JTTEE5 5:43-48
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High-Temperature Tribological Properties of Plasma-Sprayed Metallic Coatings Containing Ceramic Particles

S. Dallaire and J.-G. Legoux

Plasma-sprayed metal-base coatings containing ceramic particles were considered for high-temperature sealing of a moving metal component with a dense silica-base ceramic preheated at 800 °C. Selected metal powders (NiCoCrAlY, CuNi, CuNiIn, Ag, Cu) and ceramic particles (boron nitride, Zeta-B ceramic) were agglomerated to form suitable spray powders. Plasma-sprayed composite coatings and reference materials were tested in a modified pinion-disk apparatus in which the stationary disk consisted of a dense silica-base ceramic piece initially heated at 800 °C and allowed to cool during tests. The influence of single exposure and repeated contact with ceramic material on coefficient of friction, wear loss, and damage to the ceramic piece was evaluated.

1. Introduction

SOLID lubricants should be used instead of organic lubricants at temperatures exceeding their cracking point, except under conditions where the mating surfaces could be severely damaged by dry sliding wear. It is difficult to ensure adequate lubrication by introducing dry solid lubricants between surfaces because they do not maintain contact between the sliding surfaces (Ref 1). Plasma-sprayed ceramic-base coatings (Ref 2), metal-base coatings (Ref 3-7), and laser surface claddings (Ref 8) containing solid lubricants have been proposed to reduce wear and friction for temperatures ranging from 400 to 840 °C. Graphite and molybdenum disulfide provide lubrication to metal-base coatings up to 500 °C, and fluorides and glasses have been used with metal- and ceramic-base coatings at higher temperatures.

This work investigates the suitability of plasma-sprayed metallic coatings containing ceramic particles for sealing a heated silica-base ceramic part in contact with a steel or copper rotating drum for the containment of molten steel. Even though considerable work has been devoted to develop an adequate edge containment system, no edge dam concept has been found for scale-up beyond the pilot level (Ref 9). Seal coatings deposited on steel and copper drums should withstand repeated contact lasting 300 s against a dense silica-base ceramic material initially heated to 800 °C. They should possess as low a coefficient of friction as possible and a reduced wear rate. In addition, the seal coating should not damage the ceramic counterpiece. The sprayed coatings would be used in the as-sprayed state, having been deposited on steel or copper machinery that could not be postprocessed by grinding.

Spray metallic powders containing ceramic particles were fabricated and deposited by plasma spraying to manufacture these seal coatings. The wear properties of coated test rings were evaluated in a modified pin-on-disk apparatus in which the stationary disk consisted of a dense silica-base ceramic piece initially heated to 800 °C.

Keywords high-temperature performance, metal/ceramic coatings, sliding resistance, tribological properties

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2. Experimental Procedure

2.1 *Spray Powder Composition and Fabrication*

Spray powders of various compositions were fabricated, as no powder was commercially available to form coatings with a low coefficient of friction and high-temperature stability. The metallic component of these powders was selected for several reasons. Silver and copper were selected for their low shear strength, high thermal conductivity, and low affinity for oxygen. Copper-30Ni (wt%) alloys were considered for their shear strength and greater oxidation resistance compared to pure copper. Copper-nickel-indium is also known to exhibit high resistance to fretting wear. The NiCoCrAlY high-temperature oxidation-resistant alloy was also chosen to form spray powders. Table 1 shows the chemical compositions and particle sizes of the powders used in the fabrication of composite spray powders.

