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Microstructure and mechanical properties of hot-pressed Al_2O_3/TiC ceramic composites with the additions of solid lubricants

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Abstract

Al_2O_3/TiC ceramic composites with the additions of different solid lubricants such as MoS_2, BN, and CaF_2 were produced by hot pressing. Effect of the solid lubricants on the microstructure and mechanical properties of this ceramic composite has been studied. No trace of MoS_2 was found in the sintered Al_2O_3/TiC/MoS_2 composite owing to its low melting point and escaping during the hot-pressing process. The flexural strength, fracture toughness, and hardness of Al_2O_3/TiC/MoS_2 composite continuously decreased with the increasing of MoS_2 content. AlN phase resulted from the reaction of Al_2O_3 with BN was formed in Al_2O_3/TiC/BN composite after sintering. Significant micro-cracks resulted from the residual stress owing to the difference in the thermal expansion coefficient were found on the polished surface, and caused large mechanical properties degradation for Al_2O_3/TiC/BN composite. While Al_2O_3/TiC/CaF_2 ceramic composite showed relative higher flexural strength, fracture toughness, and hardness compared with that of Al_2O_3/TiC/MoS_2 and Al_2O_3/TiC/BN composites owing its absence porosity and finer microstructure.

Keywords: B. Composites; B. Microstructure; C. Mechanical properties; D. Al_2O_3

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, the 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 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 the 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 particles or whiskers additions to the Al_2O_3 matrix provides great improvements of its mechanical properties over the 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 behaviors [7–9].

It is well know 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 ceramic composite inappropriate for practical applications. Therefore, considerable effort has been made to improve

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the tribological performance of ceramic composites. Several researchers [14–19] have found that the incorporation of the 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.

MoS_2, BN, and CaF_2 are well known and widely used solid lubricants. They have physical (prevents adhesion), chemical (enables tribo-chemical reactions) and microstructural (lamellar structure with low shear strength) influence on a 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 [20–21], some of the ceramic composites, such as: Al_2O_3/graphite, Al_2O_3/CaF_2, Si_3N_4/BN, and TZP/graphite, have been developed and used in various applications, mechanical properties and microstructure studies on them are also extensively carried out. It has been shown that the additions of solid lubricants to ceramic matrix can improve their tribological properties.

In this paper, Al_2O_3/TiC ceramic composites with the additions of different solid lubricants such as MoS_2, BN, and CaF_2 were produced using the hot pressing techniques. The influence of MoS_2, BN, and CaF_2 solid lubricant additions on the mechanical properties and the microstructure of these ceramic composites have been studied and discussed.

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 size, purity and manufacturer. Al_2O_3/TiC (volume ratio 1:1) was used as the baseline material. Additions of solid lubricant particles, such as MoS_2, BN, and CaF_2, were added to Al_2O_3/TiC matrix. The range of solid lubricant additions to the Al_2O_3/TiC 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. 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.

2.2. Material characterization

Test pieces of 3 mm × 4 mm × 36 mm 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 [22]. On the same apparatus the

Table 1
Particle size, purity and manufacturer of the stating 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
MoS_2	<1	>98	Beijing Yili Fine Chemical Products works
BN	<1	>98	Zibo aluminum works
CaF_2	<1	>98.5	Beijing Yili fine chemical products works

Table 2
Compositions and mechanical properties of hot pressed $Al_2O_3/TiC/MoS_2$, $Al_2O_3/TiC/CaF_2$, and Al_2O_3/TiC/BN ceramic composites

Specimen	Compositions (vol.%) (volume ratio: Al_2O_3:TiC = 1:1)	Flexural strength (MPa)	Hardness (GPa)	Fracture toughness (MPa $m^{1/2}$)
1	Al_2O_3 + TiC	800	20.0	5.2
2	Al_2O_3 + TiC + 5% MoS_2	388	13.2	3.3
3	Al_2O_3 + TiC + 10% MoS_2	351	11.9	3.1
4	Al_2O_3 + TiC + 15% MoS_2	336	10.5	3.0
5	Al_2O_3 + TiC + 5% BN	307	12.7	2.5
6	Al_2O_3 + TiC + 10% BN	219	4.4	2.3
7	Al_2O_3 + TiC + 15% BN	133	2.3	2.0
8	Al_2O_3 + TiC + 5% CaF_2	478	13.2	3.4
9	Al_2O_3 + TiC + 10% CaF_2	590	15.3	3.6
10	Al_2O_3 + TiC + 15% CaF_2	418	9.6	3.3

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.

