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Mechanical and tribological properties of hot-pressed h-BN/Si_3N_4 ceramic composites

Daqing Wei *, Qingchang Meng, Dechang Jia

Institute for Advanced Ceramics, Harbin Institute of Technology, Harbin 150001, PR China

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Abstract

h-BN/Si_3N_4 ceramic composites were fabricated by hot-pressing using sub-micrometer sized α-Si_3N_4, h-BN powders and Y_2O_3–Al_2O_3 sintering additives. The microstructural analysis indicated the growth of β-Si_3N_4 grains to be hindered by h-BN particles and the diameter and aspect ratio of elongated β-Si_3N_4 grains to decrease with increasing h-BN content. As expected, this increase of h-BN content resulted in a slight decrease in the bending strength and fracture toughness and a sharp decrease in the elastic modulus and Vickers hardness of h-BN/Si_3N_4 ceramic composites. In addition, the friction coefficient of the h-BN/Si_3N_4 ceramic composites decreased with increasing h-BN content. A spalling mode of failure has been observed on the worn surface of monolithic Si_3N_4 and 10 vol.%h-BN/Si_3N_4 ceramic composite.

Keywords: B. Composites; C. Mechanical properties; C. Friction; D. Si_3N_4

1. Introduction

Si_3N_4 ceramic is promising for structural and tribological applications because it has low density, a low coefficient of thermal expansion, high strength and toughness and high resistance to wear and thermal shock [1–7]. However, the high hardness and elastic modulus of Si_3N_4 ceramic in hybrid steel/Si_3N_4 bearings result in high contact stress between bearing ball and groove, which reduces load capacity and shortens the rolling contact fatigue life of hybrid bearings [2]. In addition, in some cases, ceramic bearings are used under vacuum and exposed to a condition of elevated temperature, therefore liquid lubricants are unsuitable for these environments. In order to improve the tribological properties of ceramic materials, a self-lubricating phase such as graphite was introduced in ceramic matrixes [8,9]. However, graphite has significant effects on the mechanical properties of ceramic materials such as the strength and toughness [10].

For structural and tribological applications, the mechanical properties of the self-lubricating ceramic composite also should be taken into account besides its tribological properties. Generally speaking, the strength of the self-lubricating ceramic composite with a great quantity of a lubricating phase is not high due to the low strength of a lubricating phase. In addition, the previous investigations have indicated that the mechanic properties have a significant effect on the tribological properties of ceramic material [2,11], for instance, high fracture toughness can enhance the wear property of ceramic material [11].

It is well known that h-BN possesses a number of interesting properties such as lubrication action, low hardness and low friction coefficient. However, it has less reported that the effect of adding a small quantity of h-BN on the microstructure and tribological and mechanical properties of Si_3N_4 ceramic. In this experiment, h-BN was introduced into Si_3N_4 ceramic. The aim of adding a small quantity of h-BN is to decrease appropriately the hardness and elastic modulus of Si_3N_4 ceramic, consequently, to decrease the high contact stress between bearing ball and groove. It is also expected to maintain the high flexural strength and fracture toughness of Si_3N_4 ceramic matrix. In addition, the effects of h-BN on the

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* Corresponding author. Tel.: +86 451 8640 2040 8530;
fax: +86 451 8641 4291.
E-mail address: daqingwei@hit.edu.cn (D. Wei).

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Table 1
The compositions of raw materials (vol.%)

Specimens	$Si_3N_4 + Y_2O_3 + Al_2O_3$	h-BN
SN0	100	0
SN2	98	2
SN4	96	4
SN6	94	6
SN8	92	8
SN10	90	10

friction coefficient and wear behaviour of Si_3N_4 matrix were also investigated preliminarily.