Prior work consisted of introducing boron nitride as a solid lubricant between the hot stationary silica-base ceramic part and the cold metallic moving parts. Therefore, one issue of this work

Table 1 Chemical compositions and particle sizes of spray powder constituents

Material	Composition(a), wt%	Mean particle size, µm
NiCoCrAlY	Ni, 22.23% Co, 17.03% Cr, 12.43% Al, 0.48% Y, 0.3% impurities	20 and 60
Silver	99.99% Ag	1
CuNi	Cu, 38% Ni	25
CuNiIn	Cu, 36.8% Ni, 5.1% In, 0.13% impurities	22
Cu	99.3% Cu, 0.7% O	1
BN	99.5% BN	10
Zeta-B	Proprietary	>1

(a) Chemical compositions supplied by powder manufacturers.

was to form composite spray coatings containing boron nitride. A proprietary Zeta-B ceramic material was also mixed and agglomerated with fine copper powders for testing in this particular application.

Spray powders of different compositions were fabricated by the mechanical agglomeration of metal and ceramic powders using a polymeric binder. The powders were sieved to −106+38 μm.

2.2 *Plasma Spray Deposition*

Composite spray powders were initially sprayed to optimize spray parameters as determined with optical or scanning electron microscopy on metallographic sections. Some of the fabricated coatings with a high volume fraction of boron nitride did not exhibit sufficient strength to be tested in sliding wear conditions. The composite spray powders that produced good-quality coatings are given in Table 2.

Table 2 Compositions of spray powders

Spray powder designation	Metal volume content, %	Ceramic volume content, %
Ag-20BN	80Ag	20BN
NiCoCrAlY	100NiCoCrAlY	...
NiCoCrAlY-25BN	75NiCoCrAlY	25BN
NiCoCrAlY-40BN	60NiCoCrAlY	40BN
CuNi-25BN	75CuNi	25BN
CuNiIn-25BN	75CuNiIn	25BN
Cu/Zeta-B	45Cu	55Zeta-B

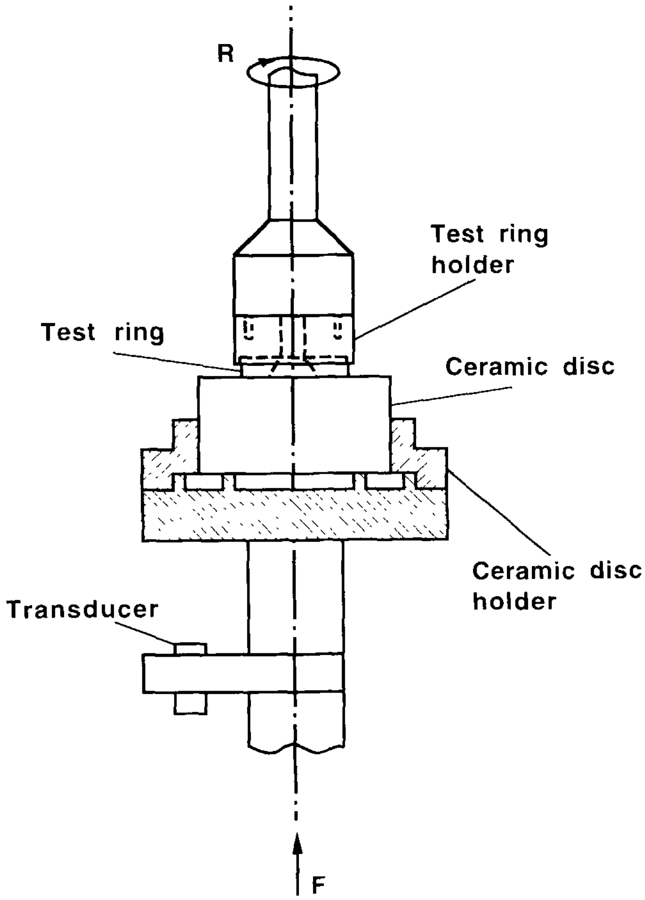


Fig. 1 Schematic of the tribometer modified to accommodate sliding rings and a preheated ceramic counterpiece

2.3 *Fabrication of Coated Rings*

Metal-base coatings for wear testing were obtained by atmospheric plasma spraying of the agglomerated powders described in Table 2 onto copper and mild steel cylindrical ring surfaces previously cleaned and grit blasted. NiCoCrAlY coatings were also deposited for comparison purposes by spraying a −74+37 μm powder with the same chemical composition given in Table 2.

