

The friction and wear characteristics of plasma-sprayed $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ from room temperature to 800°C

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The friction and wear characteristics of low-pressure plasma-sprayed (LPPS) $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ from room temperature to 800°C were studied by using a high-temperature reciprocating wear tester. At room temperature, friction of $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ composite coating against Al_2O_3 sphere was quite high, and exhibited a decrease trend with the increase of load from 30 N to 80 N. At 700°C , the composite exhibited the lowest friction and wear among all selected temperature conditions. Brittle fracture and delamination with large wear sheets were considered as the dominant wear mechanism at room temperature. At 400°C , microfracture dropping become more dominated. However, plastic deformation, formation of CaF_2 lubrication films and particle removal of Cr_2O_3 appeared as the main wear mechanisms at elevated temperatures. CaF_2 acting as an effective lubricant at 600°C and 700°C reduced the friction and wear of the composite. Cr_2O_3 particles played a very important role on controlling the size and type of microcracks and preventing or deflecting the microcrack propagation during 700°C test. Cr_2O_3 particles also acted as hard barriers to resist the scratching and high-temperature deformation of $\text{ZrO}_2\text{-CaF}_2$ matrix without increasing the friction. To a great extent, wear mainly depended on the degree of debonding and removal of Cr_2O_3 particles at 700°C .

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1. Introduction

In recent years, the increasing potential for the use of ZrO_2 ceramic coating as thermal barrier coatings in advanced engines and gas turbines and wear resistant coatings in lubrication and seal systems has focused a great attention on these materials [1–4]. The plasma spray method is most widely used to produce a considerable variety of ZrO_2 -based ceramic coatings, which showed favorable tribological behavior: high anti-wear resistance and easy to be lubricated owing to the oil storage of the pores in the coating [1–5]. However, plasma-spray processing parameters such as feed material and process operating parameters affect the coating quality such as hardness, toughness, microstructure and chemical composition distribution.

The friction and wear characteristics of plasma-spraying ZrO_2 ceramic coatings are greatly affected by the compositional and microstructural features such as microcracks, porosity, morphology and distribution of additions. The wear mechanisms of ZrO_2 -based ceramic coatings are complicated but can be classified by one of two dominant processes: brittle fracture or deformation [1–5]. With the change of wear conditions, such as load, sliding speed and temperature, etc., the transition from fracture-dominated wear to deformation-dominated wear is often accompanied by a great change

in both friction and wear. Therefore, the control of the microstructure, particularly the constituents of plasma-spray ZrO_2 -based ceramic coatings, has been recognized as an important factor in characterizing the friction and wear of ceramic coatings.

The tribological behavior of ZrO_2 ceramic coating at elevated temperatures have been extensively investigated [2, 4–6]. However, the tribological characteristics of ZrO_2 ceramic coatings with the lowest friction and wear under dry sliding conditions are still unacceptable for many high temperature applications. Thus, it is very necessary to find ways of effectively lubricating ZrO_2 ceramic coating if they are to be used extensively in tribological applications at extreme temperatures. To date, only a limited amount of experiments have been done on lubrication of ZrO_2 ceramic coating. These studies utilized several kinds of solid lubricants (CaF_2 , BaF_2 or silver) as additives or a well-adhering soft metallic coating as a boundary film [4, 7]. Results of these studies clearly showed deficiencies of the current state of high-temperature lubrication of ceramic coatings. Improved tribological characteristics of ZrO_2 ceramic coating at elevated temperature were reported through solid lubrication method [4]. The friction and wear coefficients of plasma-sprayed coatings of $\text{ZrO}_2\text{-CaF}_2$ with and without silver additives showed that,

both coating combinations had fairly high wear rates at room temperature, but wear rates were much lower for the ZrO₂-CaF₂ coating at 650°C. Friction coefficients were 0.40 at room temperature and 0.26 at 650°C for the ZrO₂-CaF₂ coating in sliding contact with two flat nickel base superalloy rub blocks. But no further data were obtained for higher temperature test or against other different counterface materials. To the best of our knowledge, some compositional modifications for a solid lubricant, which generally possess adequate thermophysical properties and stable thermochemistry at elevated temperatures as well as low shear strength properties, specifically for ZrO₂ ceramic coating must be designed.

This paper investigated the feasibility of using CaF₂ and Cr₂O₃ as solid lubricants for low-pressure plasma-sprayed (LPPS) ZrO₂ ceramic coating at elevated temperatures. Chrome oxide was a known high temperature lubricant which cannot further oxidize upon exposure to high temperature, while calcium fluoride had been widely used in a number of high-temperature applications primarily as a component of self-lubricating composites [4, 7–10]. Further studies were carried out to analyze the friction and wear mechanisms of ZrO₂-Cr₂O₃-CaF₂ against 10 mm sintered Al₂O₃ ceramic sphere at elevated temperature up to 800°C.

2. Experimental procedure

The substrate material was stainless steel AISI 304 which was machined into $\phi 25$ mm \times 7 mm circular plates. The chemical composition of substrate was (wt.%): 0.06C, 0.5Si, 1.0Mn, 18.5Cr, 9.0Ni and balance Fe. The coating material studied was a mixture of 8 wt.% Y₂O₃ stabilized ZrO₂(YPSZ), Cr₂O₃ and CaF₂ powders with a particle size of 10–45 μ m. The selection of YPSZ as coating material was based on its wide use in industry and its commercial availability. The commercial YPSZ, Cr₂O₃ and CaF₂ powders were blended and ball-milled in ratio of 60 : 20 : 20 by weight to form composite powder.

The composite coatings (marked by ZCF) have been deposited on steel AISI 304 by low-pressure plasma spray (LPPS). Before spraying, the substrate material was sand-blasted with aluminum oxide grits and then cleaned in an ultrasonic bath with benzine and acetone. All substrates were plasma-sprayed by using Ar/He plasma gases. The chamber was first evaluated to a pressure below 10 Pa, and then argon gas was added to the desired pressure. The optimum plasma spraying parameters were shown in Table I. In contrast, YPSZ ceramic coating without any additives was also low-pressure plasma-sprayed on steel AISI 304.

