstable for T800 after about five minutes and copious wear debris was generated. The formulated coating PS121 was much better than T800 alone but was inferior to either PS106T or PS120. CoMo had the most stable friction characteristics of the unformulated coatings with a fairly high but stable friction coefficient of 0.4 over the entire test duration. Friction stability apparently carried over to PS130 which had a very stable friction coefficient of about 0.3 but transferred heavily to the uncoated counterface.

Wear at Room Temperature

A - Continuous vs Intermittent Contact. - Figure 6 gives the combined wear coefficients for experiments in which coated shoes were run against uncoated disks compared to the case where uncoated shoes were run against coated disks. The combined wear coefficient is the sum of the wear coefficients for the shoes and disk in each experiment. The significant difference in the two configurations is that, with coated shoes, continuous sliding occurs on only a small area of the coating while, with coated disks, only transient sliding contact occurs on any area element of the coating during each shaft revolution.

For all three coatings evaluated in this manner, lower total disk and rub shoe wear occurred when the disks were coated. In all subsequent tests, therefore, only the disks were coated.

B - Effect of Coating Composition. - Figure 7 gives the wear at room temperatures for coatings of three cobalt alloys and coatings of these alloys combined with silver and calcium fluoride. Wear for the nichrome base coating, PS106, is included for comparison. Table III gives the individual shoe and disk wear coefficients as well as the combined wear coefficients for all of the wear tests with coated disks. As indicated in table III, some of the tests were performed in duplicate. With one exception, the data was repeatable within a factor of 2 or better.

The laves phase cobalt alloy T800 gave very high wear while, within the reproducibility of the wear data, T400 wear was about the same as PS106. Wear with the simple CoMo coating was lower than that of the reference coating although as previously shown, friction was higher. Some of the coating material transferred to the shoes to form a scab-like deposit. With PS106T coatings, very low shoe and coating wear occurred. PS120 gave only slightly higher wear. The addition of

silver and calcium fluoride to T800 (PS121) dramatically reduced wear relative to T800 alone. On the other hand, formulating CoMo with silver and calcium fluoride resulted in increased wear. Also heavy, scab-like transfer of coating material deposited on the rub shoes as it did with unformulated CoMo coatings.

Friction and Wear to 650° C

Formulated coatings containing the laves phase cobalt alloys T400 and T800 were then evaluated at 400° and 650° C. The results along with the room temperature data are summarized in table III and are shown graphically in figure 8. For the most part, friction coefficients were in the range of 0.23 to 0.32 at all three temperatures. Wear of the cobalt-base, formulated coatings was consistently lower than with the nichrome base coating PS106. Both PS106 and PS106T showed a sharp increase in wear rate at 650° C. The increased wear at 650° C was probably attributable to the softening effect of the high content of silver (35 percent) and CaF_2 (30 percent) at this temperature. It is known that CaF_2 transforms from a brittle to a ductile state above about 500° C (11). In PS120 and 121, silver and CaF_2 contents were reduced to 20 percent each and the wear did not exhibit an upward trend at 650° C. PS120 gave low wear at all temperatures. PS121 gave higher wear than PS120 by a factor of two to three but lower wear than PS106 at all three temperatures.

Oxidation at 650° C

The favorable friction and wear properties of the formulated cobalt alloy coatings were not matched by their oxidation resistance at 650° C. They were all considerably oxidized after wear tests at 650° C although no evidence of spalling or delamination was apparent.

Therefore, a brief oxidation study was performed in which coatings of T400, PS120, and PS106 were held for 20 hours in 650° C air. The degree of oxidation

was estimated by the weight increases of the specimens. A thin film of oxide can be formed on the surface of silver at 200° C, but silver oxide decomposes into silver and oxygen by simple heating at temperatures above 300° C in air (12). Therefore silver did not oxidize during these experiments. It is also known that calcium fluoride does not oxidize significantly at 650° C (13). Therefore, all weight increases were attributed to oxidation of the T400 or nichrome in the coatings. The results are summarized in table IV. Only about 2 percent of the metal oxidized in the pure T400 coating, but when the same alloy was formulated with silver and calcium fluoride in PS120, about 70 percent of the alloy oxidized during the same furnace exposure. This indicates that silver or calcium fluoride or both severely accelerate the oxidation of T400.

