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Tribological behaviors of hot-pressed Al_2O_3/TiC ceramic composites with the additions of CaF_2 solid lubricants

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Abstract

Al_2O_3/TiC ceramic composites with the additions of CaF_2 solid lubricants were produced by hot pressing. The effect of the solid lubricant on the microstructure and mechanical properties of the ceramic composite has been studied. The friction coefficient and wear rates were measured using the ring-block method, and the tribological behaviors were discussed in relation to its mechanical properties and microstructure. Results showed that additions of CaF_2 solid lubricants to Al_2O_3/TiC matrix led to a decrease in the flexural strength, fracture toughness, and hardness compared to a conventional Al_2O_3/TiC composite. The friction coefficient of Al_2O_3/TiC/CaF_2 ceramic composites when sliding against both cemented carbide and hardened steel decreased with an increase in CaF_2 content up to 15 vol.%. The reason is that the CaF_2 released and smeared on the wear surface, and acted as solid lubricant film between the sliding couple. When the content of CaF_2 solid lubricant is less than 10 vol.%, the wear rate of Al_2O_3/TiC/CaF_2 composites decreases with an increase in CaF_2 content, with further increases in CaF_2 content, the wear rate of Al_2O_3/TiC/CaF_2 composites increases rapidly. This is due to the large degradation of mechanical properties in samples with high CaF_2 contents.

Keywords: Al_2O_3; Wear resistance; Composites; Mechanical properties; TiC; CaF_2

1. Introduction

Ceramics have intrinsic characteristics, such as: high melting point, high hardness, and good chemical inertness, that make them promising candidates for high temperature structural and wear-resistance components. Nowadays advanced ceramics are widely used in cutting tools, dies for drawing or extrusion, seal rings, valve seats, bearing parts, and a variety of high temperature engine parts, etc.[1–3] However, the use of single-phase ceramics, even when fully densified, in high temperature structural or wear applications is limited by the variability of their mechanical strength and their poor fracture toughness. Their susceptibility to brittle fracture can lead to unexpected catastrophic failure. Considerable improvement in mechanical properties of single-phase ceramic materials has been achieved by incorporating one or more other components into the base material to form ceramic-matrix composites (CMC).[4–6] The reinforcing component is often in the form of particles or whiskers. Ceramic composites are of increasing interest with oxide matrices, particularly Al_2O_3 being dominant. Al_2O_3-based ceramic composites are potential substitutes for more traditional materials due to their high hardness, excellent chemical and mechanical stability under a broad range of temperatures, and high specific stiffness. The use of various particle or whisker additions to the Al_2O_3 matrix provides great improvements in mechanical properties over monolithic Al_2O_3. Some of these composites, e.g. Al_2O_3/TiC, Al_2O_3/TiB_2, and Al_2O_3/SiC_w, have been used in various engineering applications and offer advantages with respect to friction and wear behaviour.[7–10]

It is well known that the friction coefficient of Al_2O_3-based ceramic composites under dry sliding conditions is relative high.[10–13] Sometime, these properties render this

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ceramic composite inappropriate for practical applications. Therefore, considerable effort has been made to improve the tribological performance of ceramic composites. Several researchers[14–19] have found that the incorporation of solid lubricants in the ceramic matrix to develop the self-lubricating ceramic composites can improve their tribological properties. Self-lubricating ceramic composites, consisting of a supporting ceramic matrix surrounding dispersed pockets of one or more softer lubricating species, have been used in a wide range of high temperature tribological applications.