TABLE I Plasma spraying parameters used in this investigation

	ZCF composite powder	YPSZ powder
Arc voltage	45 V	45 V
Arc current	750 A	750 A
Primary gas, pressure	Ar, 0.343 MPa	Ar, 0.343 MPa
Auxiliary gas, pressure	He, 1.03 MPa	He, 1.03 MPa
Powder feed rate	15–20 g/min	15–20 g/min
Spraying distance	150–200 mm	150–200 mm

Wear testing of ZrO₂-Cr₂O₃-CaF₂ composite was carried out by using a standard SRV wear test system with reciprocating motion against a 10 mm Al₂O₃ ceramic sphere. The coating specimen was located in the testing chamber in a fixed specimen holder. The load affecting the specimen was generated by a motor spring system and recorded by a measuring unit. The oscillating, horizontal movement was generated by a moving coil drive. The force transducer thus enabled measurements of the frictional forces at the sliding surface and recorded the course of the coefficient of friction during the complete test run. Test temperatures from room temperature to 900°C can be easily controlled by thermocouple. The wear conditions were given as 30–80 N load, 10 Hz frequency, test temperature from room temperature to 800°C, 1 mm stroke and 1 hour test duration. All the test runs were conducted without lubrication in laboratory air. The wear tracks of the composite were also investigated by a surface texture measuring instrument to obtain the wear depth. The average wear depth of the composite and coefficient of friction were determined from three repeated wear measurements of 1 h duration each at the given test conditions. At all different test runs, the average wear depth and friction coefficient were plotted with error bars representing the high and low observed values to evaluate the scatter and repeatability of the friction and wear data.

Microstructural characterization and worn surfaces of the as-sprayed layers were observed by using optical microscope and JEOL-JSM6400F scanning electron microscope equipped with energy dispersive X-ray analysis system (EDX) and operated at 10 kV. For SEM observations, plasma sprayed specimens were carefully sectioned using an abrasive wheel flooded with water. The cross-sectioned samples were grinded and then polished successively by using a standard metallographic procedure. Before grinding an epoxy adhesive was applied to ensure that the coatings didn't peel off during grinding and polishing.

3. Results

3.1. Microstructure of the composite coating

The typical features of as-sprayed ZrO₂-Cr₂O₃-CaF₂ composite with a thickness of about 440 μ m were shown in Fig. 1. The composite layer exhibited a less porous, lamellar structure containing melted, partially melted and a very few unmelted powder particles. The main defect structures in the composite were pores, microcracks and internal boundaries. Under the identical plasma-spray conditions shown in Table I, only 0.2 mm YPSZ coating without any additives was obtained by using original YPSZ commercial powder. No evidence demonstrated that CaF₂ solid lubricants are partially damaged by high-temperature plasma-spray stream as observed by image analysis on the polished cross-section. Partial damage of CaF₂ solid lubricants during plasma spraying was reported in several plasma-sprayed surface composites, such as Cr₂O₃-CaF₂ [8] and NiO-CaF₂ [9] systems, mainly because of the great difference in their fusion points between ceramic matrix and solid lubricants, which resulted in different evaporation rates. Backscattering image photographs

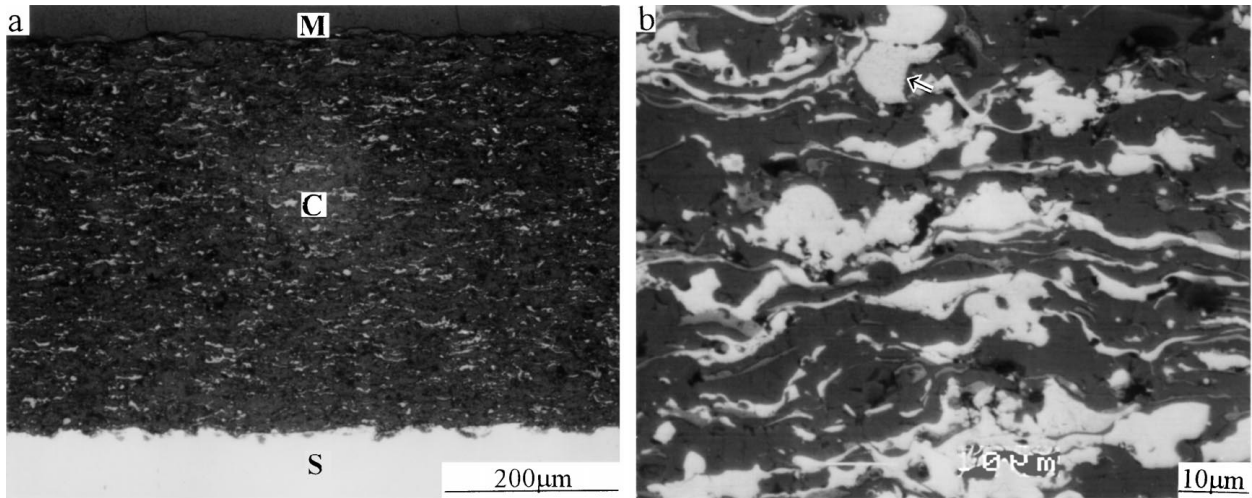


Figure 1 Typical features of as-sprayed $ZrO_2-Cr_2O_3-CaF_2$ composite: a-cross section; b-backscattering image micrograph showing the morphology and distribution of different constituents in the composite (M-mounting material, C-composite coating and S-substrate).