Table 3 presents the deposition parameters for each coating and the characteristics of the coatings formed. During spraying, the copper or steel cylindrical rings were fixed on a water-cooled substrate holder. A good surface finish after spraying was desired because the actual components would not be subjected to grinding after coating deposition. Depending on the sprayed material, the deposition efficiency was between 57 and 90% and the surface roughness (R_a) was between 4 and 9 μm.

2.4 *Performance Evaluation*

Friction and wear testing were carried out using a pin-on-disk tribometer (Fig. 1) modified to accommodate the sintered 99.9% fused-silica disks previously heated to 800 °C. Disks were 90% dense and their mean surface roughness (R_a) was 3 μm. The rotating coated specimens mated against the hot stationary ceramic disk. A normal load of 3.15 kN was applied through the stationary spindle by dead-weight loading. The friction torque was continuously recorded during all tests, and data were converted to obtain frictional force. The coefficient of friction at the end of the test and the range of its fluctuation were reported.

A typical experiment can be described as follows. A plasma-coated cylindrical ring having an area of 516 mm^2 was first mounted on the rotary spindle. Then the ceramic disk, heated to 800 °C, was placed in the stationary holder, the load applied, and the specimen maintained in rotation (104 rev/min) for the duration of the test. Two types of tests were performed. Samples were subjected to sliding wear for a period of 3600 s, the ceramic disk being allowed to cool to a temperature of 50 °C. This test was termed type 1. The type 2 test consisted of exposing the test rings for three 300 s periods, the ceramic counterpiece cooling to 355 °C. The temperature profiles during these tests are shown in Fig. 2. The wear debris was swept off after each sliding wear test. The wear loss of the coated specimens was determined by weighing them before and after the test.

3. Results

3.1 *Weight Loss after Sliding Wear Tests*

Figures 3 and 4 show the coating weight loss after type 1 and type 2 tests, respectively. As shown in Fig. 3, the CuNiIn-25BN coating performed better than the CuNi-25BN, NiCoCrAlY-

25BN, and NiCoCrAlY-40BN coatings. The NiCoCrAlY coating presented the lowest weight loss and the CuNi-25BN the highest, reaching 1470 mg.

Most of the coatings and reference materials increased their weight loss with the exposure period for repeated tests at 800 °C (Fig. 4). However, the NiCoCrAlY coating had roughly the same weight loss after each exposure. The Ag-20BN coating delaminated upon the second exposure. The Cu/Zeta-B ceramic experienced the lowest total weight loss for the three exposure periods.

3.2 *Coefficient of Friction*

The coefficient of friction varied widely between 0.05 and 0.45, depending on the tested material and the type of thermal exposure. Among coatings exposed to the type 1 test, the Ag-20BN coating had the lowest coefficient of friction (0.07), whereas the NiCoCrAlY-25BN coating and copper exhibited the highest (0.4), as shown in Fig. 5.

Upon exposure to three thermal cycles, the plasma-sprayed coatings and bare copper ring behaved differently. Indeed, as shown in Fig. 6, the coefficients of friction of all plasma-sprayed coatings containing boron nitride particles (NiCoCrAlY-40BN and -25Bn, CuNiIn-25BN, CuNi-25BN, and Ag-20BN) increased with the thermal cycles. The NiCoCrAlY coating and metal samples (copper and steel) were not sensitive to thermal cycles. The plasma-sprayed Cu/Zeta-B ceramic coating showed a coefficient of friction of 0.05 after the first exposure. This decreased to 0.03 after the third thermal cycle and represented the lowest observed in this study.

