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Wear behavior and self tribofilm formation of hot-pressed Al_2O_3/TiC/CaF_2 ceramic composites sliding against cemented carbide

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Abstract

Al_2O_3/TiC ceramic composites with the additions of CaF_2 solid lubricants were produced by hot pressing. Sliding wear tests against cemented carbide were performed on these ceramic composites using the ring-block method. The friction coefficient and wear rates were measured. Results showed that the friction coefficient and the specific wear rate decreased with the increase of CaF_2 content up to 10 vol.%, with further increases in CaF_2 content, both the friction coefficient and the wear rate increased rapidly. SEM observations showed that self tribofilms were consistently formed on the wear surfaces. Two types of tribofilms are present on the worn surface depending on the CaF_2 content. A dense self tribofilm with a smooth surface associated with small friction coefficient and low wear rate was formed by the releasing and smearing of CaF_2 solid lubricants on the wear surface when with low CaF_2 content (less than 10 vol.%). This dense self tribofilm acted as solid lubricant film between the sliding couple, protected the ceramics from severe wear by brittle microfracture, and thus significantly reduced the friction coefficient and the wear rate. A broken tribofilm associated with high friction coefficient and large wear rate was formed when with high CaF_2 content (more than 10 vol.%). The reason is that large degradation of mechanical properties occurred in samples with high CaF_2 contents.

Keywords: B. Composites; C. Wear resistance; D. Al_2O_3; Self-lubrication

1. Introduction

Advanced ceramic materials exhibit high hardness, high stiffness, excellent chemical and mechanical stability, which make them promising candidates for wear-resistance components. They have excellent prospects for tribological applications especially under severe conditions. 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]. Consequently, clarification of wear behaviors of ceramic materials has received much attention over the last two decades.

It is well known that the friction coefficient of Al_2O_3 based ceramic composites under dry sliding conditions is relative high [4–6]. Sometime, these properties render this ceramic composite inappropriate for practical applications. Therefore, considerable effort has been made to improve the tribological performance of ceramic composites. Several researchers [7–12] 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 microstructural (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 [7–12], some of the ceramic composites, such as: Al_2O_3/CaF_2,

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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

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.

Numerous studies have been conducted on the friction and wear behaviors of self-lubricating ceramics. Most of them have revealed that thin layers, so called tribofilms, are observed on the wear surfaces. Actual wear often occurs at the contact interfaces where a tribofilm is present. Tribofilm might play an important role in the sliding wear behaviors of ceramics. Several researches have addressed the characterization of the tribofilms and their role on the wear behaviors [13–15]. Their results showed that sliding couples that form a stable and adherent film exhibit much less wear rate than couples that do not form a stable and adherent film.

In the present study, 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, mechanical properties, and tribological behaviors of this ceramic composite has been studied. Detailed observations and analyses have been conducted to clarify the formation mechanism of the self tribofilms and their effects on the friction and wear behavior of these ceramic composites.

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.

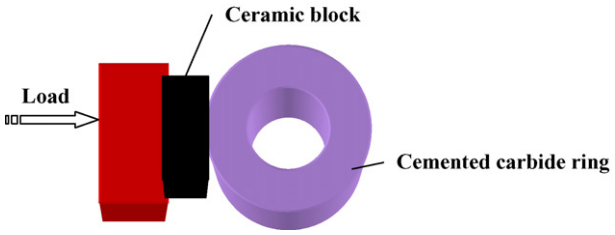


Fig. 1. Schematic diagram of the friction and wear test apparatus (dimension: ceramic block 15 mm × 12 mm × 5 mm, cemented carbide ring specimen Ø50 mm × Ø35 mm × 15 mm).

The combined powders were prepared by wet ball milling in alcohol for 60 h with cemented carbide balls. Following drying, the final densification of the combined powders 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.

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 [16]. 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.

2.3. Friction and wear tests

Friction and wear tests were conducted with a MRH-3 high-speed ring-block tribometer. 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 (Ø50 mm × Ø35 mm × 15 mm) was made of YG8 (WC + 8 vol.% Co) cemented carbide with a hardness of HRA 89. 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

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

Specimen	Compositions (vol.%) (volume ratio: Al_2O_3:TiC = 1:1)	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

block is fixed, while the cemented carbide ring is rotated with a speed of 200–600 r/min. A normal load of 70 N was applied 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 [17] is defined as the volume loss, V, divided by the applied normal load, P, times the sliding distance, L.

$$W = \frac{V}{PL} \quad (1)$$

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

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).