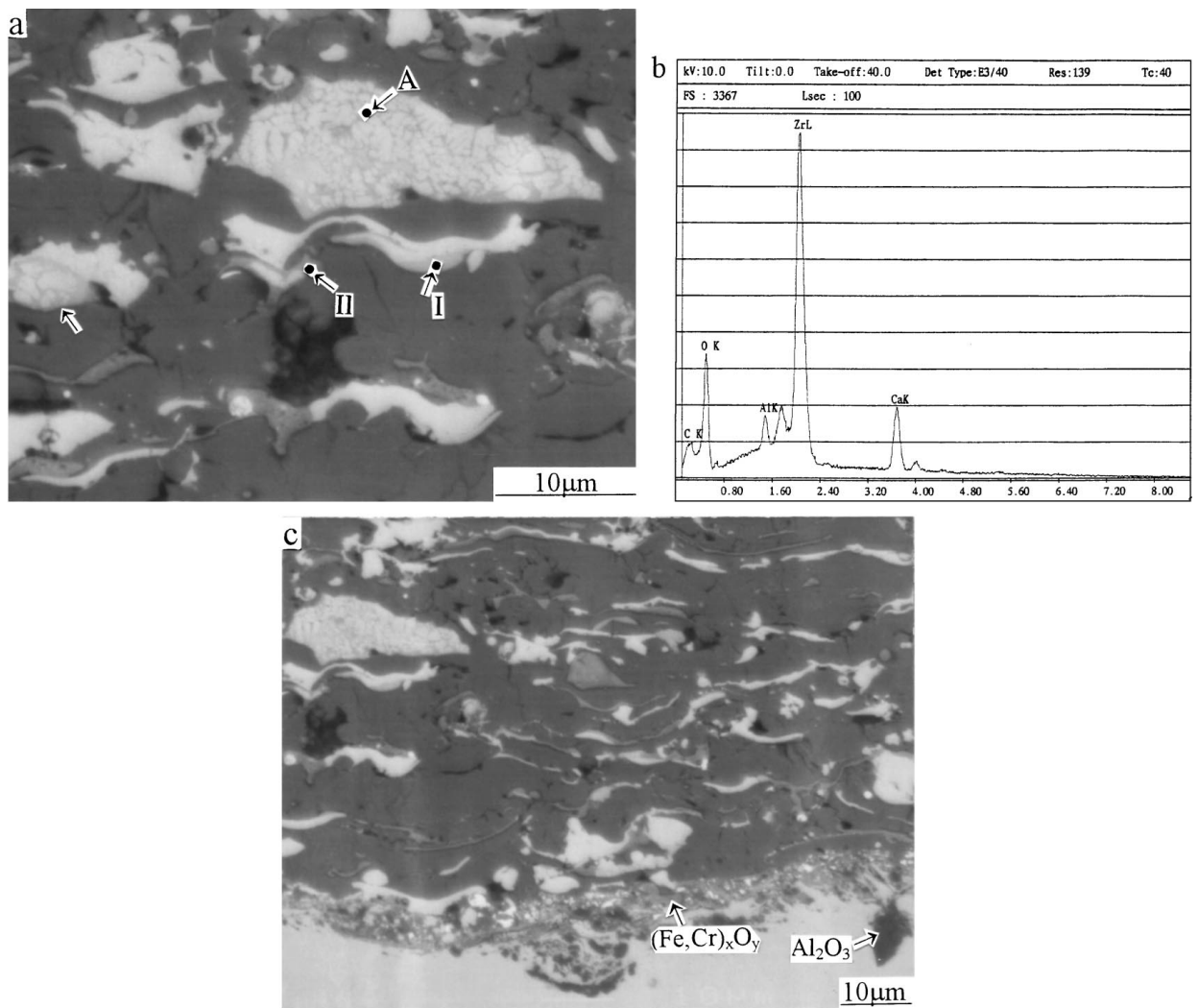


Figure 2 Backscattering images showing fine structure in ZrO_2 lamellae and interfacial morphology between the composite and substrate: a-equiaxed or dendritic grains in ZrO_2 splats; b-EDX spot analysis showing the presence of small amounts of aluminum and calcium at the measurement position marked by character A within the fine ZrO_2 grains of a; c-backscattering image micrograph showing the interfacial features with a different gray levels.

shown in Fig. 1b illustrated the morphology and distribution of different constituents in $ZrO_2-Cr_2O_3-CaF_2$ composite. ZrO_2 (white regions) and Cr_2O_3 (gray regions) constituents were observed as fine typical lamellae structures with different gray levels, while CaF_2

constituent mainly exhibited darker regions with a great volume fraction in the back-scattered electron(BSE) mode. Microcracking was easily observed to be within both ZrO_2 and CaF_2 constituents at high magnification. Backscattering image shown in Fig. 2 revealed the

fine structure of ZrO_2 constituent in the composite and the coating/substrate interfacial features. Some resolidified structure featured by fine equiaxed or dendritic grains were observed in the ZrO_2 lamellae as shown in Fig. 2a,c and Fig. 1b indicated by arrows and were considered to have formed during the solidification process of the molten splats. EDX spot analysis (Fig. 2b) at the measurement position marked by character A within these ZrO_2 splats showed that small amounts of aluminum and calcium were also detected except zirconium and oxygen elements. It was surprising that no fluorine element was detected. This indicated that calcium existed within these grains in the form of calcium oxide. Carbon peak came from the carbon film spattered on the surface for SEM observations. The locally compositional variations may be beneficial to the formation of fine grains. Within some fine ZrO_2 lamellae (Fig. 2a), Al_2O_3 or Cr_2O_3 were detected at the measurement positions indicated by character I and II. The region II containing chrome oxide within ZrO_2 lamellae appeared darker color compared with the region I containing high Al_2O_3 concentration in ZrO_2 splat. Aluminum oxide inclusion coming from the original powder or ball-mixing process formed a preferential combination with zirconia in the composite.