CaF_2 is a well known and widely used solid lubricant. It has physical (i.e. it prevents adhesion), chemical (i.e. it enables tribo-chemical reactions) and micro-structural (i.e. it has a lamellar structure with low shear strength) influences on the tribological contact of working surfaces. The mechanism behind their effective lubricating performance is understood to be owing to easy shearing along the basal plane of the hexagonal crystalline structures. Also they are useful additions in the production of self-lubricating ceramic composites, and are used in different anti-wear applications. In earlier studies,[19–22] some of the ceramic composites, such as: Al_2O_3/CaF_2, Al_2O_3/graphite, Si_3N_4/BN, and TZP/graphite, have been developed and used in various applications, mechanical properties and microstructural studies on them have also been extensively carried out. It has been shown that the additions of solid lubricants to the ceramic matrix can improve their tribological properties.

The increasing use of these alumina ceramic composites in a variety of applications in contact with themselves or with other materials has engendered a need for understanding the tribological behavior of these materials. In this paper, Al_2O_3/TiC ceramic composites with additions of CaF_2 solid lubricants were produced by hot pressing. The effect of the solid lubricants on the microstructure and mechanical properties of this ceramic composite has been studied. Their tribological behaviours were investigated using the ring-block method. The friction coefficient and wear rates were measured, and the wear mechanisms were discussed in relation to their mechanical properties and microstructures.

2. Experimental procedure

2.1. Materials and processing

The starting powders used to fabricate the ceramic composites are listed in Table 1 with their particle sizes, purities and manufacturers. Al_2O_3/TiC (volume ratio 1:1) was used as the baseline material. Additions of CaF_2 solid lubricant particles were added to Al_2O_3/TiC matrix. The range of solid lubricant additions to the Al_2O_3/TiC matrix was from 0 to 15 vol.% as listed in Table 2.

The combined powders were prepared by wet ball milling in alcohol for 60 h with cemented carbide balls, completed with colloidal and ultrasonic processing techniques for the particle dispersion. Filter pressing was used to consolidate the multi-component slurries into green bodies approximately 60 mm in diameter and 20 mm thick. Following drying, the final densification of the compacted powder was accomplished by hot pressing with a pressure of 32 MPa in argon atmosphere for 15 min to produce a ceramic disk. The sintering temperature employed for hot pressing was 1700 °C.

Table 1
Particle size, purity and manufacturer of the starting powders

Starting powder	Average particle size (μm)	Purity (%)	Manufacture
Al_2O_3	1–2	>99.9	Zibo Aluminum Works
TiC	1–2	>99.5	Zhuzhou Cemented Carbide Works
CaF_2	<1	>98.5	Beijing Yili fine Chemical Products Works

2.2. Material characterization

Test pieces of 3 mm × 4 mm × 36 mm in dimension were prepared from the disk by cutting and grinding using a diamond wheel and were offered for measurement of flexural strength, Vickers hardness and fracture toughness. Three-point bending mode was used to measure the flexural strength over a 30 mm span at a crosshead speed of 0.5 mm/min. Fracture toughness measurement was performed using indentation method in a hardness tester (ZWICK3212) using the formula proposed by Cook and Lawn.[23] On the same apparatus, the Vickers hardness was measured on polished surface with a load of 98 N. Data for hardness, flexural strength, and fracture toughness were gathered on five specimens and averaged.

XRD (D/max-2400) analysis was undertaken to identify the crystal phases present after sintering. The microstructures of sintered materials and the worn regions of the ceramic blocks were examined using scanning electron microscopy (HITACH S-570).

2.3. Friction and wear tests

Friction and wear tests were conducted with a MRH-3 high-speed ring-block tribometer (made in China). The schematic diagram of this equipment is shown in Fig. 1. The block specimen (15 mm × 12 mm × 5 mm) was made of ceramic materials having a polished surface with a surface roughness of 0.08 μm. The ring specimen (Ø 50 mm × Ø 35 mm × 15 mm) was made of cemented carbide (WC/8 vol.% Co) with a hardness of HRA 89, and 45# hardened steel with a hardness of HRC 45. The ring surface was polished to produce a final surface roughness of 0.05 μm. Both the block and the ring were rinsed with hexane, and then ultrasonically cleaned in fresh hexane, followed by ultrasonic cleaning with acetone. The ceramic block is fixed, while the cemented carbide or hardened steel ring is rotated with a speed of 200–600 rpm. A normal load of 70 N was ap-