3. Results and discussion

3.1. Microstructure and mechanical properties

The mechanical properties of Al_2O_3/TiC/CaF_2 ceramic composites with different content of CaF_2 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.

The typical microstructure from the polished surface of hot-pressed Al_2O_3/TiC/CaF_2 ceramic composite is shown in Fig. 3.

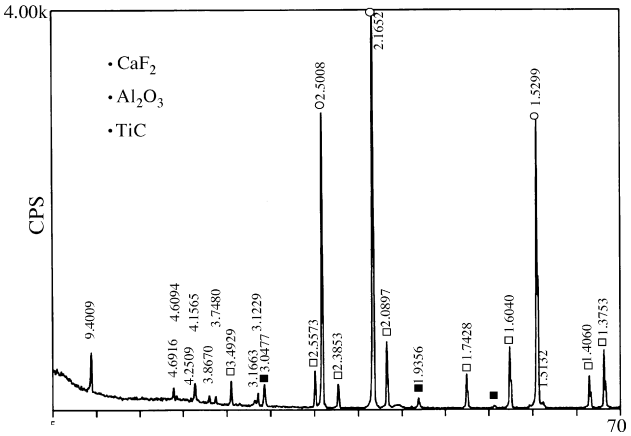


Fig. 2. X-ray diffraction analysis of the Al_2O_3/TiC/CaF_2 ceramic composite after sintering at 1700.

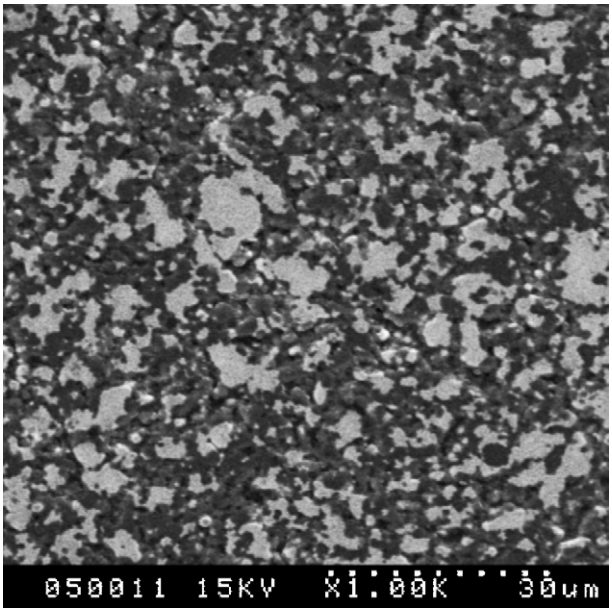


Fig. 3. Typical microstructure of the polished surface of Al_2O_3/TiC/CaF_2 ceramic composite.

The black areas were identified by EDX analysis as Al_2O_3, and the white phases with clear contrast were TiC and CaF_2. 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.

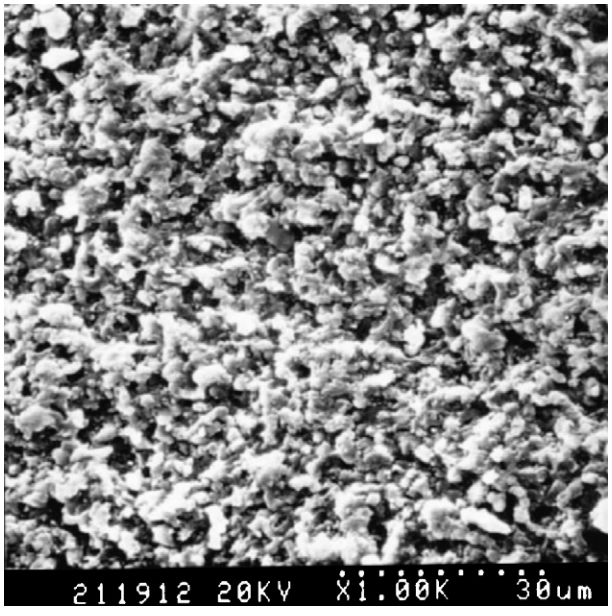


Fig. 4. SEM micrograph of the fracture surface of Al_2O_3/TiC/CaF_2 ceramic composite.