Observations on polished cross-sections (Fig. 1a) showed that the coating/substrate interface exhibited a perfect connection. High magnification BSE photograph (Fig. 2c) showed more complicated microstructures with different gray levels from the composite constituents. Many fine ZrO_2 and CaO particles were detected at the interface regions. Oxygen concentration at the interface was quite higher than that within the coating. EDX spot analyses demonstrated that oxidized products of iron and chromium at the interface were observed due to high-temperature plasma-spray stream. These oxidized products were also found to be very thin and discontinuous at the interfaces. Large and dark particles as shown in Fig. 2c near the interfacial regions were aluminum oxide, which were considered to come from the sand blasting process.

3.2. Friction and wear characteristics of the composite coating at room temperature

The average friction coefficient of $ZrO_2-Cr_2O_3-CaF_2$ composite against 10 mm sintered Al_2O_3 ceramic sphere at room temperature as a function of load was shown in Fig. 3. At room temperature, large variations in friction coefficient were distinctly observed during different wear runs, which seemed to depend greatly on the severe surface fracture process of lamellar splats in as-sprayed coatings. Friction coefficients were quite high, between 0.64 and 1.1, at room temperature and different loads. The average values and errors in friction coefficient were determined from three repeated wear measurements under the identical wear conditions. With the increase of test time, the composite coating exhibited a distinct increase trend in friction coefficient at all test loads. A similar increase value of 0.2 in friction coefficient was clearly observed after

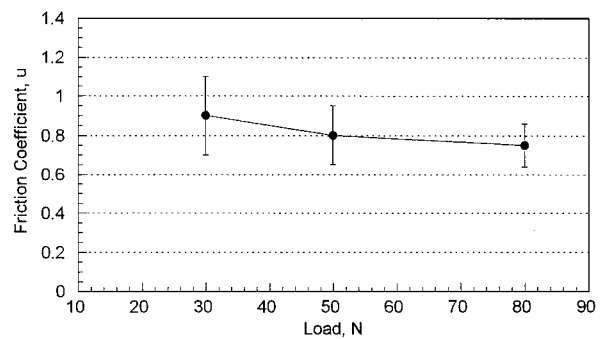


Figure 3 Average friction coefficient of $ZrO_2-Cr_2O_3-CaF_2$ against 10 mm sintered Al_2O_3 ceramic sphere at room temperature as a function of load.

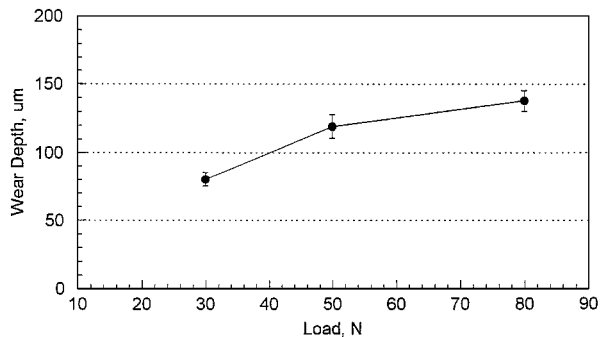


Figure 4 Wear depth of $ZrO_2-Cr_2O_3-CaF_2$ composite at room temperature and different loads.

60 min test duration at all load levels. With the increase of load from 30 N to 80 N, the composite exhibited a decrease trend in friction coefficient from 0.9 ± 0.2 to 0.75 ± 0.11 .

Wear depth of $ZrO_2-Cr_2O_3-CaF_2$ composite at room temperature and different loads was shown in Fig. 4. The average wear depth of the composite was between $80 \pm 3.0 \mu m$ and $137.5 \pm 7.5 \mu m$ at room temperature. With the increase of load from 30 N to 80 N, the coatings exhibited an increase trend in wear depth because of the increasing real tribocontact area, although low friction coefficients were obtained at higher loads.

3.3. Effects of test temperature on friction and wear characteristics of the composite

Fig. 5 showed the average friction coefficient of the composite as a function of test temperature against Al_2O_3 ceramic sphere at 50 N load. At room temperature, the average friction coefficient was quite high (0.8 ± 0.15). When temperature was increased to $400^\circ C$, friction coefficient of the composite slightly decreased to 0.75 ± 0.2 . At $600^\circ C$, the average friction coefficient of the composite was 0.45 ± 0.1 . A minimum value of 0.4 ± 0.05 was reached at $700^\circ C$. When temperature was up to $800^\circ C$, friction coefficient increased to a value of 0.5 ± 0.1 . With the increase of test time, friction coefficients of the composite were quite stable at elevated temperatures from $600^\circ C$ to $800^\circ C$. Fig. 6 showed friction coefficient of the composite at 80 N load and different test temperatures. It can be

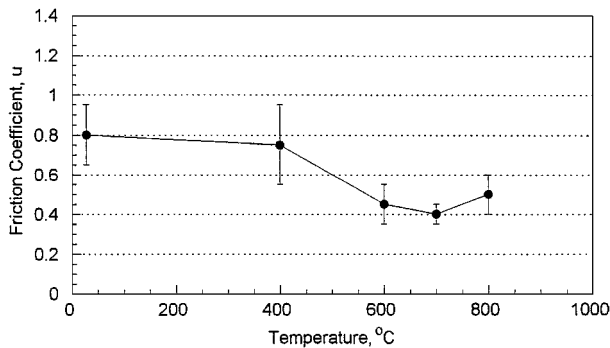


Figure 5 Average friction coefficient of the composite against sintered Al_2O_3 ceramic sphere at 50N load as a function of test temperature.

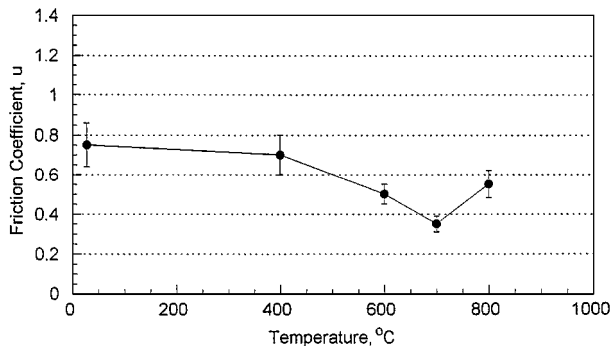


Figure 6 Average friction coefficient of the composite against sintered Al_2O_3 ceramic sphere at 80N load as a function of test temperature.