XRD (D/max-2400) analysis was undertaken to identify the crystal phases present after sintering. The microstructures of sintered materials were studied on fracture surfaces and polished section by scanning electron microscopy (HITACHI S-570) and optical microscopy.

3. Results and discussion

3.1. X-ray diffraction phase analysis

Fig. 1(a) and (b) show the X-ray diffraction analysis of the Al_2O_3/TiC/MoS_2 ceramic composite before and after sintering at 1700 °C for 20 min. When compared Fig. 1(a) with Fig. 1 (b), it can be seen that no trace of MoS_2 was found in the sintered specimens. As the solid lubricant MoS_2 is a low melting phase, its melting point is only 1185 °C. When the Al_2O_3/TiC/MoS_2 ceramic composite was hot pressed at 1700 °C, the MoS_2 may be molten and escaped owing to high temperature during the hot-pressing process.

Fig. 2 shows the X-ray diffraction analysis of the Al_2O_3/TiC/BN ceramic composite after sintering at 1700 °C for 20 min. It is obvious from Fig. 2 that AlN are newly formed phases, and are resulted from the reaction of Al_2O_3 with BN. No trace of BN was found in the sintered materials when these phases had been added in the powder compacts prior to sintering, showing that a complete reaction occurred during sintering. The reaction formulas are as follows [23]:

$$Al_2O_3 + 2BN \rightarrow 2AlN + B_2O_3 \quad (1)$$

Fig. 3 shows the X-ray diffraction analysis of the Al_2O_3/TiC/CaF_2 ceramic composite after sintering at 1700 °C for

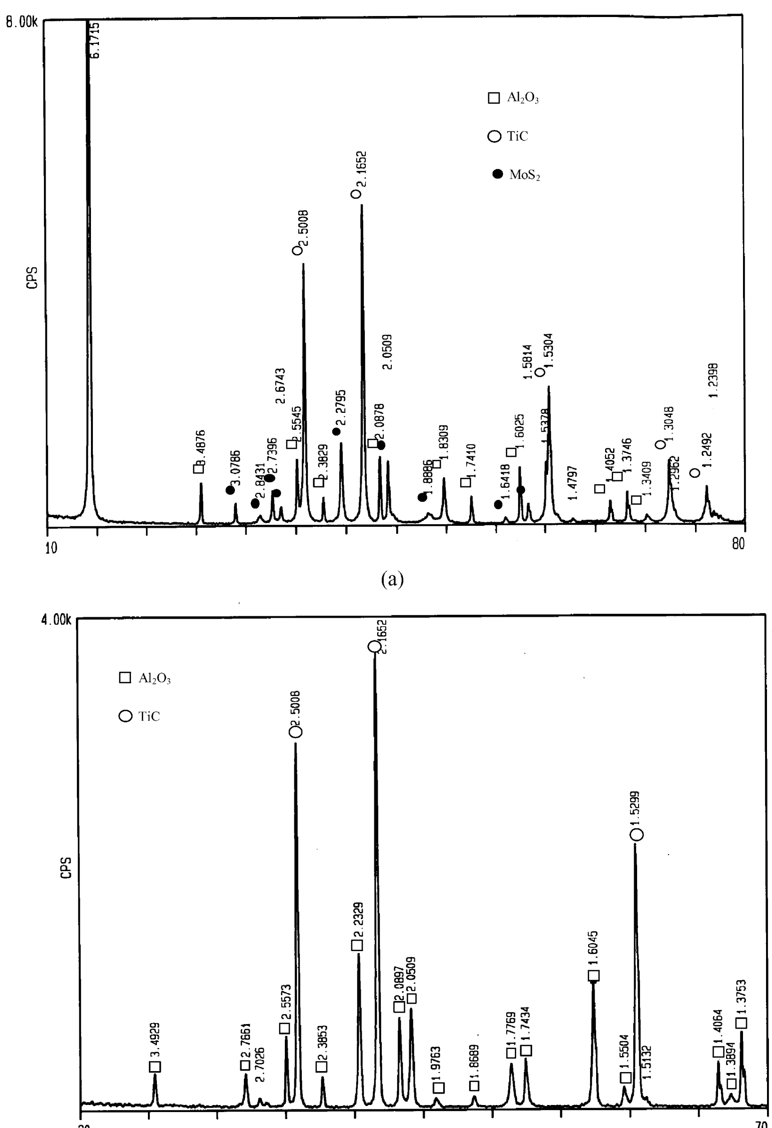


Fig. 1. X-ray diffraction analysis of the Al_2O_3/TiC/MoS_2 ceramic composite, (a) before sintering, and (b) after sintering at 1700 °C.