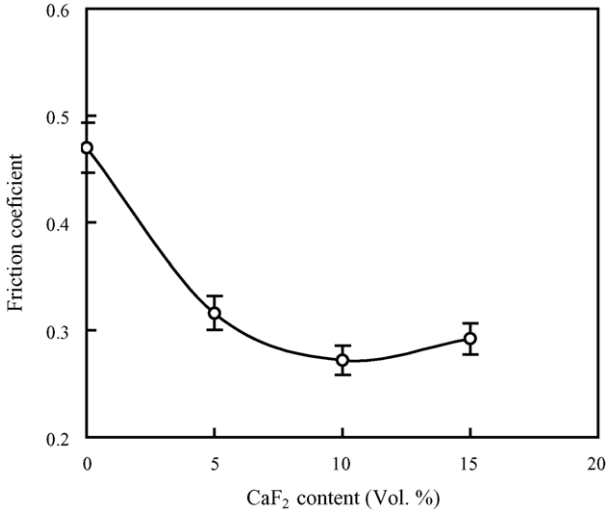


Fig. 5. Effect of the CaF_2 content on the friction coefficient of the Al_2O_3/TiC/CaF_2 ceramic composites (sliding speed $v = 400$ r/min).

3.2. Friction coefficient and specific wear rates

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.%, 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 showed a little increase. 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. 6 illustrates the effect of the sliding speed on the friction coefficient of the ceramic composite. 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.

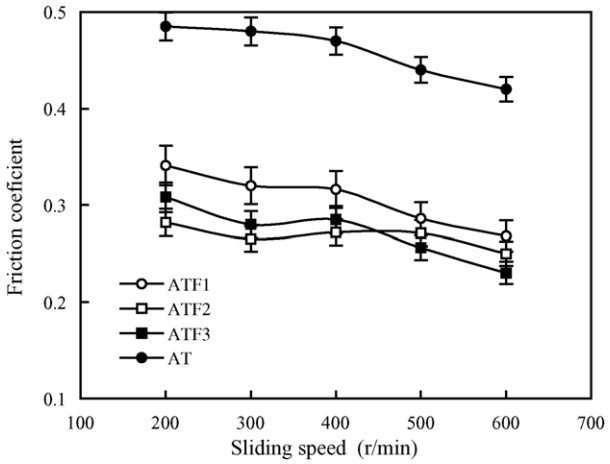


Fig. 6. Effect of the sliding speed on the friction coefficient of the ceramic composites.

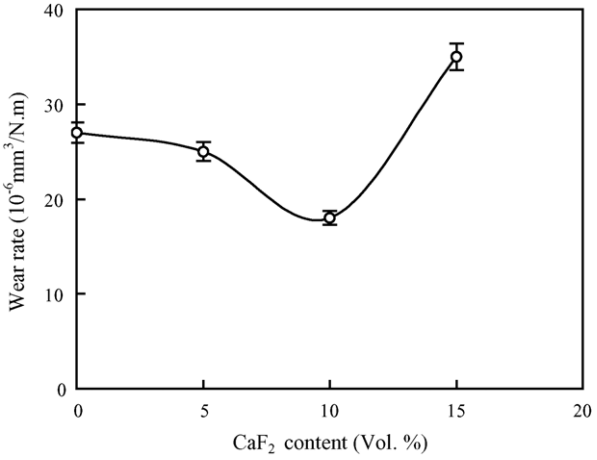


Fig. 7. Effect of the CaF_2 content on the wear rate of the Al_2O_3/TiC/CaF_2 ceramic composites (sliding speed $v = 400$ r/min).

Fig. 7 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.

3.3. Wear surface studies

Typical SEM micrograph of the worn surface of Al_2O_3/TiC composite without CaF_2 solid lubricants is shown in Fig. 8. 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 and smeared appearance. This suggests that the primary wear mechanism of Al_2O_3/TiC composite is abrasive wear.

Fig. 9(a) and (b) shows the SEM micrographs of the worn surface of ATF2 ceramic composite with 10 vol.% of

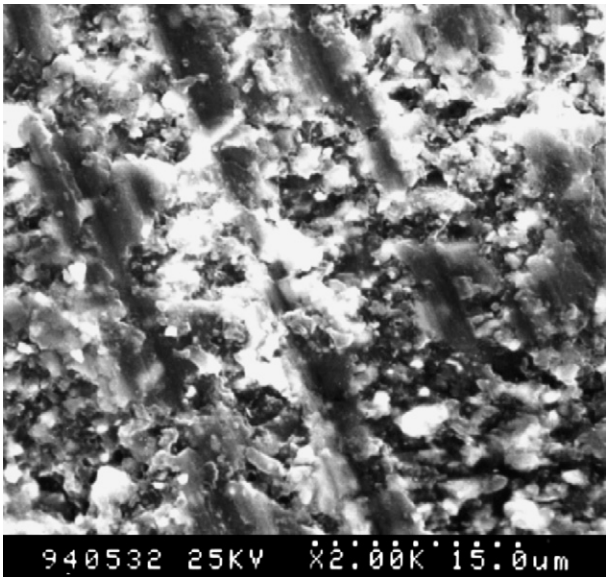


Fig. 8. SEM micrograph of the worn surface of the Al_2O_3/TiC composite without CaF_2 solid lubricants (sliding speed $v = 400$ r/min).