2. Experimental

Six kinds of compositions were designed, as shown in Table 1; the mass ratio of Si_3N_4, Y_2O_3 and Al_2O_3 was 94:4.5:1.5. Powders of α-Si_3N_4 (85%αSi_3N_4 phase, Shanghai Institute of Material Research, China), h-BN (99.5%, Beijing Chemical Factory, China), Y_2O_3 (99.9%, Shanghai Yuelong Chemical Factory, China) and Al_2O_3 (99.5%, Beijing Chemical Factory, China) were mixed and ball-milled in alcohol for 24h. After the slurry was dried, the powders were hot-pressed in flowing N_2 at 1800 °C for 1 h in a h-BN-coated graphite die. To minimize the effect of relative density on the mechanical and tribological properties, a high hot-pressure of 40 MPa was applied to fabricate h-BN/Si_3N_4 ceramic composites of a high relative density.

The relative density was calculated on the basis of the theoretical and bulk density measured by the Archimedes's method. Microstructure of h-BN/Si_3N_4 ceramic composites was characterized using a Hitachi S-570 scanning electron microscope (SEM). Bending strength was determined by three point bend testing (test bars 4 mm × 3 mm × 36 mm), with a bending span of 30 mm and a cross-head speed of 0.5 mm/min at room temperature on a universal testing machine (Instron-5569). Fracture toughness was determined by the single-edge-notched beam (SENB) method (test bars 2 mm × 4 mm × 20 mm) on a universal testing machine (Instron-5569). Elastic modulus was measured using a universal testing machine (Instron-5569). The Vickers hardness was measured using a hardness testing machine (HBV-30A) with a load of 30 kN held for 15 s. The friction coefficient was measured using friction and wear testing machine (CJS111A) with a load of 4 N. The polished and worn surfaces of specimens were characterized using a Hitachi S-570 SEM.

3. Results and discussion

3.1. Effect of h-BN on the relative density and microstructure

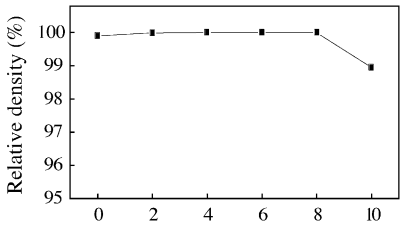

Fig. 1. Effect of h-BN content on the relative density of h-BN/Si_3N_4 ceramic composites.

The effect of h-BN content on the relative density and microstructure of h-BN/Si_3N_4 ceramic composites were investigated. Fig. 1 shows the relative density change of h-BN/Si_3N_4 ceramic composites with the different addition of h-BN content. The h-BN/Si_3N_4 ceramic composites are densified completely as the addition of h-BN content is less than or equal to 8 vol.%. However, the relative density of h-BN/Si_3N_4 ceramic composite with 10% h-BN volume content reduces slightly as shown in Fig. 1. Due to the low-chemically active nature of h-BN in h-BN/Si_3N_4 ceramic composite, therefore h-BN reduces the sinter ability of SN10, leading to the decrease in relative density of SN10. Nevertheless, the h-BN/Si_3N_4 ceramic composites with a small quantity of h-BN maintain high relative density.

Fig. 2 shows SEM micrographs of the microstructure of h-BN/Si_3N_4 ceramic composites. The microstructure of SN0 primarily consists of coarse elongated β-Si_3N_4 grains with high aspect ratios, equiaxed β-Si_3N_4 grains and intergranular phase as shown in Fig. 2a. However, when 10 vol.%h-BN is introduced into the Si_3N_4 matrix, a number of short and rod-like β-Si_3N_4 grains are observed as shown in Fig. 2f.

The formation of elongated β-Si_3N_4 grain can be explained by the anisotropic grain growth. Due to the lower boundary energy in the *c*-direction than in *a*-direction of hexagonal crystal, the energetically more favorable nucleation takes place on the surface of the basal plane [12]. That results in a higher growth rate in the *c*-direction and the formation of elongated grain. In addition, as can be seen from Fig. 2, the diameter and aspect ratio of elongated β-Si_3N_4 grains in composites decrease with increasing h-BN content. That is due to the growth of β-Si_3N_4 grains to be hindered by h-BN particles. In the grain growth stage of microstructural evolution, the growth of the β-Si_3N_4 nucleus is limited by h-BN particles as the β-Si_3N_4 nucleus contacts h-BN particles in the growth direction of the β-Si_3N_4 nucleus, thereby β-Si_3N_4 nuclei are unable to develop sufficiently in time. However, nucleation takes place continually. This suggests that the rate of nucleation increase relatively, resulting in microstructure refining. Therefore, the diameter and aspect ratio of β-Si_3N_4 grains decrease with increasing h-BN content.

