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Mechanical and Tribological Properties of Plasma-Sprayed Cr_3C_2-NiCr, WC-Co, and Cr_2O_3 Coatings

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Mechanical properties such as Young's moduli and fracture toughness of plasma-sprayed Cr_3C_2-NiCr, WC-Co and Cr_2O_3 coatings were measured. The tribological properties of the three kinds of coatings were investigated with a block-on-ring self-mated arrangement under water-lubricated sliding. Furthermore, the influences of the mechanical properties on the tribological properties of the coatings were also examined. It was found that the Young's moduli, bend strengths and fracture toughness of the coatings were lower than the corresponding bulk materials, which may be attributed to the existence of pores and microcracks in the coatings. Among the three kinds of coatings, the magnitude of wear coefficients, in decreasing order, is Cr_3C_2-NiCr, WC-Co and Cr_2O_3, and the wear coefficient of Cr_2O_3 coating was less than 1×10^{-6} $mm^3N^{-1}m^{-1}$. The wear mechanisms of the coatings were explained in terms of microcracking and fracturing, and water deteriorated wear performance of the coatings. The higher the fracture toughness and the lower the porosity and length of microcracking of the coating, the more the wear-resistance of the coating.

Keywords Cr_3C_2-NiCr, Cr_2O_3, fracture toughness, tribological property, WC-Co, Young's modulus

1. Introduction

In today's materials design, ceramic coatings play an increasingly important role in applications where high temperature, corrosion, oxidation, and wear come into play (Ref 1). It is necessary to understand the mechanical and tribological properties of the coatings for successful applications as structural components.

Young's modulus and fracture toughness are basic mechanical properties for characterizing coating performance. For example, the stress-strain behavior, contact stress field, surface hardness, coating delamination, cracking, bending, and residual stress state of coated systems all depend on the Young's modulus of the coating (Ref 2-4). Some years ago, Young's moduli of thermal spray coatings were often estimated by referring to the corresponding bulk materials (Ref 5, 6). Recently, the Young's moduli of the coatings have been reported to be far lower than the corresponding bulk materials (Ref 2, 7-9). Fracture toughness characterizes the resistance of a material to crack propagation or to damage including mechanical, thermal shock, and stress corrosion (Ref 10). Several fracture toughness testing techniques such as the double-cantilever beam, the single-edge notch beam, the double torsion, and the indentation technique have been developed on the basis of fracture mechanics. Except for the indentation technique, the applications of the other fracture toughness testing techniques for thermal spray coatings are not feasible because the required specimen thickness and geometry may be very difficult to achieve. There is limited data about the fracture toughness of thermal spray coatings (Ref 6). Therefore, the determination of these mechanical properties have assumed greater importance for thermal spray ceramic coatings being considered as structural components.

Plasma sprayed Cr_3C_2-NiCr, WC-Co, and Cr_2O_3 are traditionally wear-resistant coatings. There have been some reports about the tribological properties of the coatings under dry friction or oil lubrication conditions (Ref 11, 12). However, there are applications where ceramic coatings are used in fluid environments (Ref 13, 14). Thus, it is also very important to identify the influence of such environments on mechanical properties and the tribological property of the coatings.

The purpose of this paper is (1) to present mechanical properties such as Young's modulus and fracture toughness of plasma sprayed Cr_3C_2-NiCr, WC-Co, and Cr_2O_3 coatings that were measured adopting methods introduced in Ref 3 and 10, (2) to investigate tribological properties of the coatings under water-lubricated sliding, and (3) to discuss the influence of mechanical properties on tribological properties of coatings.

2. Experimental Procedure

2.1 Coating Process

Coatings of Cr_3C_2-NiCr, WC-Co, and Cr_2O_3 were applied by atmosphere plasma spray using optimized spray parameters as shown in Table 1. The coatings for measurement of mechanical properties were sprayed on aluminum plates of 10 by 15 by 2 mm up to 3.0 mm thick and then removed from the substrates. The coatings for tribological tests were deposited on 1Cr18Ni9Ti stainless steel formed to the specific dimensions.