Oxidation of nichrome in PS106 was also accelerated but not as much as T400 in PS120. The nichrome in PS106 was about 40 percent oxidized after 20 hours at 650° C. In additional oxidation test of PS106 at 900° C, oxidation was 78 percent complete or roughly equivalent to that of PS120 at 650° C. Therefore, for short duration application, the upper temperature limit for PS120 is about 650° C and for PS106 it is about 900° C. For long duration applications, the upper temperature limits would be lower by perhaps 100° to 150° C. A much more extensive oxidation study would be required to be more definitive than this.

CONCLUSIONS

Three cobalt-base alloys were compared to nichrome as matrix metals for composite self-lubricating coatings. Other components of the coatings were silver for achieving satisfactory low temperature friction and wear and calcium fluoride, a high-temperature solid lubricant. The major observations in this program follow.

1. In base line tests with unformulated cobalt alloy coatings, moderate to high wear and friction coefficients from 0.4 to 0.6 were observed under dry unlubricated conditions.

2. Coatings of the same cobalt alloys combined with silver and calcium fluoride gave much reduced wear and friction coefficients from 0.2 to 0.3 at room temperatures, 400° and 650° C. Wear was less and friction about the same as obtained with analogous coatings which contained nichrome instead of a cobalt alloy.

3. Oxidation sets the upper temperature limit for the cobalt base, composite coatings. They appear to be limited by oxidation of the cobalt alloys to an estimated 500° C for long duration use and to about 650° C for limited duration in an air atmosphere. The pure cobalt alloy coatings have much better oxidation resistance. The accelerated oxidation appears to be either a catalytic effect of the silver content and/or a fluxing action of calcium fluoride on the oxides of the cobalt alloys.

4. Nichrome oxidation is also accelerated in the composite coatings but to a lesser degree. The nichrome-base coating in general could be used for long duration to a least 750° C and for limited air exposures to 900° C.

5. The overall evaluation for the composite coatings studied in this program is that the cobalt alloys are superior to nichrome as matrix metals in regard to wear resistance but are inferior in regard to oxidation resistance at 650° C.

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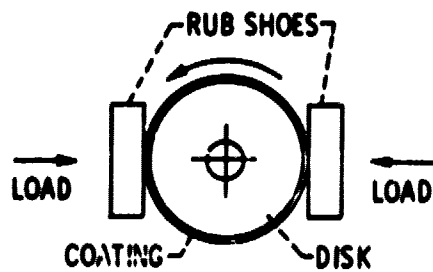


Figure 1. - Specimen configuration.

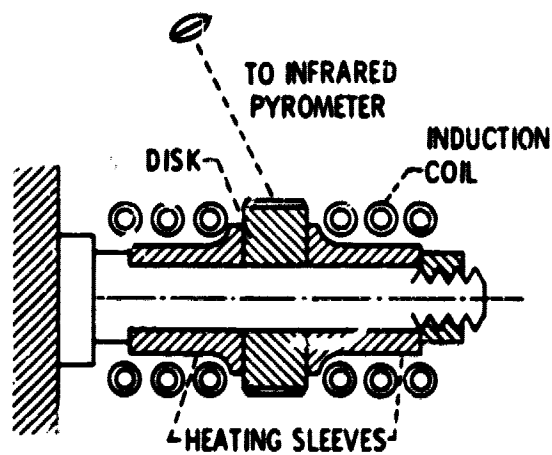


Figure 2. - Disk heating schematic.

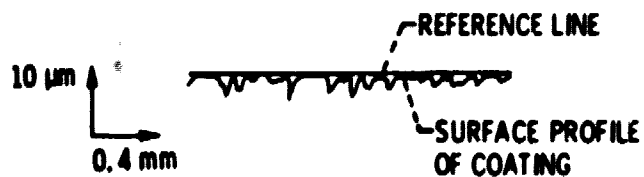


Figure 3. - Stylus profilometer trace of PS120 plasma-sprayed coating (after grinding) showing predominant contribution of porosity to surface roughness.