3.2. Effect of h-BN on the mechanical properties

3.2.1. Flexural strength

Fig. 3 shows the relation of the flexural strength of h-BN/Si_3N_4 ceramic composites versus h-BN content. The bending strength of h-BN/Si_3N_4 ceramic composites decreases with

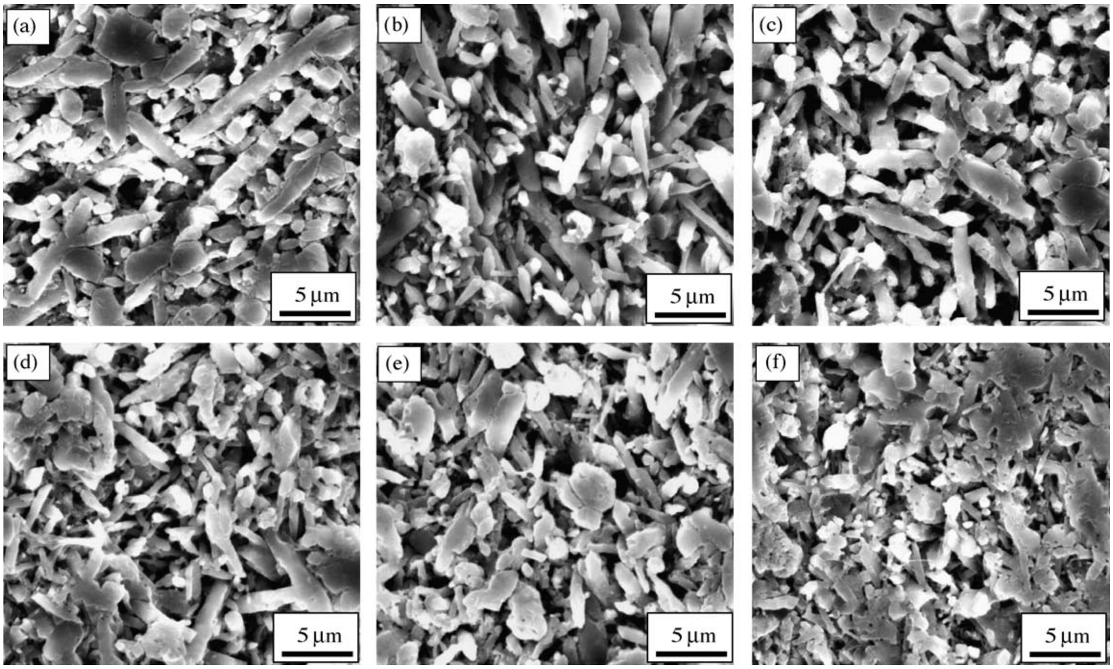

Fig. 2. SEM micrographs of the etched surface of (a) SN0, (b) SN2, (c) SN4, (d) SN6, (e) SN8 and (f) SN10.

increasing h-BN content as shown in Fig. 3, which is mainly due to the low strength of h-BN and weak interface between h-BN and Si_3N_4 grains.

Nevertheless, the bending strength of h-BN/Si_3N_4 ceramic composites decreases slightly with increasing h-BN content, which is due to the reduction of β-Si_3N_4 grain size. Generally speaking, the strength of Si_3N_4 ceramic can be enhanced by reducing the grain size of β-Si_3N_4 [13]. According to the microstructural analysis, the diameter and aspect ratio of β-Si_3N_4 grains in composites decrease with increasing h-BN content. Therefore, the strength has a tendency to be improved with the reduction of β-Si_3N_4 grain size. This result reveals that Si_3N_4 ceramic still has a high bending strength as a small quantity of h-BN is incorporated into Si_3N_4 ceramic matrix. High strength of h-BN/Si_3N_4 ceramic composites is necessary for its structural application.