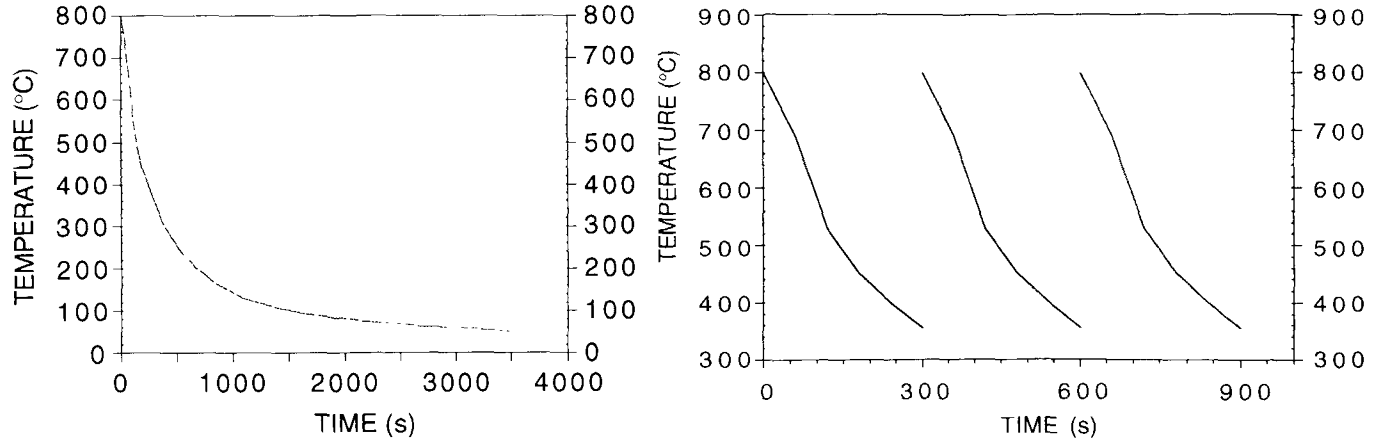
In comparing the coefficients of friction of materials after testing, it should be observed that the NiCoCrAlY-40BN, NiCoCrAlY-25BN, Ag-20BN, and Cu/Zeta-B ceramic plasma-sprayed coatings exhibited a higher coefficient of friction after the type 1 test than after the type 2 test. On the other hand, the NiCoCrAlY, CuNi-25BN, and CuNiIn-25BN plasma-sprayed coatings had a lower coefficient of friction after the type 1 test.

3.3 *Fluctuation in the Coefficient of Friction*

Nearly every coating and reference material experienced fluctuations in its coefficient of friction for all tests. Exceptions

Table 3 Plasma spray deposition parameters and coating characteristics

Spray powder	Arc gas, L/s	Arc voltage, V	Arc current, A	Spray distance, mm	Thickness, µm	Deposition efficiency, %	Number of passes	Surface roughness (R_a), µm
Ag-20BN	Ar 0.8	33	500	63.5	508	57	20	6
NiCoCrAlY	Ar-He 0.8-3.0	50	700	101.6	630	73	20	9
NiCoCrAlY-25BN	Ar-He 0.8-3.0	50	500	76.2	574	77	15	4
NiCoCrAlY-40BN	Ar-He 0.8-3.0	50	500	76.2	551	65	20	5
CuNi-25BN	Ar-He 0.8-3.0	50	500	76.2	599	63	15	4.5
CuNiIn-25BN	Ar-He 0.8-3.0	50	500	76.2	927	90	15	4
Cu/Zeta-B	Ar-He 0.8-3.0	50	500	76.2	475	60	20	5.5



(a) (b)

Fig. 2 Thermal cycles imposed on sliding wear experiments (a) 3600 s exposure to a temperature decreasing from 800 to 550 °C (type 1 test). (b) Three 300 s exposures to a temperature decreasing from 800 to 355 °C (type 2 test)