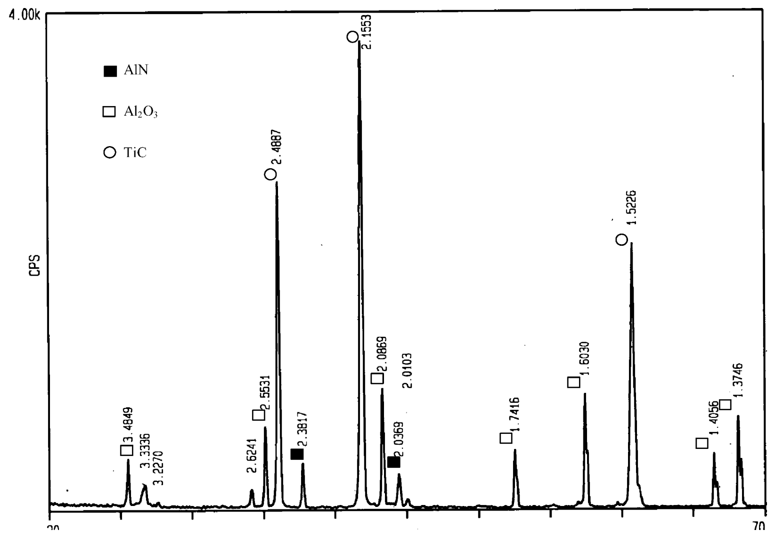


Fig. 2. X-ray diffraction analysis of the Al_2O_3/TiC/BN ceramic composite after sintering at 1700 °C.

20 min. It can be seen that Al_2O_3, TiC, and CaF_2 are all existed in the sintered specimens.

3.2. Microstructural characterization

Fig. 4(a) and (b) show the typical microstructure from the polished surface of hot pressed Al_2O_3/TiC/MoS_2 ceramic composite, specimens were etched using a hot-solution of phosphoric acid. It is obvious that there are a lot of obvious pores or cavities of varying diameter and morphology located on the polished surface. The probability of finding such features on the polished surface was significantly greater. This may be resulted from the melt formation for the low melting phase MoS_2 and it is escaping during the hot-pressing processes.

Fig. 5(a) shows the typical microstructure from the polished surface of hot-pressed Al_2O_3/TiC/BN ceramic composite, which reveals quite a number of cracks on the polished surface. Fig. 5(b) shows the cracks clearly at higher magnification. As chemical reaction was took place during hot pressing process. New phase AlN resulted from the reaction of Al_2O_3 with BN was existed in the sintered specimens. Since there was large thermal expansion coefficient mismatch among Al_2O_3, TiC, and AlN in this composite (as can be seen in Table 3), the cracks on the polished surface were thought to be caused by the residual stress generated by the difference in the thermal expansion coefficient of Al_2O_3, TiC, and AlN.

The typical microstructure from the polished surface of hot-pressed Al_2O_3/TiC/CaF_2 ceramic composite is shown in Fig. 6(a) and (b). The black areas as identified by EDX analysis is of TiC and CaF_2, and the white phases with clear contrast are of Al_2O_3. As can be seen that TiC and CaF_2 particles are quite uniformly distributed throughout the microstructure. It is indicated that porosity is virtually absent, and the solid lubricant phases were uniformly dis-