3.2.2. Fracture toughness

The effect of h-BN content on the fracture toughness of h-BN/Si_3N_4 ceramic composites was investigated. Fig. 3 shows the relation of the fracture toughness of h-BN/Si_3N_4 ceramic composites versus h-BN content. As can be seen from this figure, the monolithic Si_3N_4 has high fracture toughness. However, the fracture toughness of h-BN/Si_3N_4 ceramic composites deceases slightly with increasing h-BN content.

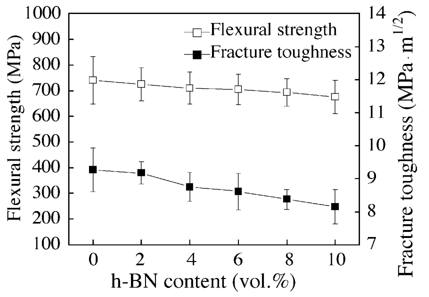

Fig. 3. Effect of h-BN content on the flexural strength and fracture toughness of h-BN/Si_3N_4 composites.

Many investigators have demonstrated that the fracture toughness of β-Si_3N_4 ceramic is strongly dependent upon grain morphology [14–16]. The improved fracture toughness of β-Si_3N_4 ceramic is the result of a reinforcing phenomenon from the whisker-like β-Si_3N_4 grains, similar to the behavior observed in whisker-reinforced ceramics. It has been demonstrated that the fracture toughness of Si_3N_4 ceramic can be enhanced by increasing the diameter and aspect ratio of elongated β-Si_3N_4 grains [1,17–20]. In addition, other factors can also affect the fracture toughness such as volume fraction of the bridging grains and the compositions and properties of the boundary phase [21].

As mentioned above, the fracture toughness of β-Si_3N_4 ceramic is strongly dependent upon β-Si_3N_4 grain morphology. That the monolithic Si_3N_4 has high fracture toughness is mainly attributed to large numbers of coarse elongated β-Si_3N_4 grains with high aspect ratios, yielding various toughening mechanisms such as grain bridging, crack deflection and pull-out of the elongated β-Si_3N_4 grains. As shown in Fig. 4a, many coarse voids due to the pull-out of the elongated β-Si_3N_4 grains were observed on the fractured surface of monolithic Si_3N_4. However, with increasing h-BN content, the diameter and aspect ratio of elongated β-Si_3N_4 grains decrease, which weakens the toughening mechanisms of elongated β-Si_3N_4 grains. Therefore, the fracture toughness of h-BN/Si_3N_4 ceramic composites decreases with increasing h-BN content.

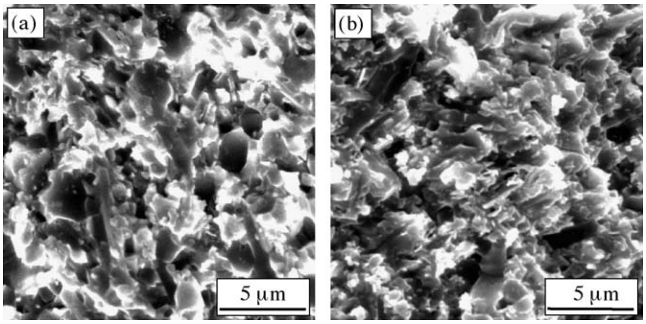

Fig. 4. SEM micrographs of the fractured surface of (a) SN0 and (b) SN10.