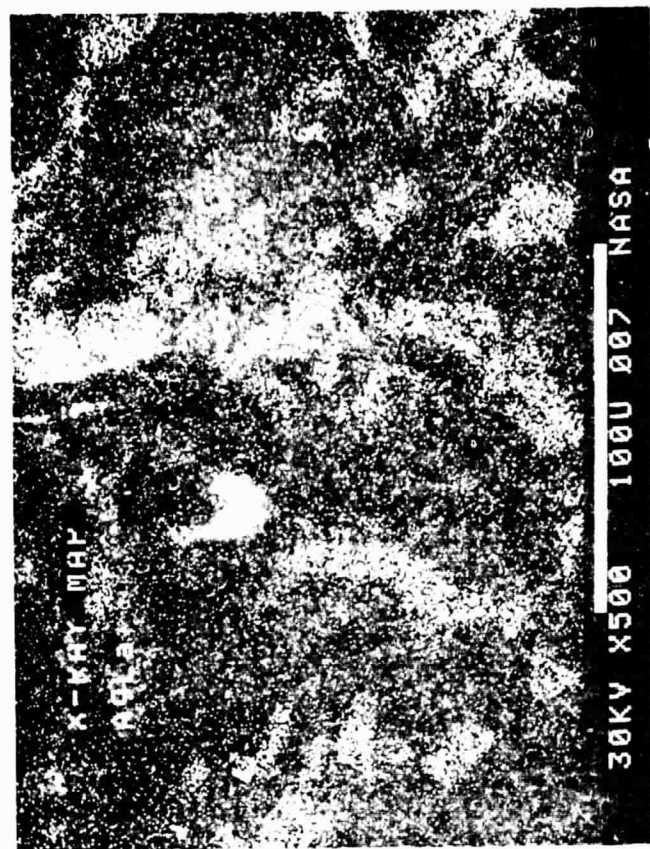
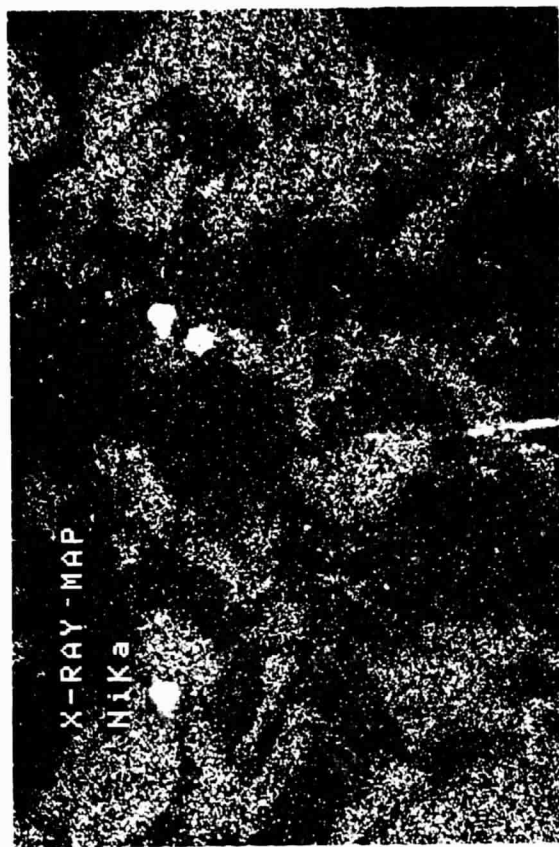


Figure 4. SEM and X ray maps showing distribution of components in PS106.