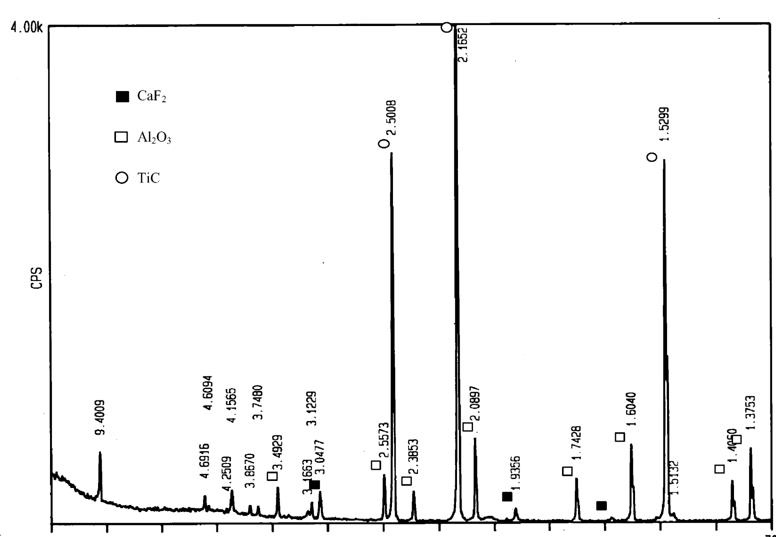
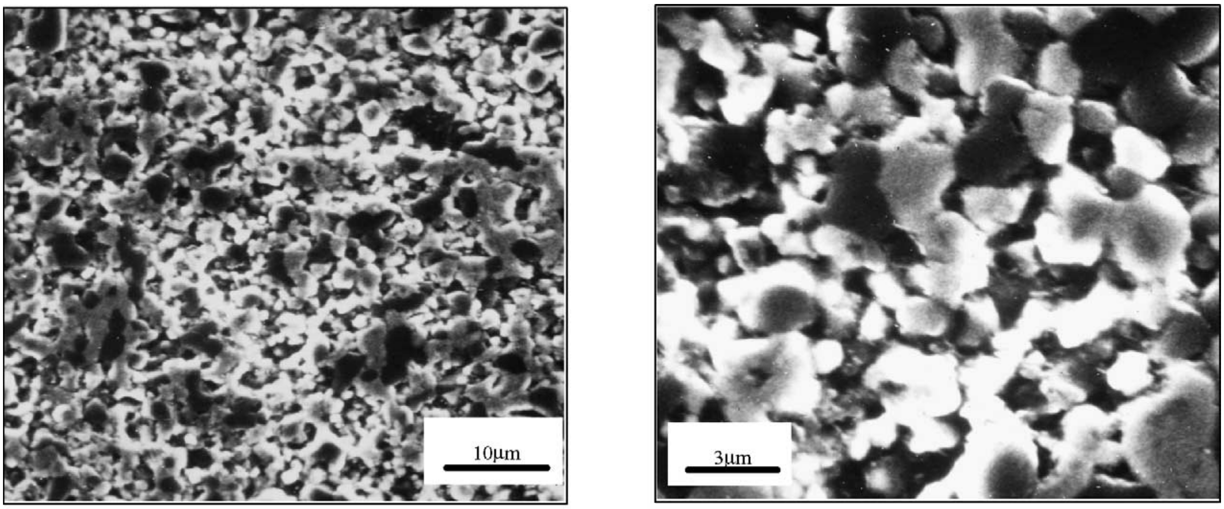
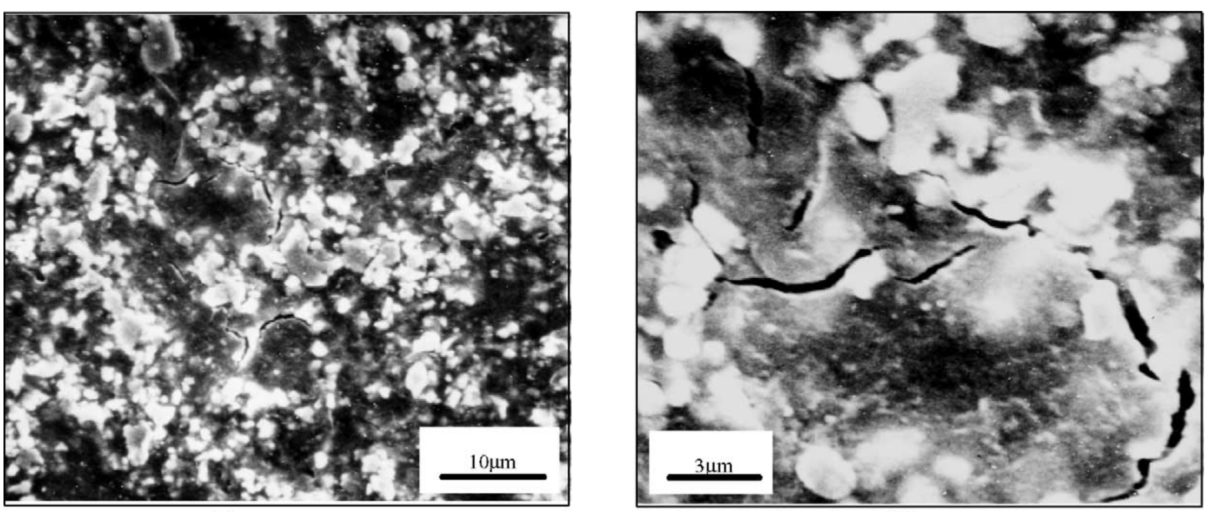