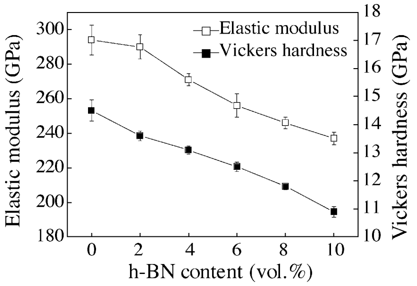

Fig. 5. Effect of h-BN content on the elastic modulus and Vickers hardness of h-BN/Si_3N_4 ceramic composites.

In contrast to the fractured surface of SN0, even though no large number of coarse β-Si_3N_4 grains of SN10 was pulled out as shown in Fig. 4b, no significant reduction in fracture toughness was observed. This is due to a crack deflection originated from the effect of h-BN particles on crack propagation. When the crack tip contacts the h-BN particle, cracks will propagate within the h-BN particles or along the interface between h-BN and Si_3N_4 grains due to the weak interface between h-BN and Si_3N_4 grains. Other investigators have shown that adding a small quantity of h-BN to Si_3N_4 can increase the fracture toughness of Si_3N_4 ceramic matrix [22]. However, in this investigation the β-Si_3N_4 grain size is a key factor in determining the fracture toughness. Therefore, the fracture toughness of h-BN/Si_3N_4 ceramic composites decreases due to the reduction in the diameter and aspect ratio of elongated β-Si_3N_4 grains. Nevertheless, the extent of reduction in fracture toughness of h-BN/Si_3N_4 ceramic composites is not significant owning to the effect of h-BN particles on crack propagation.

3.2.3. Elastic modulus and Vickers hardness

Fig. 5 shows the relation of the elastic modulus and Vickers hardness of h-BN/Si_3N_4 ceramic composites versus h-BN content. The elastic moduli of SN0 and SN10 are 293.5 and 236.6 GPa, respectively. As can be seen from this figure, the elastic modulus of h-BN/Si_3N_4 ceramic composites decreases sharply with increasing h-BN content. That is caused by the low elastic modulus of h-BN and the weak interface between h-BN and β-Si_3N_4 grains.

The Vickers hardness of h-BN/Si_3N_4 ceramic composites decreases sharply with increasing h-BN content as shown in Fig. 5. The Vickers hardness of SN0 and SN10 are 14.5 and 10.9 GPa, respectively. The sharp decrease in Vickers hardness of h-BN/Si_3N_4 ceramic composites can be explained by the low hardness of h-BN and the weak interface between h-BN and Si_3N_4 grains. The h-BN has a laminated crystal structure similar to graphite and the bond strength between layers is minimal due to the molecular linkage. Therefore, h-BN has lower hardness and is easily broken along interlayers. As a weak phase, the addition of h-BN leads to the reduction in the Vickers hardness of h-BN/Si_3N_4 ceramic composites. In addition, the reduction in Vickers hardness is also related to the weak interface between h-BN and Si_3N_4 grains.