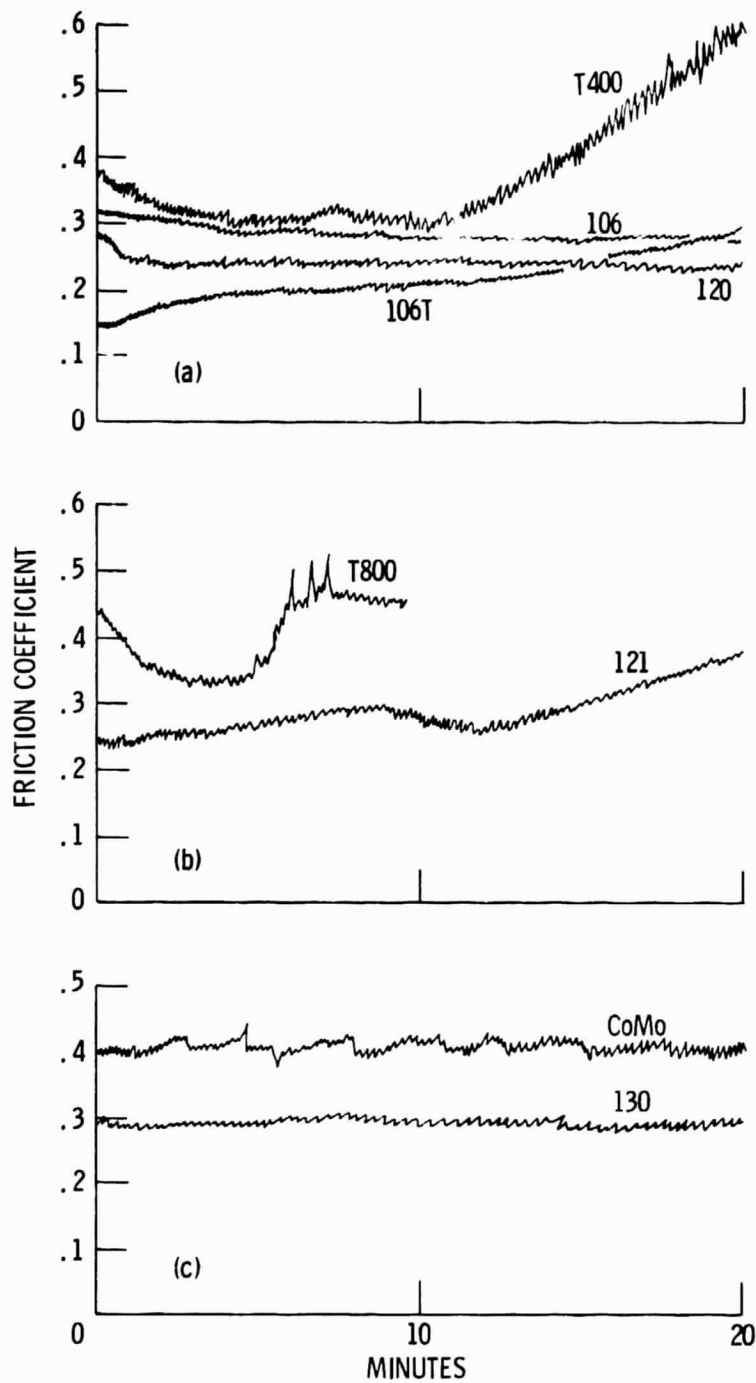


Figure 5. - Friction with cobalt alloys alone and combined with silver and calcium fluoride. Room temperature, 27.4 cm/sec, 222 N (50 lb) per shoe.