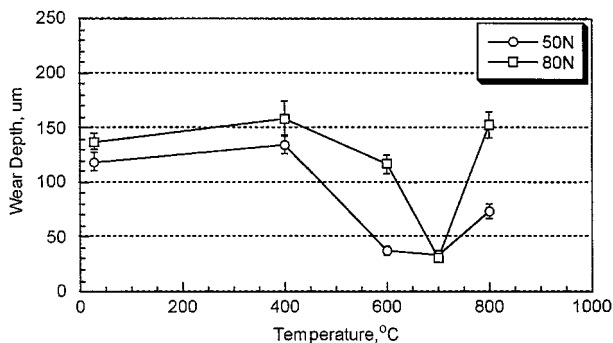


Figure 7 Effect of test temperature on the wear depth of $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ composite coating at different test loads.

seen that when test load was increased to 80 N, friction coefficient of the composite continued to decrease to a minimum value of 0.35 ± 0.04 at 700°C . But at 80 N load, higher values of friction coefficient at 600°C and 800°C were found than those obtained at 50 N load. This phenomenon was different from the results obtained at room temperature with the increase of test load.

Fig. 7 showed the effect of test temperature on the wear depth of the composite at different test loads. At room temperature and 50 N, wear depth of the composite was $119 \pm 8.5 \mu\text{m}$. When temperature was increased to 400°C , wear depth of the composite increased to $135 \pm 9.0 \mu\text{m}$. At 600°C , the average wear depth was about $37 \mu\text{m}$. Wear depth of the composite at 50 N load had a minimum value of $33 \pm 4.0 \mu\text{m}$ at 700°C . But when temperature was up to 800°C , wear depth increased to a high value ($73 \pm 6.5 \mu\text{m}$). When test load was increased to 80 N, wear depth of the composite con-

tinued to decrease to a minimum value of $30 \pm 2.5 \mu\text{m}$ at 700°C . But at 600°C and 800°C , wear depth were quite high ($116.5 \pm 9.0 \mu\text{m}$ and $153 \pm 12.0 \mu\text{m}$), respectively. The repeated high-temperature test runs demonstrated that no significant variations in friction and wear can be found at the same temperature level. The friction and wear measurements, which were much more sensitive to the temperature changes, may result from the internal structural changes and the brittle to ductile transitions of CaF_2 at elevated temperatures.

3.4. Observations of worn surfaces of the composite coating

Worn surfaces of selected $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ composite were observed by optical microscope and SEM. The worn surfaces of the composite at 50 N load and different test temperatures were shown in Fig. 8. At room temperature, typical brittle fracture was observed on the worn surface without evidence of plastic deformation (Fig. 8a). Large wear debris and fine wear particles on the tribocontact surfaces were considered to result from microcracking, crack propagation, fracture and delamination. Fig. 8b illustrated the worn surface of the composite after 400°C wear test. No distinct brittle cracking, splat pull-out and delamination was observed on the worn surface. Many fine fracture pits and microfracture dropping wear were found on the worn surface as well as mild scratching and plastic deformation. The fine multiangular debris were formed by microfracture of the cracked lamellae and are thought to be mainly generated by surface fatigue during sliding. When temperature was increased to 600°C , small amounts of fracture pits and white particles were observed on the worn surface (Fig. 8c) as well as evidence of mild plastic deformation. Discontinuous surface films seemed to cover the worn surface by extensive plastic deformation.

The worn surface of the composite after 700°C wear test was shown in Fig. 8d. Worn surface was entirely covered with smooth material transfer films containing many fine particles. EDX spot analysis demonstrated that these fine particles consisted mainly of Cr_2O_3 particles together with the evidence of a few fine ZrO_2 particles. Smooth surface films were detected to be CaF_2 lubrication films together with small amounts of ZrO_2 . The worn surface of $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ composite at 800°C was shown in Fig. 8e. Severe plastic plowing and deformation were clearly evident. The flash temperature might be sufficiently high to greatly soften the asperities in contact and the asperities were severely deformed under initial high contact stress. Fracture of ZrO_2 splats was also observed in the surficial layer partially covered with smooth CaF_2 films.

3.5. Wear behavior of Cr_2O_3 in the composite at high temperature

Higher magnification SEM micrographs as shown in Fig. 9 were obtained on the worn surfaces of the composite after 700°C wear test in order to evaluate the wear behavior of Cr_2O_3 at high temperature. Microcracks were observed in the dark regions together with many