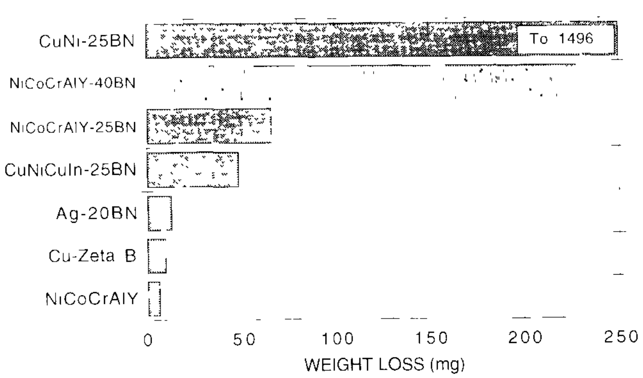


Fig. 3 Weight loss of sliding rings after a 3600 s exposure to a temperature decreasing from 800 to 50 °C (type 1 test)

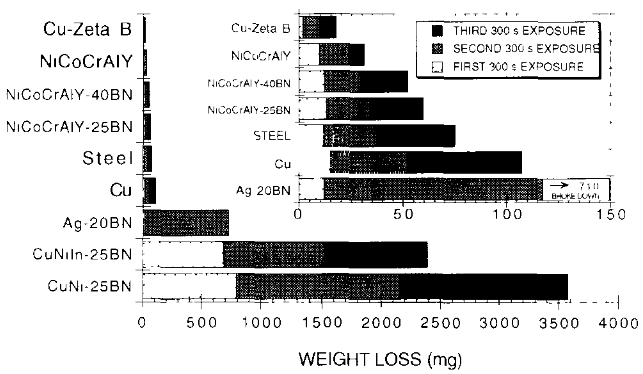


Fig. 4 Weight loss of sliding rings after three 300 s exposures to a temperature decreasing from 800 to 355 °C (type 2 test). The inset figure shows more detail for the low-weight-loss test results.

were the Ag-20BN coating for the type 1 test and the Cu/Zeta-B ceramic coating for the three exposures of the type 2 test.

3.4 *Damage to the Ceramic Part*

With the exception of the plasma-sprayed Cu/Zeta-B ceramic coating, all the coatings and materials damaged the ceramic counterpiece. The NiCoCrAlY dug out a deep wear track of the same dimensions as the coated ring, although this coating did not wear much in both types of tests. The Ag-20BN coating did not scratch the ceramic disk, but transferred material to it during the first 300 s sliding test (type 2). Except for the plasma-sprayed Cu/Zeta-B ceramic coating, all the coatings left a residue that smeared and impregnated the wear track. During sliding the plasma-sprayed Cu/Zeta-B ceramic produced debris consisting of a very fine, loose dust that did not adhere to the ceramic part.

3.5 *Damage to Sliding Rings*

All the coated and bare rings were covered with scars on their surfaces with the exception of steel, plasma-sprayed CuNiIn-25BN, and Cu/Zeta-B ceramic coatings after the type 1 test, and plasma-sprayed NiCoCrAlY-25BN, NiCoCrAlY-40BN, and Cu/Zeta-B ceramic coatings after the type 2 test. The worn surfaces of these coated rings was partly (for NiCoCrAlY-25 and -40BN) or mostly (for Cu/Zeta-B ceramic) smooth.

4. Discussion

4.1 *Exposure for 3600 s at a Temperature Decreasing from 800 to 50 °C*

During the type 1 test, sliding rings were exposed only once at 800 °C and slid for 2100 s against the dense silica-base material which was at less than 100 °C (Fig. 2). Therefore, they received less heat than in the 300 s exposure test. In this low-temperature cycle, the CuNiIn-25BN coating performed better than the CuNi-25BN and NiCoCrAlY-40 and -25BN coatings, as shown in Fig. 3. The lubricating and antiseizure properties of indium are responsible for this low coefficient of friction (0.17) and lower wear loss at low temperature (Fig. 3 and 5). Due to its malleability, the Ag-20BN plasma-sprayed coating showed a low coefficient of friction (0.07) and a low weight loss. The NiCoCrAlY coating presented the lowest weight loss and a coefficient of friction lower than 0.09. This coating, however, severely damaged the ceramic part. Most likely, the large amount of debris trapped in the wear track formed a pad of particles that presented less contact area and reduced the coefficient of friction at the end of the test.