Table 2
Compositions and mechanical properties of hot pressed Al_2O_3/TiC/CaF_2 ceramic composites

Specimen	Compositions (vol. %) (Al_2O_3:TiC = 1:1, v/v)	Flexural strength (MPa)	Hardness (GPa)	Fracture toughness ($MPa.m^{1/2}$)
AT	Al_2O_3 + TiC	800 ± 43	20.0 ± 0.6	5.2 ± 0.3
ATF1	Al_2O_3 + TiC + 5% CaF_2	478 ± 32	13.2 ± 0.8	3.4 ± 0.2
ATF2	Al_2O_3 + TiC + 10% CaF_2	590 ± 29	15.3 ± 0.7	3.6 ± 0.3
ATF3	Al_2O_3 + TiC + 15% CaF_2	418 ± 33	9.6 ± 0.5	3.3 ± 0.3

plied in all the tests. Each test was run over a period of 10 min. The friction coefficient was calculated by dividing the measured tangential force by the applied normal force. The mass loss of the worn ceramic blocks was measured with an accurate electron balance (minimum 0.001 mg). The wear rate W is defined as the volume loss (V), divided by the applied normal load (P), times the sliding distance (L):

$$W = \frac{V}{PL} \tag{1}$$

where the W has the units of volume loss per unit force per unit distance (mm^3/N m).

3. Results and discussion

3.1. Microstructure and mechanical properties of Al_2O_3/TiC/CaF_2 ceramic composites

The mechanical properties of Al_2O_3/TiC/CaF_2 ceramic composites with different content of solid lubricants are listed in Table 2. It can be seen that that additions of CaF_2 solid lubricants to the Al_2O_3/TiC matrix led to a decrease in the flexural strength, fracture toughness, and hardness compared to a normal Al_2O_3/TiC composite. The flexural strength of Al_2O_3/TiC composite with 10 vol.% CaF_2 exhibited a maximum value of 590 MPa, and with further increasing of CaF_2 content it showed a downward trend. The trend of the fracture toughness and the hardness is the same as that of the flexural strength. Fig. 2 illustrates the X-ray diffraction analysis of the Al_2O_3/TiC/CaF_2 ceramic composite after sintering at 1700 °C for 15 min. It can be seen that Al_2O_3, TiC, and CaF_2 are all existed in the sintered specimens.

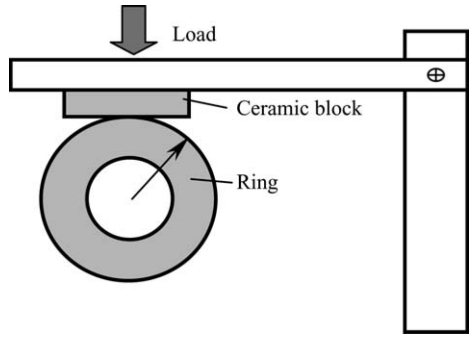

Fig. 1. Schematic diagram of the friction and wear test apparatus.

The typical microstructure from the polished surface of hot-pressed Al_2O_3/TiC/CaF_2 ceramic composite is shown in Fig. 3a. The black areas were identified by EDX analysis as TiC and CaF_2, and the white phases with clear contrast were Al_2O_3 (Fig. 3b and c). It can be seen that the TiC and CaF_2 particles are quite uniformly distributed throughout the microstructure, porosity is virtually absent, and the solid lubricant phases were uniformly distributed with the matrix with very few second phase agglomerates or matrix-rich regions.

Fig. 4 shows the SEM micrograph of the fracture surfaces of Al_2O_3/TiC/CaF_2 ceramic composite. From this SEM micrograph, different morphologies of the composite can be seen clearly. The Al_2O_3/TiC/CaF_2 composites exhibited a rough fracture surface, resulting from the mixed transgranular and intergranular fracture modes.