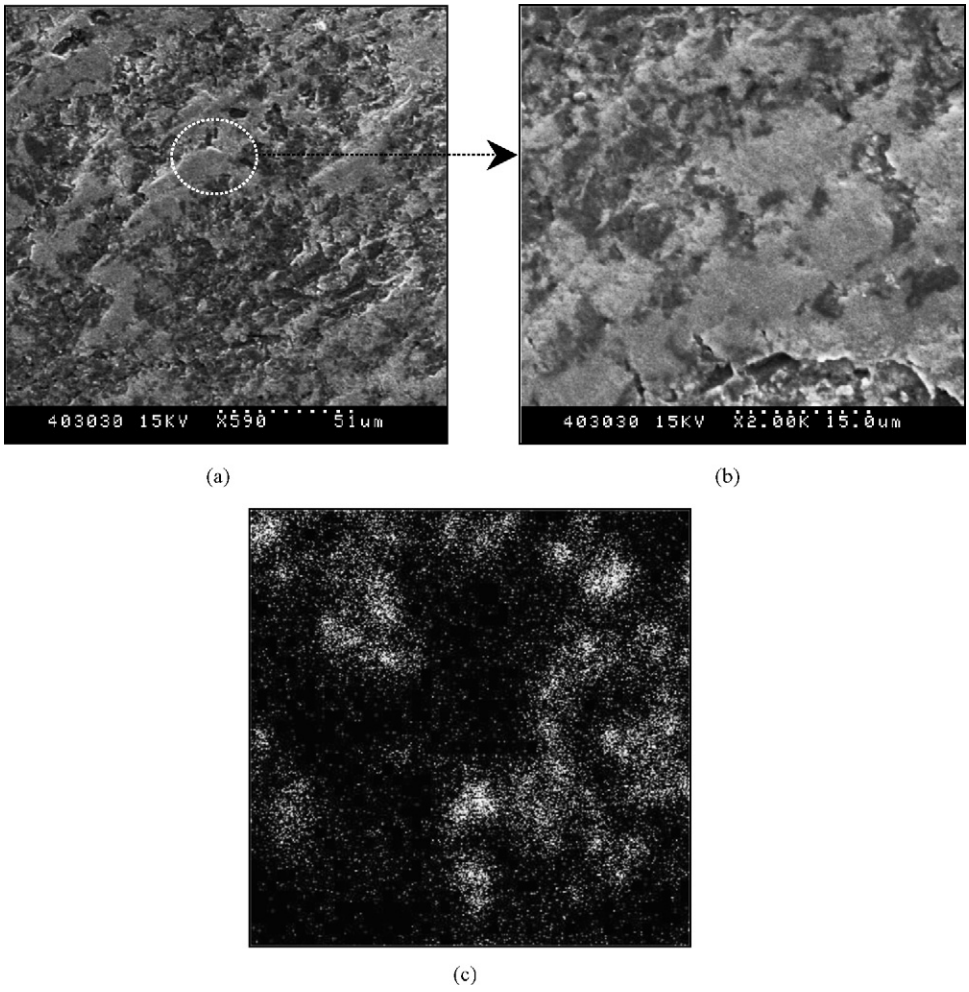


Fig. 9. SEM micrographs of (a) the worn surface of ATF2 ceramic composite, (b) enlarged SEM micrograph corresponding to (a), (c) the F element distribution corresponding to (a) (sliding speed $v = 400$ r/min).

proportion CaF_2 solid lubricants. In comparison with Fig. 8, 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. 9(c). The results indicate that CaF_2 has been released and smeared on the wear surface, and reveals the existence of a thin dense self tribofilm on the worn surface after sliding wear tests. Fig. 10 illustrates the schematic diagram of the formation process of self tribofilm on the wear track.