4.2 *Three Exposures at a Temperature Decreasing from 800 to 355 °C*

Upon exposure to thermal cycles, sliding rings behave differently. With the exception of plasma-sprayed NiCoCrAlY-25BN, NiCoCrAlY-40BN, and Cu/Zeta-B ceramic coatings, all other coatings exhibited a coefficient of friction higher after the third thermal cycle (type 2 test) than after the type 1 test. As the temperature falls between 800 and 355 °C, sliding conditions are more severe and higher weight loss is observed (Fig. 4). The coefficients of friction of plasma-sprayed NiCoCrAlY-25BN and -40BN coatings (Fig. 6), however, are lower after the third thermal cycle than those recorded for an exposure to a temperature decreasing from 800 to 50 °C (type 1 test) (Fig. 5). This indicates that these coatings possess some lubricant properties at high temperature as opposed to the plasma-sprayed NiCoCrAlY coating, although their weight losses are higher.

4.3 *Effect of Repeated Exposures*

Most of the coatings showed increased weight loss and coefficient of friction upon successive exposures to 800 °C (Fig. 4 and 6). Weight loss increases after each thermal cycle (Fig. 4), whereas the coefficient of friction increases from the previous cycle to a higher value. This result indicates that the coatings are constantly damaged when exposed to high temperatures and that no protection is afforded them. Although the oxidation temperature is different for all materials, these coatings are exposed within a temperature range where oxidation could be observed. The formation of oxides, however, can reduce both friction and wear, as observed for plasma-sprayed NiCoCrAlY-25BN, NiCoCrAlY-40BN, and Cu/Zeta-B ceramic coatings (Fig. 6).

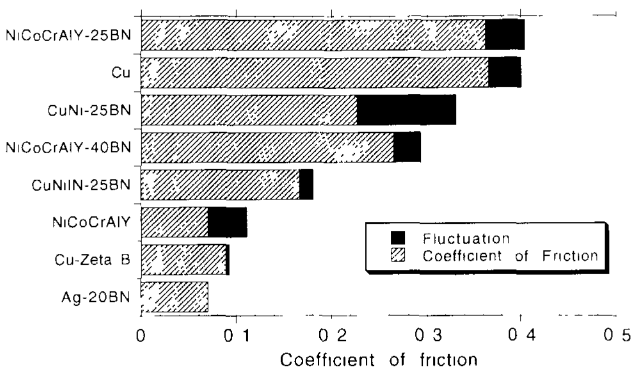


Fig. 5 Coefficient of friction of sliding rings at the end of the 3600 s exposure to a temperature decreasing from 800 to 50 °C (type 1 test)

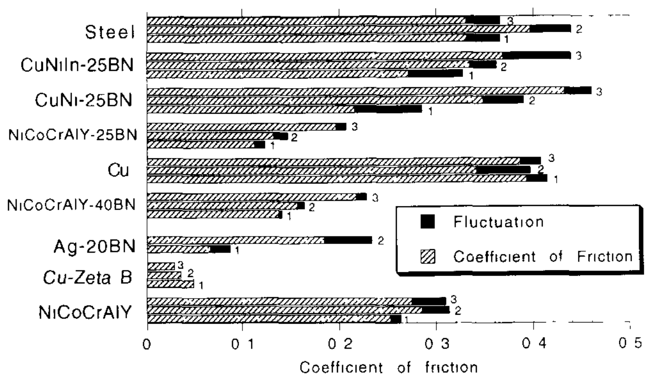


Fig. 6 Coefficient of friction of sliding rings at the end of each 300 s exposure to a temperature decreasing from 800 to 355 °C (type 2 test)

4.4 *Cause of Low Coefficients of Friction*

The low coefficients of friction observed for plasma-sprayed NiCoCrAlY-25BN, NiCoCrAlY-40BN, and particularly Cu/Zeta-B ceramic coatings are most likely due to the formation of glazes on their surface after exposure to high temperature. The gradual oxidation of these coatings produces debris, which forms a thin superficial layer that appears polished and dense. This layer is composed of different metal oxides and is most likely responsible for reducing friction and wear in oxidizing atmospheres.