3.2. Tribological behaviors of hot-pressed Al_2O_3/TiC/CaF_2 ceramic composites

The effect of the CaF_2 content on the friction coefficient of the ceramic composite is shown in Fig. 5. It can be seen that the friction coefficient continuously decreased with increases in the CaF_2 content up to 10 vol.% when conducted with a cemented carbide ring, and decreased from 0.47 for Al_2O_3/TiC to 0.27 for Al_2O_3/TiC/10 vol.% CaF_2. With further increasing CaF_2 content the friction coefficient kept almost constant. The ceramic composite without CaF_2 solid lubricants exhibited the highest friction coefficient, while the composite with 10 vol.% CaF_2 solid lubricants showed the smallest friction coefficient under the same test conditions.

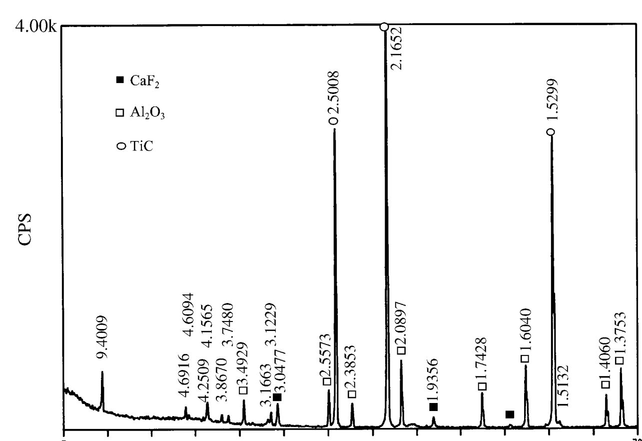

Fig. 2. X-ray diffraction analysis of the Al_2O_3/TiC/CaF_2 ceramic composite after sintering at 1700°C.