Fig. 3. X-ray diffraction analysis of the Al_2O_3/TiC/CaF_2 ceramic composite after sintering at 1700 °C.



(a) (b)

Fig. 4. Typical microstructure of the polished surface of Al_2O_3/TiC/MoS_2 ceramic composite.



(a) (b)

Fig. 5. Typical microstructure of the polished surface of Al_2O_3/TiC/BN ceramic composite.

tributed with the matrix, and there were few second phase agglomerates or matrix-rich regions.

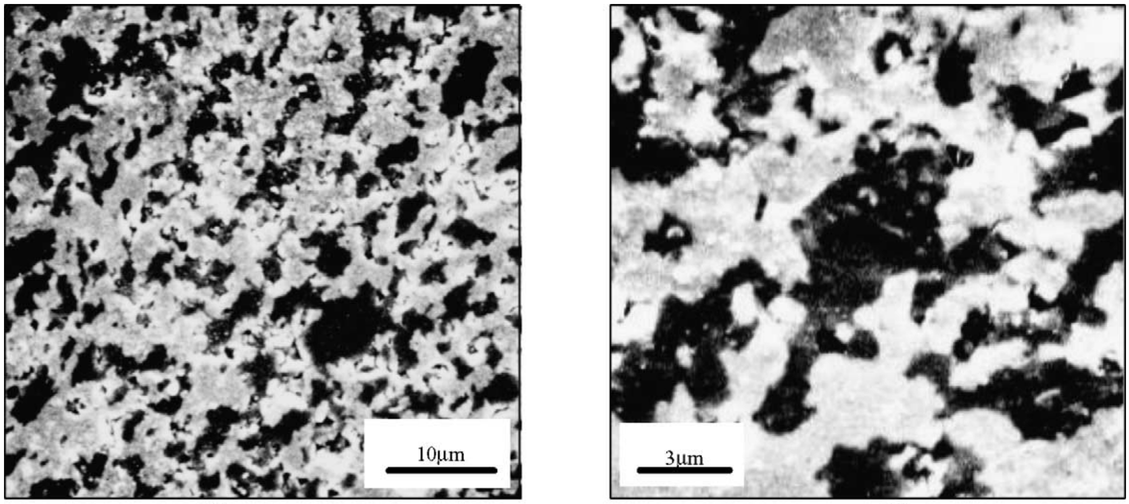
Figs. 7–9 show the SEM micrographs of the fracture surfaces of Al_2O_3/TiC/MoS_2, Al_2O_3/TiC/CaF_2, and Al_2O_3/TiC/BN ceramic composites respectively. From these SEM micrographs, different morphologies of these composites can be seen clearly. The Al_2O_3/TiC/MoS_2, Al_2O_3/TiC/BN, and Al_2O_3/TiC/CaF_2composites exhibited a rough fracture surface, resulting from the mixed transgranular and intergranular fracture mode.

3.3. Mechanical properties

The mechanical properties of Al_2O_3/TiC/MoS_2, Al_2O_3/TiC/CaF_2, and Al_2O_3/TiC/BN ceramic composites with different content of solid lubricants are listed in Table 2.