Fig. 11 shows the stress distribution in the sliding couple (ATF2/YG8) calculated by finite element method (FEM). It was found that the maximum main and shear stresses are at the center of the contact area between the sliding couple. The main stresses exhibited a maximum value of 97 MPa, and the maximum shear stress is of 135 MPa. Comparison of maximum main stress and shear stress of AT and ATF2 ceramic composites sliding against YG8 cemented carbide are listed in Table 3. It can be seen that additions of CaF_2 solid lubricants to the Al_2O_3/TiC matrix led to a decrease in main stress and shear stress compared to a normal Al_2O_3/TiC composite.

The friction coefficient between two smooth bodies sliding under elasticity-loaded conditions in an elliptical contact can be expressed as [18]:

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

where A is a constant determined by contact geometry, τ is critical shear stress at the interface, which may be a 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

Table 3
Comparison of the maximum main stress and shear stress of AT and ATF2 ceramic composites calculated by finite element method (sliding speed 400 r/min)

Specimen	Maximum main stress (MPa)	Maximum shear stress (MPa)
AT	162	169
ATF2	97	135

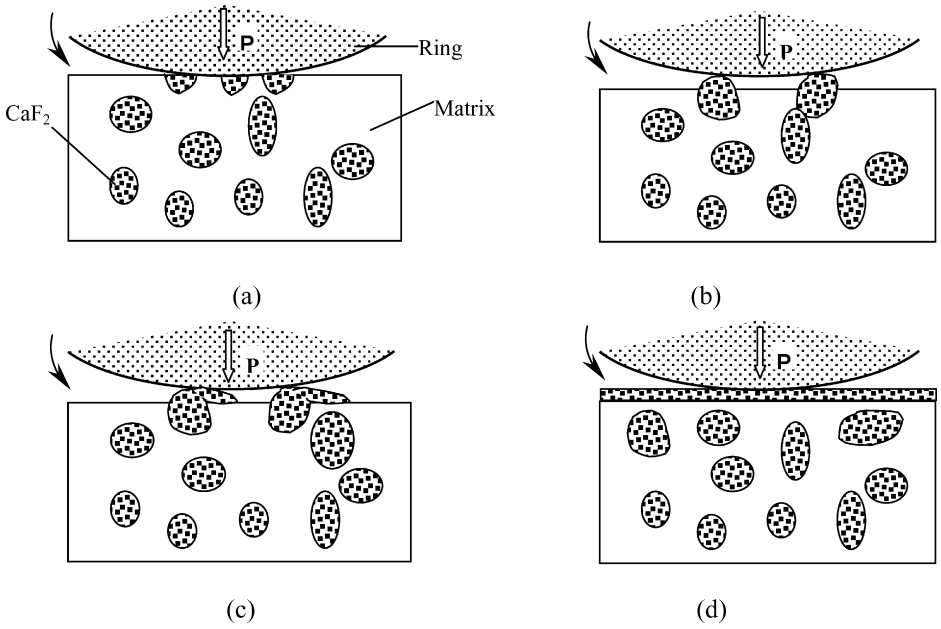


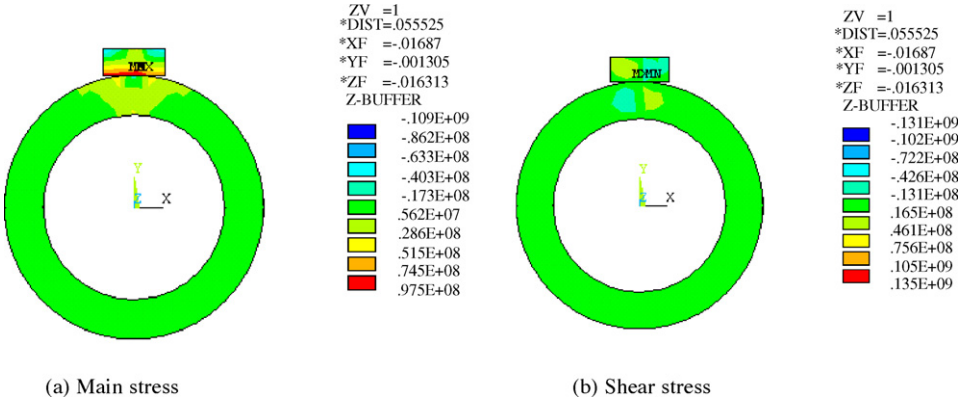
Fig. 10. Schematic diagram of the formation process of self tribofilm between the sliding couple.

shear stress. When there is a tribofilm on the wear surface, the matrix endures the load, and friction occurs on the lubricant film [19,20]. 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 sliding against cemented carbide. This may be due to the formation of a CaF_2 self tribofilm 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 self-tribofilm works as a lubricious buffer between cemented carbide ring and the ceramic block in sliding process to significantly reduce the friction coefficient and the wear rate. This means that self-lubrication can be accomplished for Al_2O_3/TiC/CaF_2 composites when with low CaF_2 content (less than 10 vol.%).