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2.2 Measurements of Mechanical Properties

The bend strengths and Young's modulus of the coatings were obtained via a three-point bend test (Ref 3) employing an Instron tester. The bend test specimens were formed into specific dimensions—40 mm long, 5 mm wide, and 1.5 mm thick.

The fracture toughness of the coatings was determined with the indentation technique (Ref 10). An Akashi Avk-A indenter (Akashi Seisakusho Ltd., Japan) was used on 20 by 10 by 1.5 mm specimens. The indentation parameters of radial crack length $2c$, impression diagonal $2a$, and hardness H were measured by the optical microscopy immediately after releasing the load. In addition, the density and porosity of the coating were measured by the Archimedean method. All of the above property parameters were the average of five identical specimens and exhibited a coefficient of variance of less than 10%.

2.3 Tribological Tests

Friction and wear tests were conducted on a block-on-ring arrangement of an MM-200 wear tester (Shanghai University, Shanghai), under deionized water (see Ref 12, 15). The rings were 40 mm outer diameter, 16 mm inner diameter, and 10 mm thick. The blocks were 30 by 7 by 6 mm with a contact width of 6 mm on the ring. The surface roughness, Ra, of both Cr_3C_2-NiCr and WC-Co coatings before the friction and wear tests were from 0.40 to 0.6 μm, and the Cr_2O_3 coating was 0.2 μm R_a after polishing. The tests were performed under the following conditions: a load of 400 N and a rotational speed of 200 rev/min, which was equal to the sliding velocity of 0.42 m/s at the contact surface of specimen. The friction coefficient was obtained from the friction torque, which was obtained directly from the tester by dividing the load by the ring radius. Wear coefficients were acquired from the wear mass loss divided by load. Prior to weighing, the specimens were cleaned in an ultrasonic bath with acetone for 30 min and then dried in an oven at 120 °C for 60 min.

An EPMA-8705QHII type scanning electron microscope (SEM; Shimadzu Corp., Shimadzu, Tokyo) was used to observe the surface morphology, and an ESCA-2 x-ray photoelectron spectrometer (XPS) analyzed the chemical compositions of the worn surfaces of the coatings.

3. Results and Discussion

3.1 Coating Characteristics

Figure 1 indicates the SEM micrographs of the coating surfaces after polishing. As indicated in Fig. 1, the coatings contained some pores and microcracks, which typically occur in the plasma spray process. Among the three kinds of coatings, the porosity and length of microcracks of both Cr_3C_2-NiCr and WC-Co coatings were higher than those of the Cr_2O_3 coating.

3.2 Mechanical Properties

Table 2 lists the mechanical properties of the coatings. It should be pointed out that only the bend strength but not Young's modulus of the WC-Co coating was measured via three-point bend tests. In order to compute the fracture toughness of the coating, the

Table 1 Optimized plasma spray parameters

Code	Coating material	Plasma Power, kW	Plasma gas flow rate, L/min	Powder feed rate, g/min	Spraying distance, mm
CRC	Cr_3C_2-25wt%NiCr	18	40 (argon) + 5 (hydrogen)	50	100
WCC	WC-17wt%Co	21	48 (argon) + 4 (hydrogen)	60	100
CRO	Cr_2O_3	32	50 (nitrogen) + 5 (hydrogen)	40	110