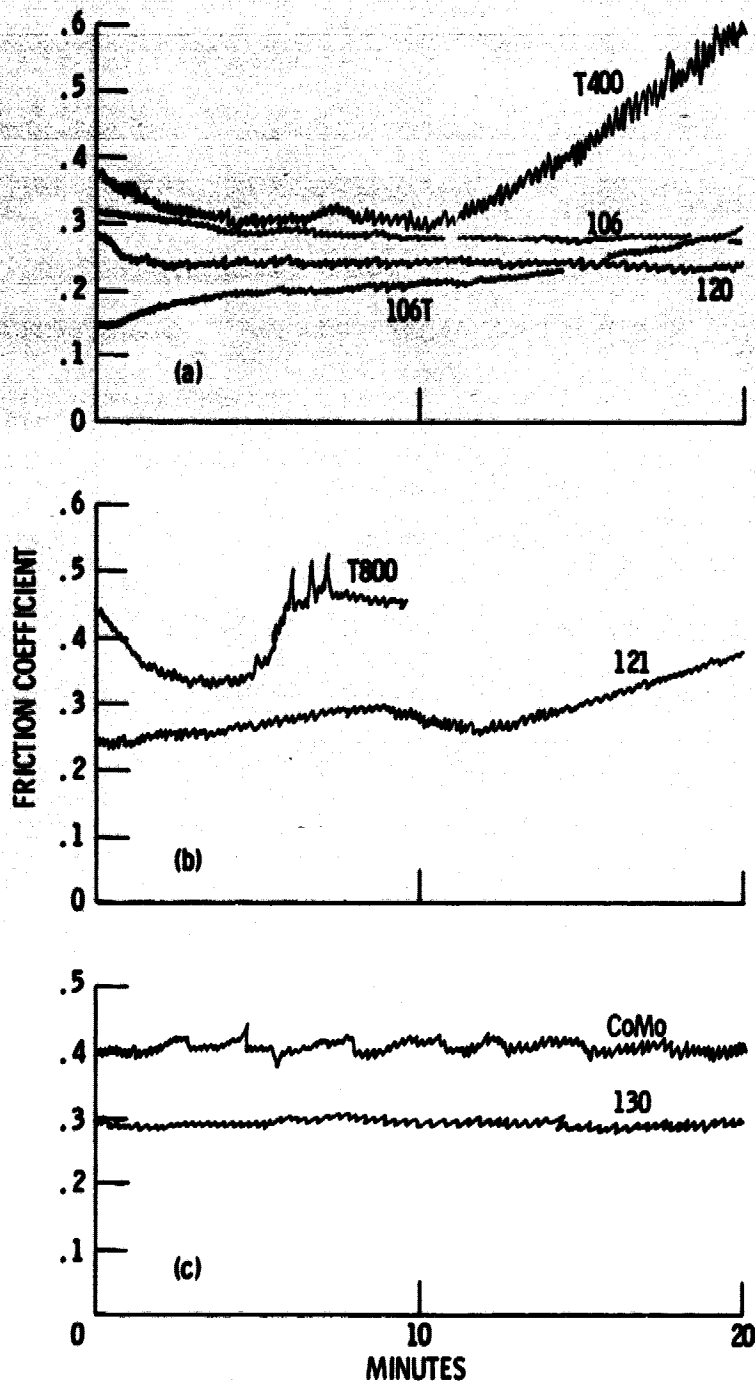


Figure 5. - Friction with cobalt alloys alone and combined with silver and calcium fluoride. Room temperature, 27.4 cm/sec, 222 N (50 lb) per shoe.

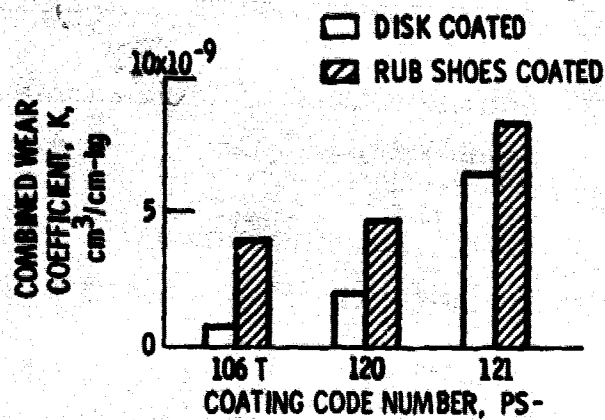


Figure 6. - Comparative effect of coating rub shoes or disks on combined shoe and disk wear. Room temperature, 27.4 cm/sec, 222 N (50 lb) load per shoe.

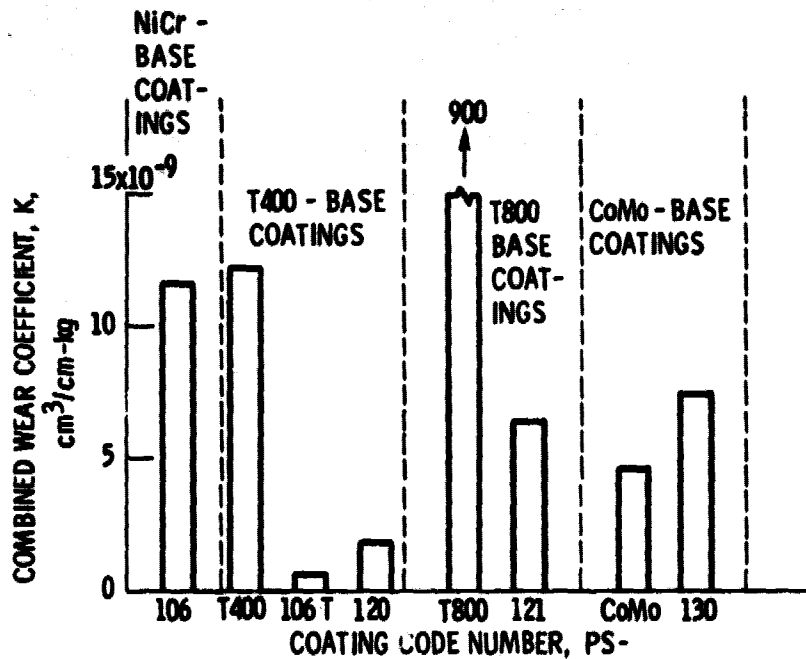


Figure 7. - Effect of coating composition on combined shoe and disk wear for uncoated shoes sliding against coated disks. Room temperature, 27.4 cm/sec, 222 N (50 lb) load per shoe.