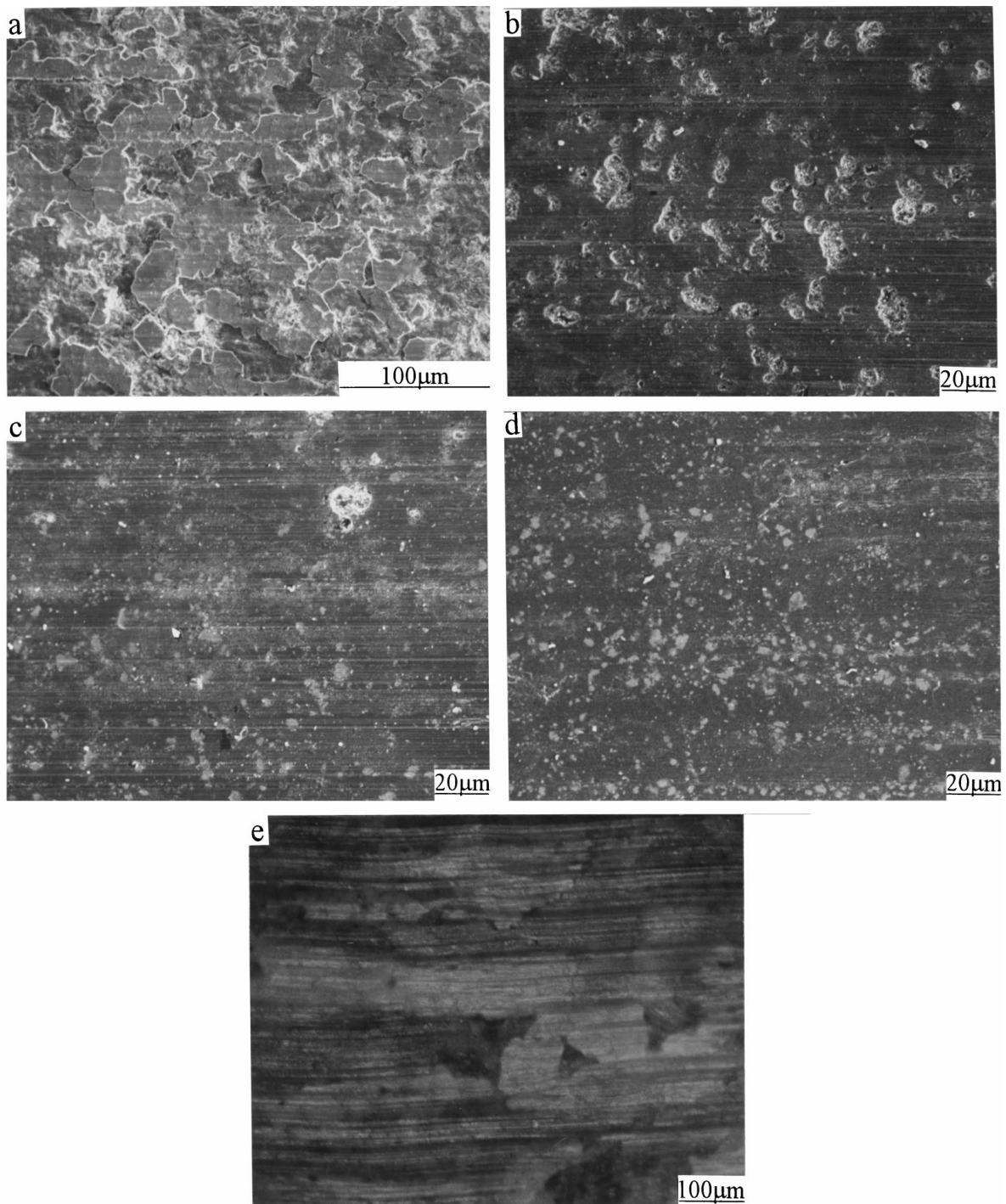


Figure 8 Worn surfaces of $ZrO_2-Cr_2O_3-CaF_2$ composite at 50N load and different test temperatures: a-room temperature; b-400°C; c-600°C; d-700°C; e-800°C.

fine particles (Fig. 9a and b). Mild plastic deformation was also observed within the large and white particle indicated by arrow in Fig. 9a. No distinct evidence of coating delamination was found on the worn surfaces. EDX spot analysis at the measurement position marked by character B in Fig. 9a demonstrated that the dark regions contained calcium, fluorine, zirconium, oxygen and a few chromium elements as shown in Fig. 9c. However, EDX spot analysis at the measurement position marked by character C in Fig. 9a indicated that large particles consisted mainly of Cr_2O_3 together with a very few calcium oxide (Fig. 9d). Microcracking with ring cracks around the Cr_2O_3 particles were produced in flat-surfaced ZrO_2-CaF_2 matrix critically loaded either

thermally or dynamically with hard Al_2O_3 asperities. Radial cracks shown in micrographs revealed cracks propagating and expanding radially from the matrix to the interfacial regions. However, these microcracks usually deflected to expand along the matrix/ Cr_2O_3 interface (also see the micrographs shown in Fig. 10). Almost no evidence of trans-particle microcrack propagation was found within large Cr_2O_3 particles. These microcracks formed preferentially on the planes of easy cleavage in the ZrO_2-CaF_2 matrix. The catastrophic cracks may grow easily by application of a shearing force during sliding. The tangential force introduced by sliding plays an important role in the Cr_2O_3 particle removal. Under sliding contact, the maximum shear