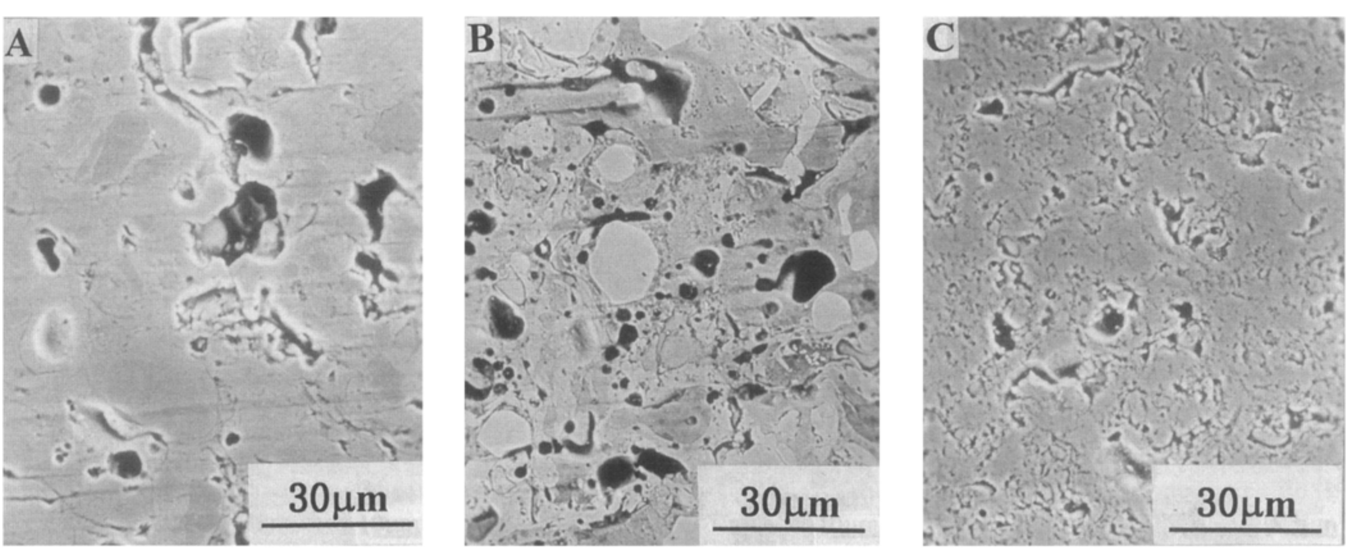

Fig. 1 SEM micrographs of surfaces of as-received coatings after polishing: A, Cr_2C_3-NiCr; B, WC-Co; C, Cr_2O_3