4.5 *Formation of Glazed Layers*

The formation of these glazed layers involves complex mechanisms involving mechanical, chemical, and thermal actions, which have been described previously (Ref 10). The glazes appear more quickly at high temperature on the surface of a material that can be more readily oxidized. A glazed surface is thought to be formed at temperatures between 100 and 400 °C below the oxidation temperature of the material, resulting in a low coefficient of friction and wear rate (Ref 10). Although copper has a low affinity for oxygen, the temperature reached during the tests is beyond its onset oxidation temperature (185 °C) (Ref 11). Blisters and ceramic particles within the coating can modify the oxidation kinetics of copper (Ref 11) and thus the composition and microstructure of the glazed layer.

4.6 *Role of Coating Uniformity*

The plasma-sprayed Cu/Zeta-B ceramic coatings are composed of very fine particles that can be pressed into the glaze and thus exhibited the best performance, showing a coefficient of friction of 0.05 after the first exposure. It further reduced to 0.03 at the end of the third exposure. The good uniformity achieved within this coating results from the small feedstock particle size and leads to good tribological behavior. Reduction in particle size has enhanced the uniformity of self-lubricating coatings (Ref 12). The NiCoCrAlY coatings containing 25 and 40 vol% BN had a coefficient of friction of 0.14 after the first thermal cycle and 0.22 after the third cycle and exhibited smooth surfaces. However, the increase in their coefficient of friction suggests that the glazed layer is unstable or that the coating strength is adversely affected by repeated exposures to high temperatures. Increasing the BN content from 25 to 40 vol% within these coatings results in the degradation of mechanical properties, as observed earlier (Ref 13).

5. Conclusions

Plasma-sprayed metallic coatings containing ceramic exhibited different behaviors when submitted to sliding against a dense silica-base ceramic preheated at 800 °C. The relative performance depended on the coating composition and the type of thermal exposure. When exposed to a temperature decreasing from 800 to 50 °C, the high-temperature oxidation-resistant NiCoCrAlY coating and coatings containing malleable metals exhibited low coefficients of friction and reduced wear losses. However, most of them severely damaged the ceramic counterpiece. After three 300 s exposures to a temperature decreasing from 800 to 355 °C, the Cu/Zeta-B ceramic, NiCoCrAlY, NiCoCrAlY-25BN, and NiCoCrAlY-40BN coatings exhibited lower weight loss. However, the tribological properties of most of these coatings, except the Cu/Zeta-B ceramic coating, irreversibly deteriorated after thermal cycling.

The plasma-sprayed Cu/Zeta-B ceramic coating exhibited the lowest coefficient of friction (less than 0.1). The formation of a glazed layer composed of oxidation products is responsible for the outstanding tribological properties of this coating. The low thermodynamic affinity of copper for oxygen and coating homogeneity due to the fineness of powder constituents most likely contribute to the formation and replenishment of this glazed layer, which lasted over the thermal cycles.

Although restricted to coatings sliding against a silica-base ceramic initially heated at 800 °C, this study can be used as a basis in the design of high-temperature self-lubricating coatings for sliding contact seals in high-performance machinery.

Acknowledgments

The authors wish to acknowledge Mr. S. Boivin for preparing the spray powders and manufacturing the sprayed coatings, S. Turenne and D. Gerbeau for participating in sliding wear tests, H. Levert for modifying the pin-on-disk apparatus, and M. Thibodeau for the microscopy analysis. The authors are also indebted to Mr. F.G. Hamel of the Strip Casting Group for discussions on the testing conditions and performance evaluation.

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