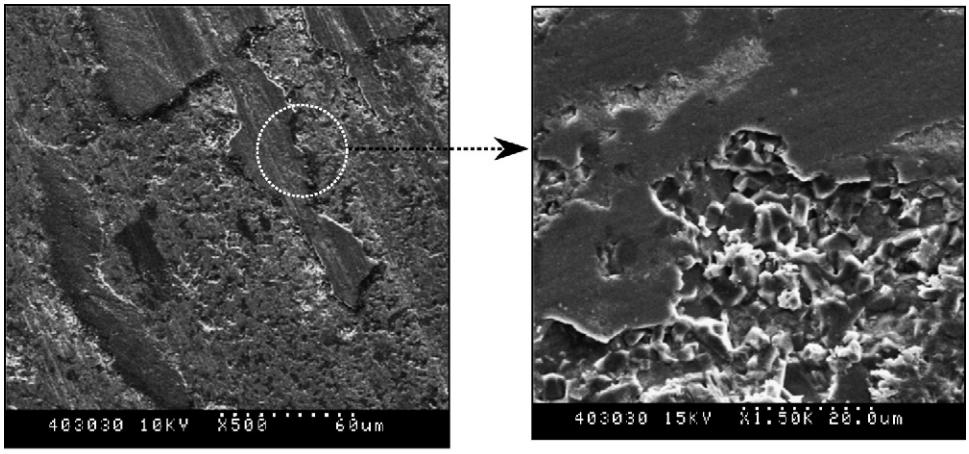
Fig. 12 shows the SEM micrograph of the worn surface of ATF3 ceramic composite with 15 vol.% proportions of CaF_2 solid lubricants. In comparison with Fig. 9, it exhibited a damaged surface, a lot of damages could be observed on the tribofilm. The results indicate that CaF_2 has been released and smeared on the wear surface, and reveals the existence of a broken tribofilm on the worn surface of after sliding wear tests.

Therefore, 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 due to the formation of a dense self tribofilm between the sliding couple, and to the decrease in main stress and shear stress compared to a normal Al_2O_3/TiC composite. 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 when with higher CaF_2 content as can be seen in Table 2, and to the formation of a broken tribofilm between the sliding couple.



(a) Main stress (b) Shear stress

Fig. 11. Stress distribution in the sliding couple (ATF2/YG8) calculated by finite element method (FEM): (a) main stress, and (b) shear stress (sliding speed v = 400 r/min).



(a) (b)

Fig. 12. SEM micrographs of the worn surfaces of (a) ATF3 (Al_2O_3/TiC/15 vol.% CaF_2) ceramic composite, (b) enlarged SEM micrograph corresponding to (a).

This means that self-lubrication could not be accomplished for Al_2O_3/TiC/CaF_2 composites when with high CaF_2 content (more than 10 vol.%).

The results show that tribofilm plays a very important role on the friction and wear behavior of Al_2O_3/TiC/CaF_2 ceramic composites. Two types of tribofilms are present on the worn surface depending on the CaF_2 content. Dense tribofilm on the surface can protect the ceramics from severe wear by brittle microfracture, and thus significantly reduces the friction coefficient and wear rate. While broken tribofilm on the surface leads to the increase in friction coefficient and wear rate.

4. Conclusions

Al_2O_3/TiC ceramic composites with the additions of CaF_2 solid lubricants were produced by hot pressing. Sliding wear tests against cemented carbide were performed on these ceramic composites. Detailed observations and analyses of the wear surface have revealed that two types of tribofilms are present on the worn surface depending on the CaF_2 content. A dense self tribofilm with a smooth surface associated with small friction coefficient and low wear rate is formed by the releasing and smearing of CaF_2 solid lubricants on the wear surface when with low CaF_2 content (less than 10 vol.%). This dense self tribofilm acted as solid lubricant film between the sliding couple, and resulted in small friction coefficient and low wear rate. A broken tribofilm associated with high friction coefficient and large wear rate is formed when with high CaF_2 content (more than 10 vol.%). The reason is that large degradation of mechanical properties occurred in samples with high CaF_2 contents

Acknowledgements

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