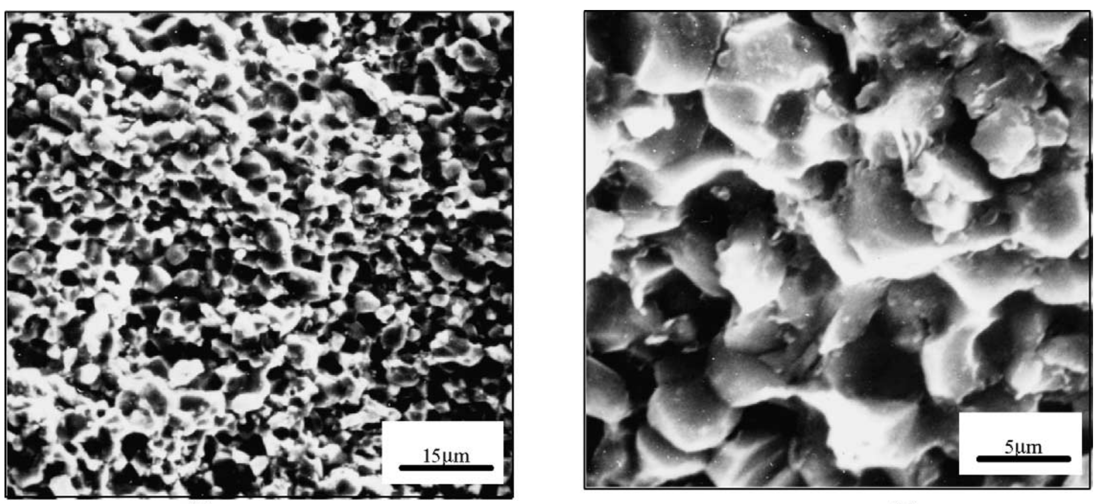
Table 3
Properties of BN, Al_2O_3, TiC, and AlN [24]

	Density (g/cm^3)	Elastic modulus (GPa)	Thermal conductivity (W/(m K))	Thermal expansion coefficient (10^{-6}/K)
Al_2O_3	3.98	407	34	8.6
BN	2.27	84	25.1	7.5
AlN	3.26	350	30	4.5
TiC	4.95	450	31.8	7.4



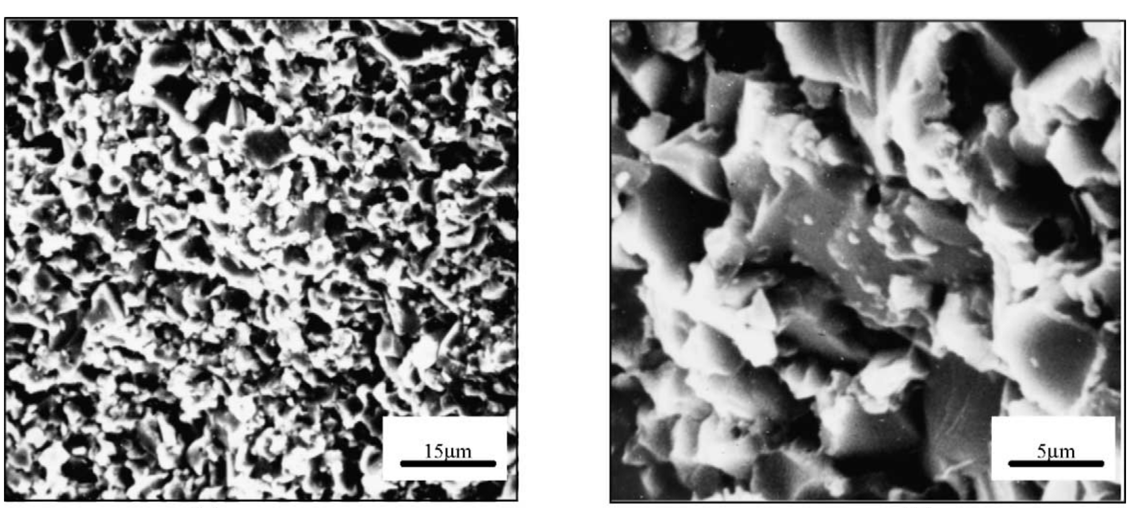
(a) (b)

Fig. 6. Typical microstructure of the polished surface of Al_2O_3/TiC/CaF_2 ceramic composite.