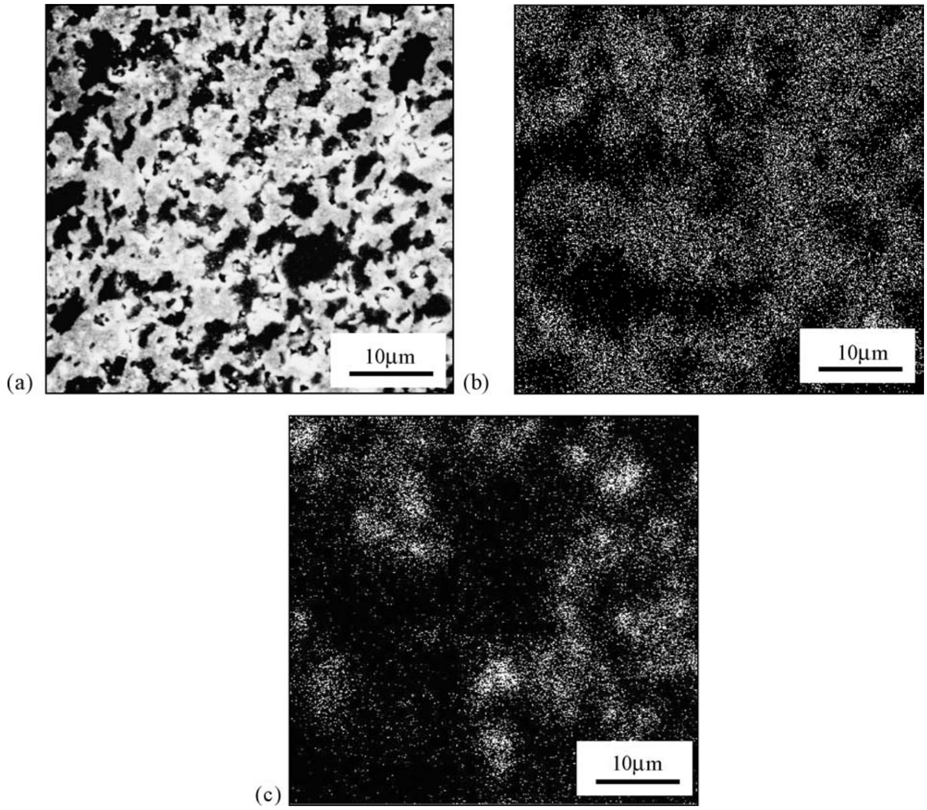

Fig. 3. Typical microstructure: (a) of the polished surface of Al_2O_3/TiC/CaF_2 ceramic composite; (b) the Al element distribution corresponding to (a); and (c) the F element distribution corresponding to (a).

The trend of the friction coefficient is similar when using a hardened steel ring.

Figs. 6 and 7 illustrate the effect of the sliding speed on the friction coefficient of the ceramic composite with cemented carbide ring and hardened steel ring respectively. It is indicated that the friction coefficient showed a downward trend with an increase in the sliding speed. The ceramic composite without CaF_2 solid lubricants exhibited a higher friction coefficient when compared with the composite with CaF_2 under all the test conditions.

Fig. 8 shows the influence of CaF_2 content on the wear rate of Al_2O_3/TiC/CaF_2 composites. It can be seen that when the CaF_2 content is less than 10 vol.%, the wear rate decreases with the increase of CaF_2 content, with further increases in the CaF_2 content, the wear rate of Al_2O_3/TiC/CaF_2 increases rapidly when sliding against both a cemented carbide ring and a hardened steel ring.

Typical SEM micrographs of the worn surfaces of Al_2O_3/TiC ceramic composite without CaF_2 solid lubricants are shown in Fig. 9. There were numerous scratches and pits on the wear surface. The wear track was mangled, and showed a "brushing-off" of debris on the worn surface. Significant surface damage can be observed in the form of a scratched

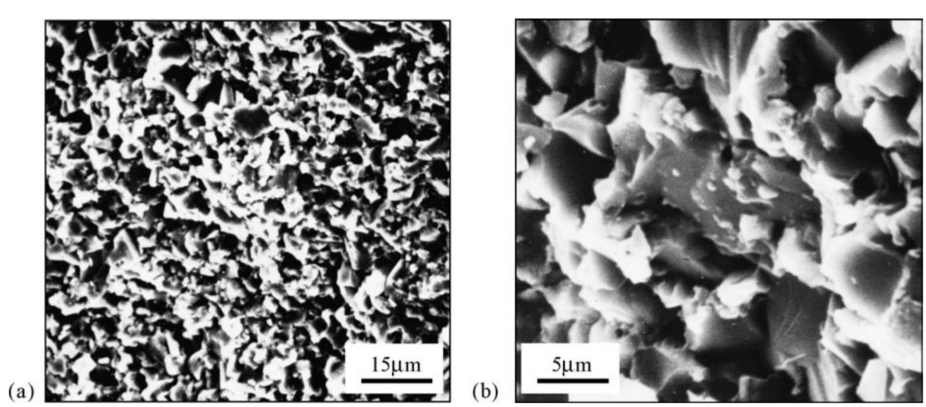

Fig. 4. SEM micrograph of the fracture surfaces of Al_2O_3/TiC/CaF_2 ceramic composite.

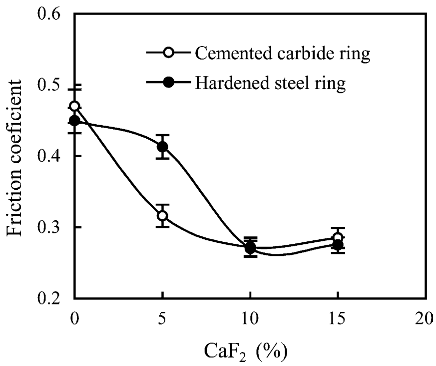

Fig. 5. Effect of the CaF_2 content on the friction coefficient of the Al_2O_3/TiC/CaF_2 ceramic composites (sliding speed v = 400 rpm).