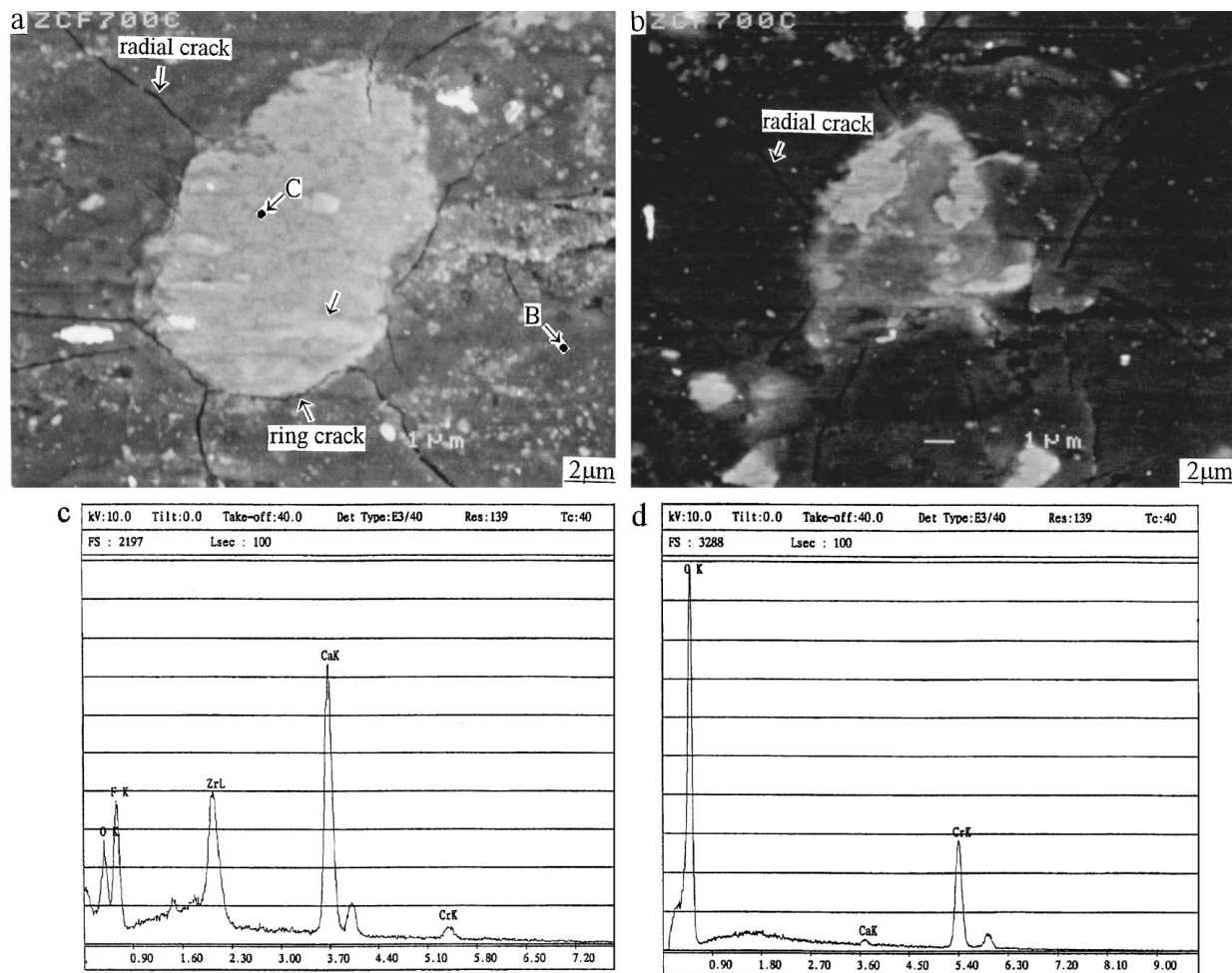


Figure 9 Wear behavior of Cr₂O₃ particles on the worn surfaces of ZrO₂-Cr₂O₃-CaF₂ composite during 700°C wear test: a, b-high magnification micrographs showing the radial microcracks and ring microcracks around Cr₂O₃ particles; c-EDX spot analysis showing the composition of dark regions at the measurement position marked by character B in a; d-EDX spot analysis showing the composition of large particle at the measurement position marked by character C in a.

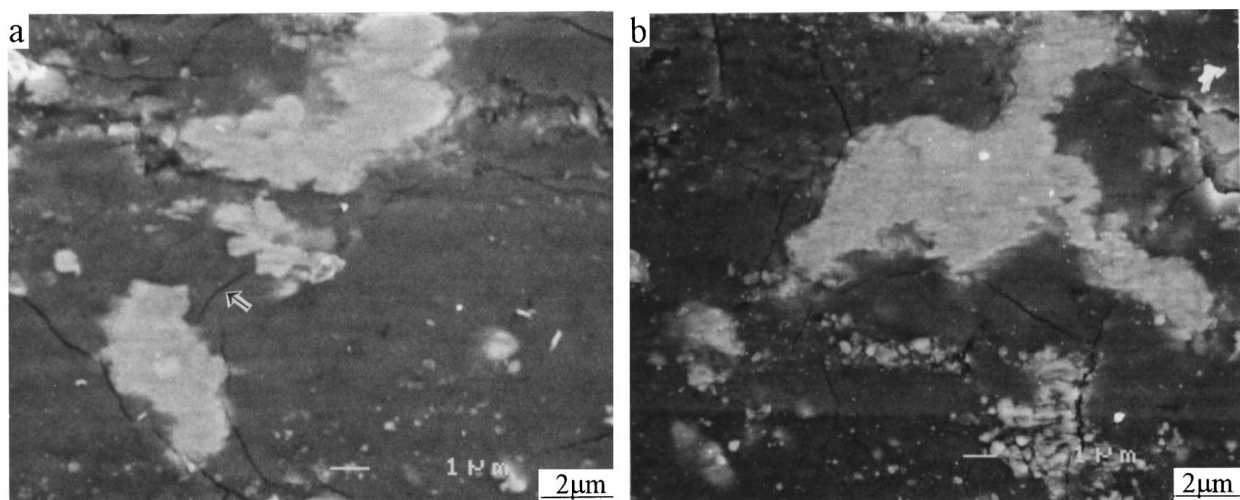


Figure 10 Clustering of Cr₂O₃ particles during the reciprocating wear sliding at 700°C: a-flower-like cluster and crack bridging connection between Cr₂O₃ particles; b-connection and growth of particles.

stress was at the near-interfacial regions of subsurface layers located just underneath the Cr₂O₃ particles. This stress caused subsurface cracks to propagate along the particle boundary. Eventually, these cracks opened to the surface and led to the removal of Cr₂O₃ particles. The rate of the crack propagation depended on the

stress level at the particle boundaries. The size of cracks was controlled by the distribution of Cr₂O₃ particles. Once Cr₂O₃ particles are detached from the surface, further sliding may lead to the local delamination of coating matrix because of the stress redistribution in the contact.

Clear evidence was presented in this investigation, which showed the aggregation of Cr_2O_3 particles (Fig. 10a and b). Flower-like particle clusters, which were clearly visible in these micrographs, were considered to be caused by the reciprocating wear sliding. Possible mechanism can be envisaged for the high cohesive affinity between fine Cr_2O_3 particles. No microcracking was observed within the particle clusters, which suggested a high aggregation strength in clusters.