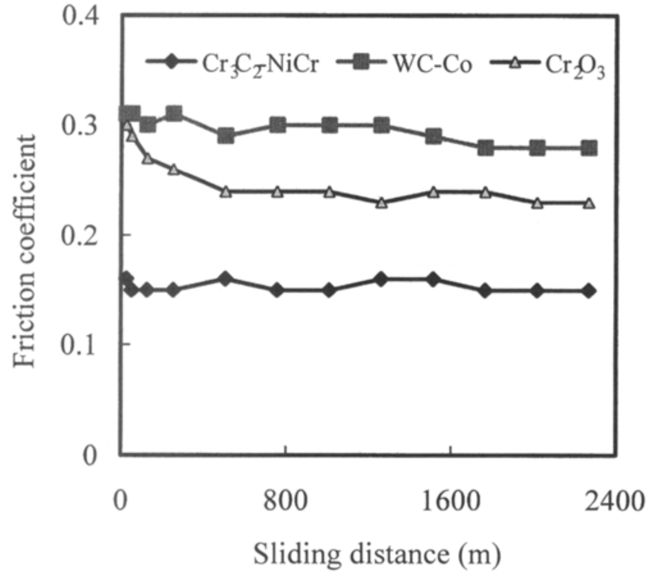

Fig. 2 Friction coefficient of different friction pairs

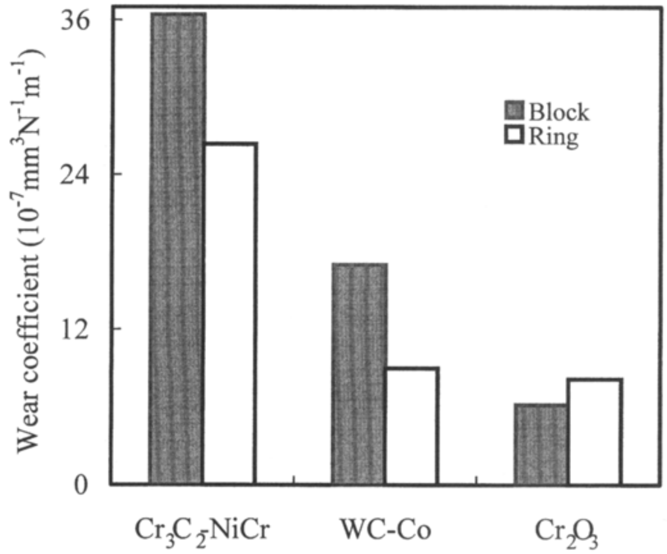

Fig. 3 Wear coefficient of different friction pairs

Table 2 Results of measurements of mechanical properties of the three kinds of coatings

Coating	Density, Mg/m^3	Porosity, %	Microhardness, GPa	Bend strength, MPa	Young's modulus, GPa	Fracture toughness, $MPa\sqrt{m}$
CRC	6.16	10.7	9.6	60	126	5.4
WCC	13.87	10.8	12.1	...	113	8.4
CRO	4.52	4.7	10.0	75	132	3.5

Table 3 XPS results of the worn surfaces of the block specimen

	Binding energy, eV			
Specimen	$Cr2p_{3/2}$	$Ni2p_{3/2}$	$W4f_{7/2}$	$Co2p_{3/2}$
Cr_3C_2-NiCr coating fresh surface	573.9	852.8	...	...
Cr_3C_2-NiCr coating worn surface	574.3, 576.5 (I)	852.8, 855.8 (I)	...	...
WC-Co coating fresh surface	...	...	32.0 (I), 32.5, 35.3	777.9 (I), 779.6
WC-Co coating worn surface	...	...	32.0, 32.5, 35.3 (I)	777.9, 779.6 (I)
Cr_2O_3 coating fresh surface	576.5	...	...	...
Cr_2O_3 coating worn surface	576.5	...	...	...

I, intensive peak in the XPS spectrum

Young's modulus of the coating was adopted from Ref 7. From Table 2, it can be seen that the porosity of both Cr_3C_2-NiCr and WC-Co coatings were higher than that of the Cr_2O_3 coating, which agreed with the SEM micrographs of Fig. 1. The Young's modulus, bend strength, and fracture toughness of the coatings were far lower than the corresponding bulk materials (Ref 11, 16-18), which may be attributed to the existence of pores and microcracks in the coatings that lower the strength of the coatings (Ref 19). The results also agreed with the reports of Ref 2 and 7 to 9.

3.3 Tribological Properties

The friction and wear coefficients of the three kinds of self-mated coatings under water-lubricated sliding are shown in Fig. 2 and 3. Figure 2 indicated the order of friction coefficients among the three coatings was, in decreasing order, WC-Co, Cr_2O_3, and Cr_3C_2-NiCr. From Fig. 3 it can be seen that the Cr_3C_2-NiCr and WC-Co coatings exhibited the worse wear performance in water. The Cr_2O_3 coating in water appeared wear resistant, and its wear coefficient was less than $1 \times 10^{-6} mm^3/N \cdot m$; however, the friction coefficient of the coating was more than 0.2 (Fig. 2), which is the minimal criterion needed for general tribological application (Ref 20).

Figure 4 shows the SEM micrographs of the worn surfaces for the three coatings. It can be seen that all the coatings indicate cracking and particle fracturing along pores and microcracks during water-lubricated sliding. In contrast, the wear intensity of the Cr_3C_2-NiCr and WC-Co coatings was greater than that of the Cr_2O_3 coating.