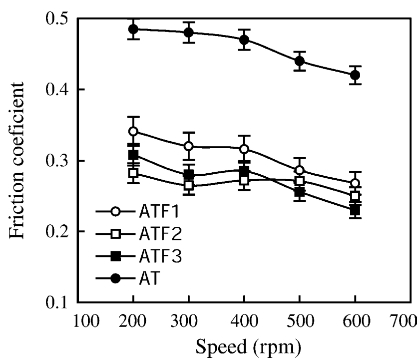

Fig. 6. Effect of the sliding speed on the friction coefficient of the ceramic composites when sliding against a cemented carbide ring.

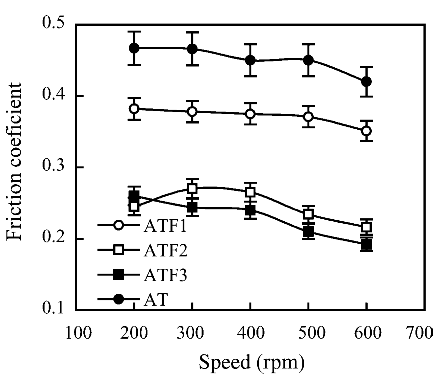

Fig. 7. Effect of the sliding speed on the friction coefficient of the ceramic composites when sliding against a hardened steel ring.

and smeared appearance. This suggests that the primary wear mechanism of this composite is abrasive wear.

Fig. 10a shows the SEM micrograph of the worn surface of the Al_2O_3/TiC ceramic composite with CaF_2 solid lubricants. In comparison with Fig. 9b, it exhibited a relatively smooth surface, both mechanical plowing grooves and scratches could not be observed, and there is no distinct crack on the wear track. A SEM/EDX map of the distribution of fluorine (i.e. with CaF_2) on the worn surface is shown in Fig. 10b. The results indicated that CaF_2 has been released and smeared on the wear surface. Fig. 11 gives SEM micrograph of the cross-sectional views of Al_2O_3/TiC/10 vol.%

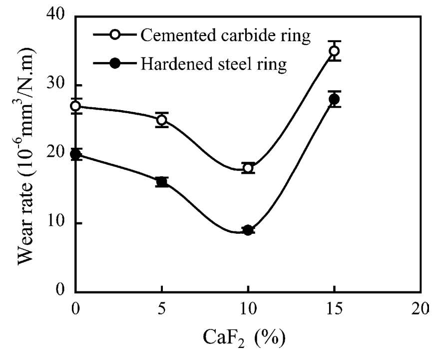

Fig. 8. Effect of the CaF_2 content on the wear rate of the Al_2O_3/TiC/CaF_2 ceramic composites (sliding speed v = 400 rpm).

CaF_2 composite before and after sliding wear tests respectively, which reveals the existence of a thin film on the worn surface of after sliding wear tests. The thickness of this film is about 0.5–1 μm. Fig. 12 illustrates the schematic diagram of the formation process of self-lubricating film on the wear track.

The friction coefficient between two smooth bodies sliding under elasticity loaded conditions in an elliptical contact can be expressed as[24]:

$$\mu = A\frac{\tau}{P^{1/3}}\left(\frac{3}{4E'}\right)^{2/3} \qquad (2)$$

where A is a constant determined by contact geometry, τ is critical shear stress at the interface, which may be an lubricant film, P is the normal load, and E' the effective elastic modulus of the contact materials.

For a given contact geometry Eq. (2) shows that the friction coefficient varies linearly with critical shear stress. When there is a lubricant film on the wear surface, the matrix endures the load, and friction occurs on the lubricant film.[25,26] As the lubricant film on the wear surface had a much smaller critical shear stress than the substrate and thus resulted in a reduced friction coefficient according to Eq. (2).