4. Discussion

For plasma-sprayed $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ composite, the presence of surface and subsurface defects such as some microcracks, impurities, pores and internal boundaries in the surfacial layers, generally dictated the zones from which wear damage and wear particles were generated. The extent and distribution of such defects, to a large extent, determined the size of the wear damage and wear particles generated. This was observed in the scanning electron microscope. Brittle fracture and delamination of coating material were demonstrated to be the dominated wear mechanism of $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ composite at room temperature, which produced relatively high friction coefficient and material removal rates described previously.

At 400°C , worn surface featured by many fine fracture pits together with mild scratching and plastic deformation suggested a microfracture mechanism of the cracked lamellae. However, microfracture dropping taken from this wear process exhibited no distinct changes in friction and wear as associated with this wear mechanism transition.

When temperature was increased to 600°C , CaF_2 seemed to become the dominant material in the composite with high temperature lubrication properties. The fluoride underwent a brittle to ductile transition at about 550°C resulting in a reduction in shear strength and increasing its effectiveness as a lubricants [4]. The fluorides readily wet the Al_2O_3 forming a lubricous film to reduce friction and wear when sliding the $\text{NiCr-Cr}_2\text{O}_3\text{-Ag-BaF}_2/\text{CaF}_2$ coating against Al_2O_3 at 650°C [7]. EDX demonstrated that discontinuous and smooth films containing CaF_2 lubricants were produced on the worn surface at 600°C . But a few microfracture pits were also found at those regions rich in ZrO_2 constituents. Plastic deformation and formation of CaF_2 transfer films became the dominant wear mechanism. At 700°C , CaF_2 effectively served the function of a solid lubricant at high temperatures by preventing direct contact between the worn surfaces of ceramic materials, although small amounts of microcracks were observed in $\text{ZrO}_2\text{-CaF}_2$ matrix at high magnification. Cr_2O_3 particles present in the composite played a very important role on controlling the size and type of microcracks and preventing or deflecting the microcrack propagation. Cr_2O_3 particles also acted as hard barriers to resist the scratching and high-temperature deformation of $\text{ZrO}_2\text{-CaF}_2$ matrix without distinct increasing the friction. To a great extent, wear depends mainly on the extent of debonding and removal of Cr_2O_3 particles. The dominated wear mechanism at 700°C depended on contin-

uous formation of CaF_2 films and particle removal of Cr_2O_3 particles.

The operating temperature range of CaF_2 for getting low friction coefficient was between 500°C and 950°C [10]. However, at 800°C , high temperature friction and wear was not greatly reduced by CaF_2 under this experimental condition. Under high temperature lubrication condition, however, a significant amount of heating occurred at the few asperity contacts. This often produced localized high temperatures more than 1000°C at such contact points. The flash heating could cause thermal degradation of the lubricant. CaF_2 appeared to have inadequate film strength to support load under this experimental condition of 800°C . This may be due to the inability of CaF_2 in the composite and severe softening of the composite. Severe plastic deformation appeared as the dominant wear mechanism and led to high friction and wear at 800°C wear test.

5. Conclusions

(1) Within the as-sprayed composite, ZrO_2 and Cr_2O_3 constituents were observed as fine typical lamellae structures with different gray levels in the back-scattered electron (BSE) mode, while CaF_2 exhibited darker region with a great volume fraction. Some microcracks and resolidified structure featured by fine equiaxed or dendritic grains were observed in the ZrO_2 lamellae.

(2) At room temperature, friction coefficient μ of $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ composite were quite high, and exhibited a decrease trend with the increase of load from 30 N to 80 N. But the wear loss was reversed with increasing the loads at room temperature. At 700°C , the composite exhibited lowest friction and wear among all selected test temperatures.

(3) Brittle fracture and delamination of $\text{ZrO}_2\text{-Cr}_2\text{O}_3\text{-CaF}_2$ composite were demonstrated to be the dominant wear mechanism at room temperature. At 400°C , brittle microfracture dropping become more dominated. However, plastic deformation, formation of CaF_2 lubrication films and particle removal of Cr_2O_3 appeared as the main wear mechanisms at elevated temperatures. CaF_2 acting as an effective lubricant at 600°C and 700°C reduced the friction and wear of the composite.

(4) Cr_2O_3 particles present in the composite played a very important role on controlling the size and type of microcracks and preventing or deflecting the microcrack propagation during 700°C wear test. Cr_2O_3 particles also acted as hard barriers to resist the scratching and high-temperature deformation of $\text{ZrO}_2\text{-CaF}_2$ matrix without distinct increasing the friction. To a great extent, wear depended mainly on the degree of debonding and removal of Cr_2O_3 particles at 700°C .

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References

1. C. FUNKE, J. C. MAILAND, B. SIEBERT, R. VASSEB and D. STOEVER, *Surf. Coat. Technol.* **94/95** (1997) 106.
2. H. AHN, J. KIM and D. LIM, *Wear* **203/204** (1997) 77.
3. Y. WANG, S. M. HSU and P. JONES, *Wear* **218** (1998) 96.
4. H. E. SLINEY, *Tribology International* (October 1982) 303.
5. Y. WANG, Y. JIN and S. WEN, *Wear* **128** (1988) 265.
6. J. Y. KIM, D. S. LIM and H. S. AHN, *J. Korean Ceramic Soc.* **30** (1993) 1059.
7. C. DELLACORTE, *Surf. Coat. Technol.* **86/87** (1996) 486.
8. G. H. LIU, F. ROBBEVALLOIRE, R. GRAS and J. BLOUET, *Wear* **160** (1993) 181.
9. G. D. MOORE and J. E. RITTER, *Lubrication Engineering* **30** (1974), 12,596.
10. H. E. SLINEY, T. N. STOM and G. P. ALLEN, *ASLE Trans.* **8(4)** (1965) 309

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