In order to explore the tribochemical mechanisms of the three kinds of coatings, XPS was used to analyze the worn surfaces of the coatings under water-lubricated sliding. The analytical results are given in Table 3. In comparison with standard data (Ref

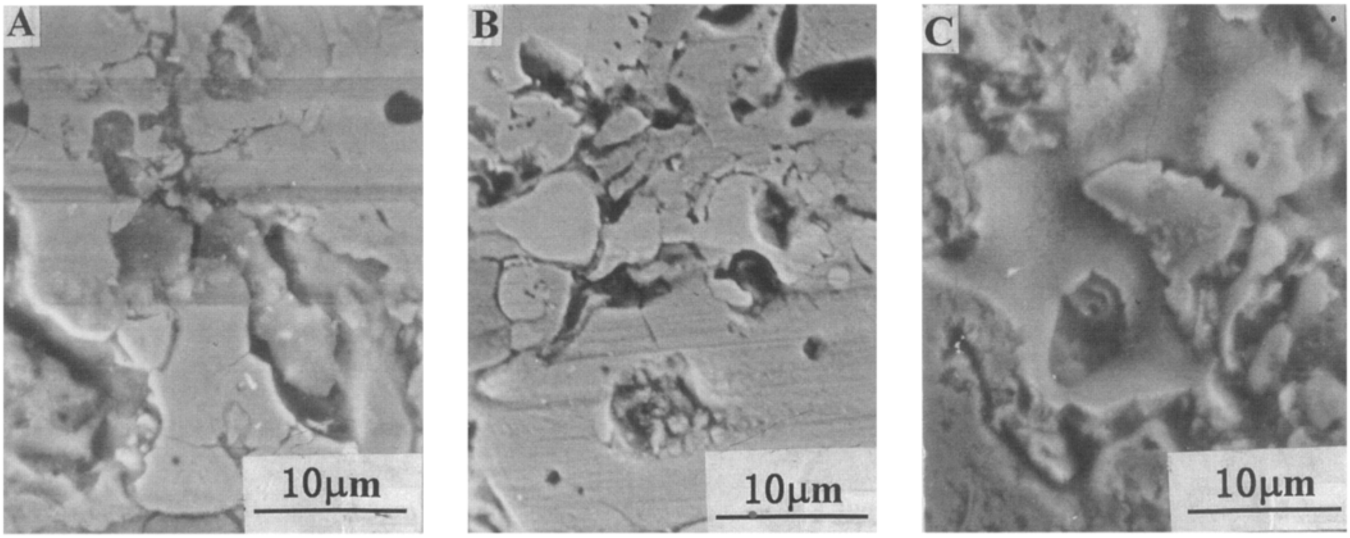

Fig. 4 SEM micrographs of the worn surfaces of: A, Cr_3C_2-NiCr; B, WC-Co;

21), binding energies agreed with the corresponding values for Cr_2O_3, Ni_2O_3, WO_2, WO_3, and CoO. Thus, it can be concluded that Cr_3C_2-NiCr and WC-Co coatings reacted with water to produce these oxides.

The stress during the block-on-ring wear test consists of a static Hertzian stress and rotational stress components. The maximum Hertzian stress, q_0, at the center of the contact surface between the self-mated coatings of modulus E and Poisson's ratio ν is calculated using (Ref 5); that is:

$$q_0 = \frac{2}{\pi(1-\nu)}\left\{\frac{PE}{2tD}\right\}^{1/2} \quad \text{(Eq 1)}$$