The increase in CaF_2 content led to a decrease in the coefficient of friction of Al_2O_3/TiC/CaF_2 ceramic composites both sliding against cemented carbide and hardened steel. This may be due to the formation of a CaF_2 lubricant film between the sliding couple. Since the CaF_2 acted as a solid lubricant, the friction coefficient decreased as the CaF_2 was released and smeared on the wear surface. This means that self-lubrication can be accomplished under these conditions.

However, when the content of CaF_2 solid lubricants is less than 10 vol.%, the wear rate of Al_2O_3/TiC/CaF_2 composites decreases with increase in the CaF_2 content, and this may be also due to the formation of a CaF_2 lubricant film between the sliding couple. With further increases in the CaF_2 content, the wear rate of Al_2O_3/TiC/CaF_2 composites increases greatly. This is attributed to the large degradation of mechanical properties with higher CaF_2 content as can be seen in Table 2.

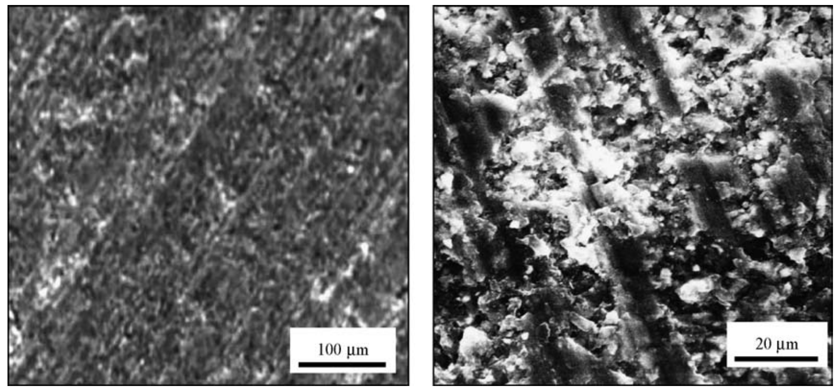

Fig. 9. SEM micrographs of the worn surfaces of the Al_2O_3/TiC composite without CaF_2 solid lubricants (the ring materials is cemented carbide, sliding speed $v = 400$ rpm).

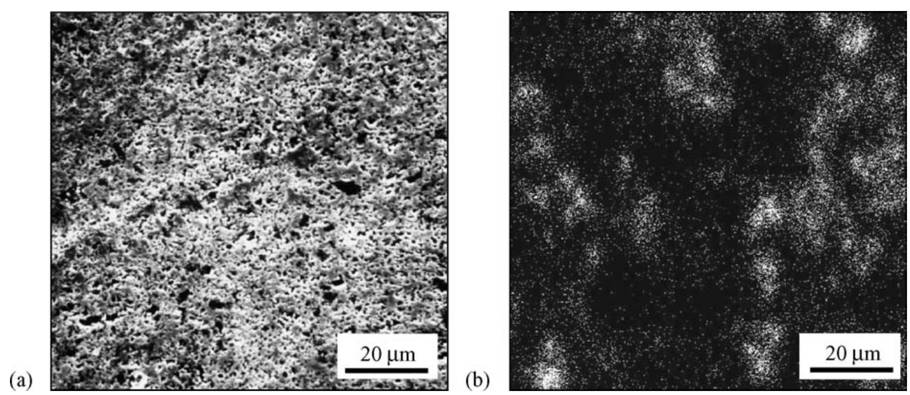

Fig. 10. SEM micrograph of: (a) the worn surfaces of the Al_2O_3/TiC/10 vol.% CaF_2 composite; (b) the F element distribution corresponding to (a).