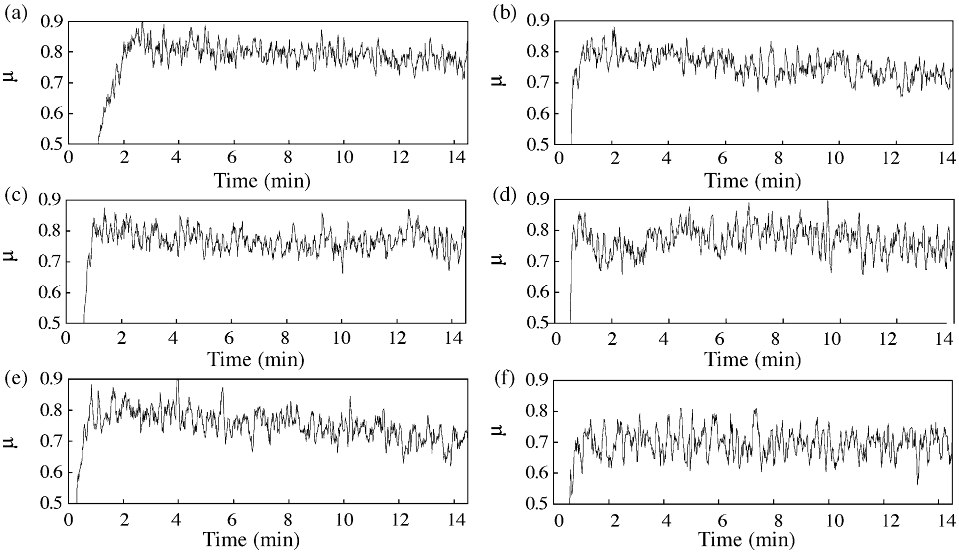

Fig. 6. The friction coefficients of (a) SN0, (b) SN2, (c) SN4, (d) SN6, (e) SN8 and (f) SN10.

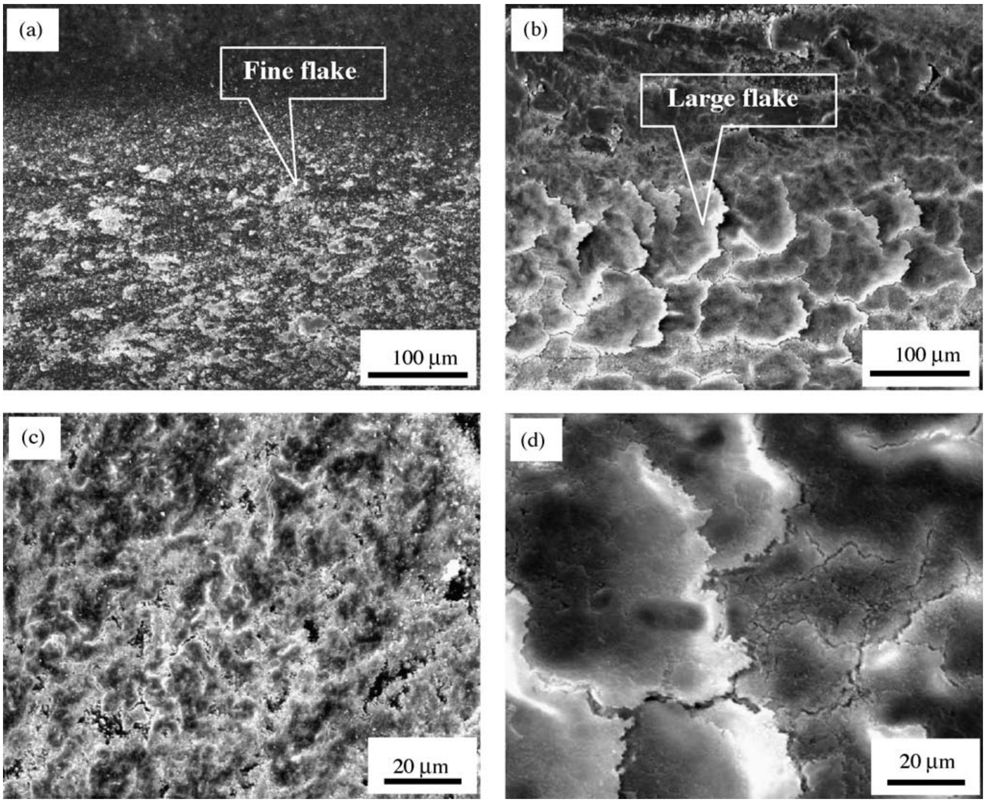

Fig. 7. SEM micrographs of the worn surfaces of monolithic Si_3N_4 and 10 vol.%h-BN/Si_3N_4 ceramic composite: (a), (c) SN0 and (b), (d) SN10.