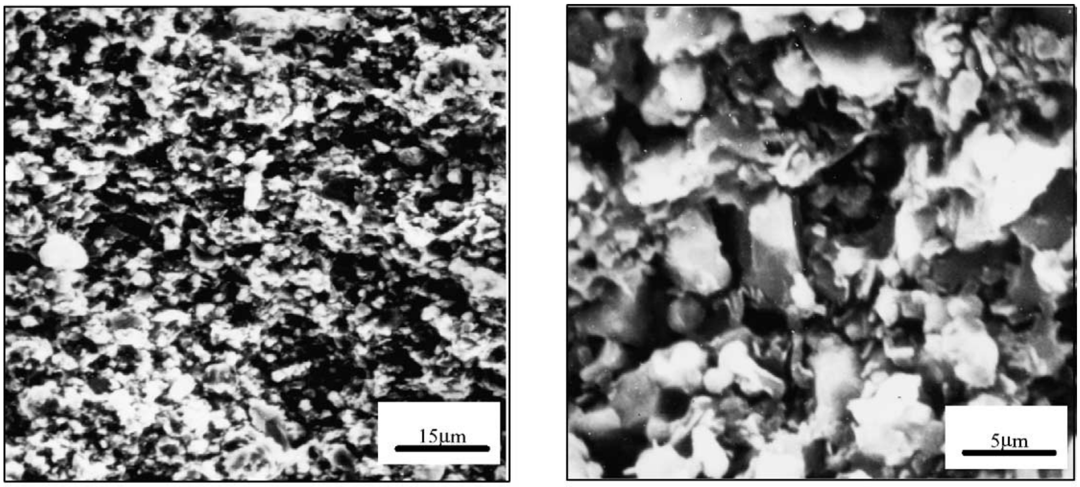
(a) (b)

Fig. 7. SEM micrographs of the fracture surfaces of Al_2O_3/TiC/MoS_2 ceramic composite.



(a) (b)

Fig. 8. SEM micrographs of the fracture surfaces of Al_2O_3/TiC/CaF_2 ceramic composite.



(a) (b)

Fig. 9. SEM micrographs of the fracture surfaces of Al_2O_3/TiC/BN ceramic composite.

It was found that the flexural strength of Al_2O_3/TiC/MoS_2 ceramic composite continuously decreased with the increasing of MoS_2 content up to 15 vol.%, and decrease from 800 MPa for hot-pressed Al_2O_3/TiC to 336 MPa for Al_2O_3/TiC/15% MoS_2 composite, representing a maximum decreasing of 464 MPa. The trend of the hardness and the fracture toughness is the same as that of the flexural strength.

The flexural strength, fracture toughness and hardness of Al_2O_3/TiC/BN ceramic composite were found to decrease with the increasing of BN content. When compared with Al_2O_3/TiC, Al_2O_3/TiC/MoS_2 and Al_2O_3/TiC/CaF_2 ceramic composites, the flexural strength, fracture toughness and hardness of Al_2O_3/TiC/BN ceramic composite is rather small (for example: hardness = 2.3 GPa, K_{IC} = 2.0 MPa $m^{1/2}$, flexural strength = 133 MPa for Al_2O_3/TiC/15% BN composite). As can be seen that there is a remarkable micro-cracks on the polished surfaces of this composite, which may serve as fracture origins. Therefore, cracks caused by the residual stress owing to the difference in the thermal expansion coefficient of Al_2O_3, TiC, and AlN may be the direct consequence of the mechanical properties degradation of this composites.

The flexural strength of Al_2O_3/TiC/CaF_2 ceramic composite exhibited a maximum value of 590 MPa for 10 vol.% CaF_2, and with further increasing 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.

4. Conclusions

Al_2O_3/TiC ceramic composites with the additions of different solid lubricants, such as MoS_2, CaF_2, and BN, were produced by hot pressing. Particular attention was paid to the effect of solid lubricants additions on the mechanical properties and microstructure. Results showed that

1. No trace of MoS_2 was found in the sintered Al_2O_3/TiC/MoS_2 composite owing to the low melting point of MoS_2. There are a lot of obvious pores or cavities located on the polished surface resulted from the melting and escaping of MoS_2 during the hot-pressing processes. The flexural strength, fracture toughness, and hardness of Al_2O_3/TiC/MoS_2 composite continuously decreased with increasing of MoS_2 content up to 15 vol.%.
2. AlN phase resulted from the reaction of Al_2O_3 with BN was formed in Al_2O_3/TiC/BN composite after sintering. Significant micro-cracks resulted from the residual stress owing to the difference in the thermal expansion coefficient were found on the polished surface, and caused large mechanical properties degradation for Al_2O_3/TiC/BN composite.
3. Al_2O_3/TiC/CaF_2 ceramic composite showed higher flexural strength, toughness, and hardness compared with that of Al_2O_3/TiC/MoS_2 and Al_2O_3/TiC/BN composites owing its porosity absent and finer microstructure.

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