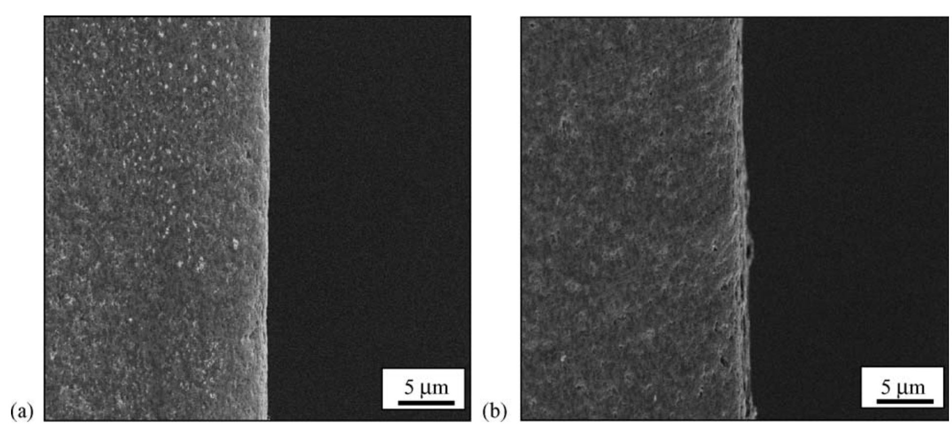

Fig. 11. Cross-sectional view SEM micrograph of the worn surface of Al_2O_3/TiC/10 vol.% CaF_2 composite: (a) before sliding wear tests and (b) after sliding wear tests (the ring materials is cemented carbide, sliding speed $v = 400$ rpm).

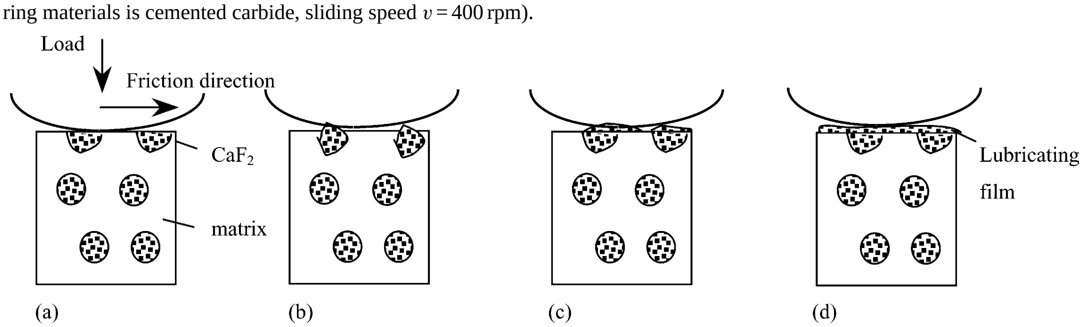

Fig. 12. Schematic diagram of the formation process of self-lubricating film between the sliding couple.

4. Conclusions

Al_2O_3/TiC ceramic composites with the additions CaF_2 solid lubricants were produced by hot pressing. Particular attention was paid to the effect of solid lubricant additions on the mechanical properties, microstructures and tribological behaviour. Results showed that:

1. Additions of CaF_2 solid lubricant to Al_2O_3/TiC matrix led to a decrease in the flexural strength, fracture toughness, and hardness as compared to the base Al_2O_3/TiC composite.
2. The friction coefficient of Al_2O_3/TiC/CaF_2 ceramic composites when sliding against both cemented carbide and hardened steel decreased with an increase in CaF_2 content up to 15 vol.%. The reason is that the CaF_2 released and smeared on the wear surface and acted as solid lubricant film between the sliding couple.
3. When the content of CaF_2 solid lubricant is less than 10 vol.%, the wear rate of Al_2O_3/TiC/CaF_2 composites decreases with increase in the CaF_2 content; with further increases in the CaF_2 content, the wear rate of Al_2O_3/TiC/CaF_2 composites increase greatly. This is due to the large degradation of mechanical properties of the composite with higher CaF_2 contents.

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