3.3. Effect of h-BN on the tribological properties

3.3.1. Friction coefficient

Fig. 6 shows the relation of the friction coefficient of h-BN/Si_3N_4 ceramic composites versus h-BN content. In all cases the friction coefficient rose quite quickly at the start of the test before reducing to a level which remained relatively constant for the remainder of the test. It can be seen that the friction coefficient of h-BN/Si_3N_4 ceramic composites has a tendency to decrease with increasing h-BN content.

h-BN has a lower friction coefficient and lubrication action, thereby the friction coefficient of h-BN/Si_3N_4 ceramic composites decreases with increasing h-BN content. In addition, the reductions in diameter and aspect ratio of elongated β-Si_3N_4 grains also result in the decrease of friction coefficient. Investigations of ZrO_2, Al_2O_3 and ZrO_2–Al_2O_3 ceramics system have shown that the frictional surface of fine-grains ceramic is more smooth and the friction coefficient is lower than that of coarse-grains ceramic [23–25]. Therefore, the reduced β-Si_3N_4 grain size is also the factor to decrease the friction coefficient of h-BN/Si_3N_4 ceramic composites (see Fig. 6).

3.3.2. Wear behaviour

The wear behaviour of SN0 and SN10 were investigated preliminarily. Fig. 7 shows the SEM micrographs of the worn surfaces of SN0 and SN10. A surface spalling mode of failure is observed on the worn surfaces of SN0 and SN10. However, the characteristic of spalling morphology on worn surface changes from fine flakes to large flakes by incorporating 10 vol.%h-BN into the Si_3N_4 ceramic matrix as shown in Fig. 7a and b. In addition, no coarse cracks are observed on the worn surface of SN0 but on that of SN10 as shown in Fig. 7c and d.

The formation of coarse cracks on the worn surface of SN10 can be explained by the surface pores and weak interface between h-BN and β-Si_3N_4 grains. Fig. 8 shows the SEM micrographs of the polished surfaces of SN0 and SN10. No evident pores are observed on the polished surface of SN0 as shown in Fig. 8a. However, as can be seen from Fig. 8b, pores are produced by incorporating 10 vol.%h-BN into Si_3N_4 ceramic matrix, which is caused by the reduction in its sinter ability. The pores of SN10 lead to the stress concentration, thereby microcracks are easily produced from the sites of pores existed by applying stress. In addition, the weak interface also

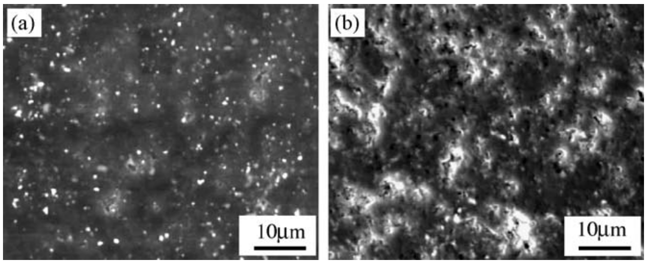

Fig. 8. SEM micrographs of the polished surfaces of (a) SN0 and (b) SN10.

results in the formation of microcracks. Eventually, the accumulation and propagation of microcracks result in the formation of coarse cracks on the worn surface of SN10.

Consequently, the propagation of coarse cracks leads to the formation of large flakes on the worn surface of SN10. In addition, as can be seen from Fig. 8d, the surface of each coarse flake is smooth, which is due to the lubrication action and low hardness of h-BN.

In order to understand thoroughly the effect of h-BN on the tribological properties of h-BN/Si_3N_4 ceramic composites, further works need to be conducted.

4. Conclusions

Hot-pressed h-BN/Si_3N_4 ceramic composites with a small quantity of h-BN can maintain high relative density.

The growth of β-Si_3N_4 grains is hindered by h-BN particles and the diameter and aspect ratio of β-Si_3N_4 grains in composites decrease with increasing h-BN content.

The aim of decreasing the hardness and elastic modulus of Si_3N_4 ceramic appropriately and maintaining its high flexural strength and fracture toughness by introducing a small quantity of h-BN into Si_3N_4 ceramic was achieved.

The friction coefficient of h-BN/Si_3N_4 ceramic composites decreases with increasing h-BN content due to the lubrication action of h-BN and the reduced β-Si_3N_4 grains size. A spalling mode of failure has been observed on the surface of SN0 and SN10.

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