where D is the ring diameter, t the test block width, and P the applied load. The Poisson's ratios of thermal sprayed ceramic coatings ranges from 0.20 to 0.30 (Ref 2, 3, 5, 7); therefore, a Poisson's ratio of 0.25 was used for Cr_3C_2-NiCr, WC-Co, and Cr_2O_3 coatings to compute the maximum Hertzian contact stress for the three friction pairs (Fig. 5). The bulk porosity lowers the tensile strength and leads to large particle removal of the coatings (Ref 19). Among the three kinds of coatings, although Cr_3C_2-NiCr and WC-Co coatings possessed higher fracture toughness than Cr_2O_3 coating, they also exhibited higher porosity and microcrack length. It is possible that microcracking and particle fracture were easier for the Cr_3C_2-NiCr and WC-Co coatings than for the Cr_2O_3 coating. Therefore, the wear coefficients of both Cr_3C_2-NiCr and WC-Co coatings were higher than that of Cr_2O_3 coating (Fig. 3). Compared with the Cr_3C_2-NiCr coating, the WC-Co coating suffered higher Hertzian contact stress (Fig. 5), but it exhibited a higher fracture toughness than the Cr_3C_2-NiCr coating (Table 2). Thus, it is also reasonable that the wear coefficient of the WC-Co coating was lower than that of the Cr_3C_2-NiCr coating (Fig. 3).

Absorption of polar H_2O molecules on the oxide solid surface induces stress corrosion (Ref 22, 23). Cr_3C_2-NiCr and WC-Co coatings reacted with H_20 and formed Cr_2O_3, Ni_2O_3, WO_2, WO_3, and CoO. As both Cr_3C_2-NiCr and WC-Co coatings possessed relatively higher porosity and density of microcracks, a continuous and dense surface film of oxides could not be pro-

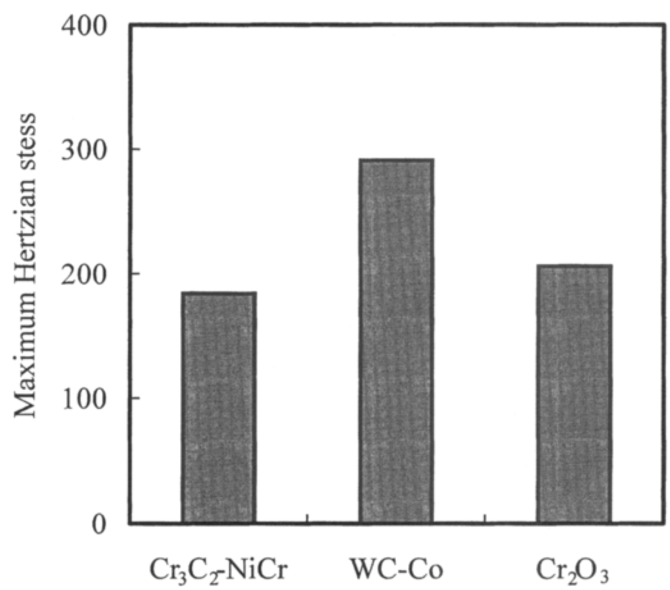

Fig. 5 Maximum Hertzian contact stress of the three kinds of friction pairs

duced on the worn surface and protect the coatings during water-lubricated sliding. This resulted in the fact that H_2O molecules can be absorbed on surfaces of Cr_3C_2-NiCr, WC-Co, and Cr_2O_3 coatings and caused stress corrosion, which aggravated microcracking and particle fracture; thereby deteriorating the wear performance for three coatings. Therefore, although the experimental conditions were somewhat different, the wear coefficients of the coatings under water-lubricated sliding were greater than under dry friction conditions (Ref 11, 12).

4. Conclusions

The Young's modulus, bend strength, and fracture toughness of all of the Cr_3C_2-NiCr, WC-Co, and Cr_2O_3 coatings were lower than the corresponding bulk materials, which may be attributed to the existence of pores and microcracks in the coatings.

Among the three kinds of coatings, the order of wear coefficient was Cr_3C_2-NiCr, the highest, and then WC-Co, followed by Cr_2O_3. The Cr_2O_3 coating indicated wear-resistance, and its wear coefficient was less than $1 \times 10^{-6} mm^3/N \cdot m$.

The wear mechanisms of the coatings were explained in terms of microcracking and fracture, and water deteriorated the wear performance of the coatings. The higher the fracture toughness and the lower the porosity and length of microcrack of the coating, the more wear-resistant the coating.

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