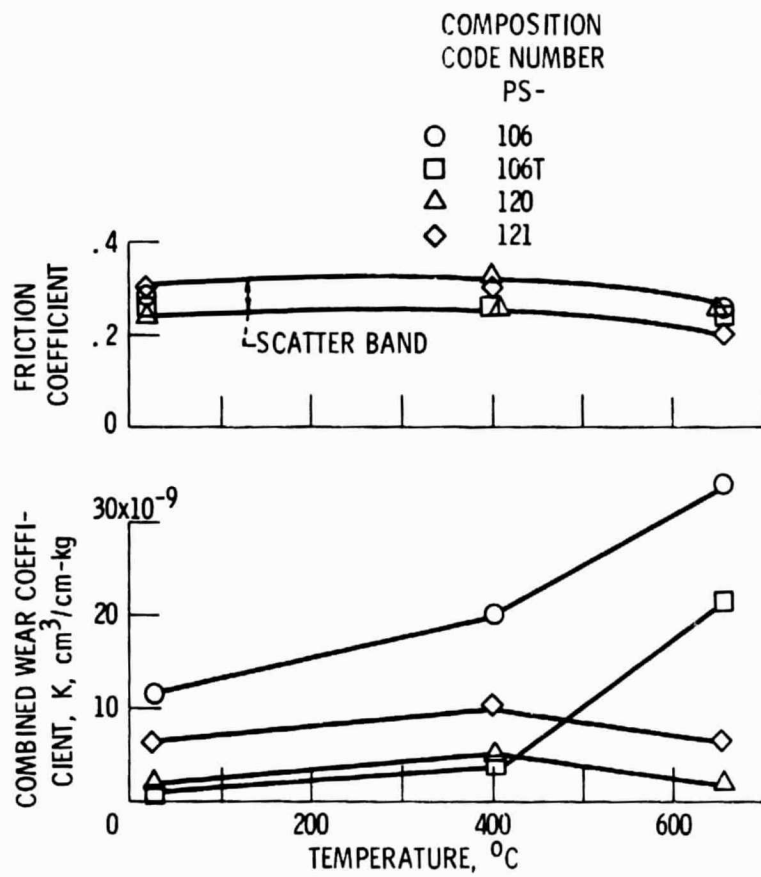


Figure 8. - Effect of temperature on typical friction and wear coefficients of some plasma sprayed coatings. 27.4 cm/sec, 222 N (50 lb) per shoe.

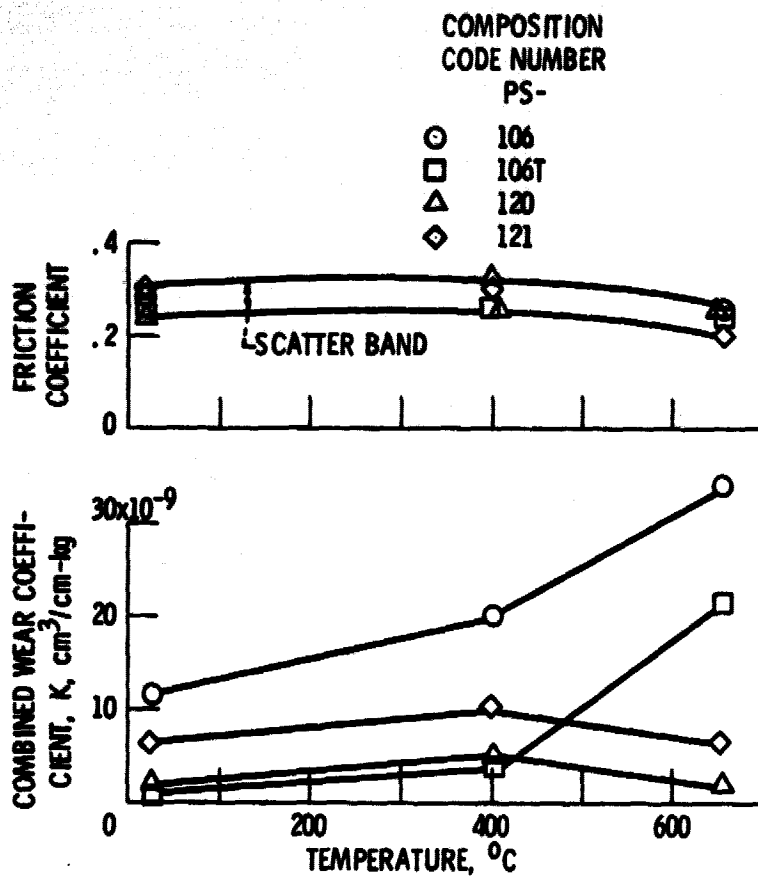


Figure 8. - Effect of temperature on typical friction and wear coefficients of some plasma sprayed coatings. 27.4 cm/sec, 222 N (50 lb) per shoe.

TABLE I. - CHEMICAL COMPOSITIONS OF
 PLASMA-SPRAYED COATINGS ON
 INCONEL 750 DISKS

[Bond coat: 0.008 cm thick NiCr
 (80-Nickel-20Chromium), lubricant coating: 0.01 cm composition indicated below.]

Coating code number PS-	Composition, wt %
T400	62Co-28Mo-8Cr-2Si
T800	52Co-28Mo-17Cr-3Si
CoMo	75Co-25Mo
106	35NiCr-35Ag-30CaF ₂
106T	35T400-35Ag-30CaF ₂
120	60T400-20Ag-20CaF ₂
121	60T800-20Ag-20CaF ₂
130	60CoMo-20Ag-20CaF ₂

TABLE II. - PLASMA SPRAY PARAMETERS

[Torch SG-1 design, hopper wheel continuously stirred powders at 1.4 to 2.0 rpm.
 Argon for both arc gas and powder carrier gas.]

Coating code number PS-	Argon gas flow rate		Electrical settings		Torch to target distance cm	Powder feed port on touch
	Arc m ³ /hr	carrier m ³ /hr	volts	amps		
T400 } T800 } CoMo }	1.84	0.28	33	600	11.4	Rear
106	1.27	.37	24	350	5.1	Front
106T } 120 } 121 } 130 }	1.84	.28	31	450	11.4	Front
NiCr	1.56	.31	28	350	12.5	Front

TABLE III. - DATA SUMMARY, FRICTION, AND WEAR FOR RENE 41 DOUBLE SHOES SLIDING ON VARIOUS PLASMA-SPRAYED

COATINGS AT 27.4 cm/sec UNDER 222 N (50 lb) LOAD PER SHOE

Coating code number PS-	Wear coefficient, $\text{cm}^3/\text{cm kgx}10^9$ and friction coefficients,											
	Room temperature				490° C				650° C			
	Coating	Shoes	Total	μ	Coating	Shoes	Total	μ	Coating	Shoes	Total	μ
T-400 laves Phase alloy	11.0	0.4	11.4	0.45	2.7	1.6	4.3	0.5				
	13.0	Transfer	13.0	$\pm .15$								
T-800 laves Phase alloy	890	1.6	892	0.40								
	930	2.6	933	$\pm .05$								
CoMo (75Co-25Mo)	4.2	Transfer	4.2	0.40								
	4.3		4.7	$\pm .02$								
106 (NiCr matrix)	7.0	4.6	11.6	0.28 $\pm .02$	20.0	Transfer	20.0	0.25 $\pm .02$	34.0	Transfer	34.0	0.25 $\pm .02$
106T (T400 matrix)	0.5	0.1	0.6	0.25 $\pm .02$	1.6	1.9	3.5	0.28 $\pm .02$	19.0	1.7	20.7	0.24 $\pm .02$
120 (T400 matrix)	0.9	0.2	1.1	0.25	2.3	2.5	4.8	0.3	1.4	Transfer	1.4	0.2
	2.4	.4	2.8	$\pm .02$								
121 (T800 matrix)	5.9	0.5	6.4	0.30 $\pm .02$	6.5	3.7	10.2	0.3 $\pm .02$	6.0	0.3	6.3	0.2 $\pm .1$
130 (CoMo matrix)	7.0	Transfer	7.0	0.27								
	7.8		7.8	$\pm .03$								

Note: The term "transfer" in shoe wear column indicates coating material transferred from disk to rub shoe wear measurements irrelevant.

TABLE IV. - ESTIMATED PERCENTAGES OF COBALT OR NICKEL

ALLOY CONTENT OF COATINGS THAT OXIDIZED IN 20 HOUR

FURNACE EXPOSURE

Percent T400 or NiCr Oxidation

	650° C	900° C
T400 (laves phase cobalt alloy)	2	Not tested
PS120 (60T400-20Ag-20CaF ₂)	70	Not tested
PS106 (35NiCr-35Ag-30CaF ₂)	40	78

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