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Microstructure of hot-pressed h-BN/Si_3N_4 ceramic composites with Y_2O_3–Al_2O_3 sintering additive

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Abstract

The microstructure of hot-pressed h-BN/Si_3N_4 ceramic composites with Y_2O_3–Al_2O_3 sintering additive was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). SEM examination shows the diameter and aspect ratio of elongated β-Si_3N_4 grains in the composites to decrease with increasing h-BN content. TEM shows some β-Si_3N_4 grains in the composites to be unable to develop sufficiently and integrally since h-BN flake limits the growth space for β-Si_3N_4 grain and reduces the diffusion rate of Si and N in the liquid glass phase. XRD and TEM reveal that the hot-pressed composites are composed of β-Si_3N_4, h-BN, $Y_2Si_3O_3N_4$ and a glassy phase mainly containing Y and Si. The phase composition of the Si_3N_4 ceramic matrix is unaffected by h-BN addition.

Keywords: A. Grain growth; B. Composites; B. Microstructure; D. Si_3N_4

1. Introduction

Si_3N_4 ceramic has long been regarded as one class of promising structural materials for wide applications due to its high strength, as well as high fracture toughness, high resistance to thermal shock and chemical attack [1–3]. In order to satisfy some severe requirements for gas turbine, automotive engine and aircraft components, a small amount of h-BN was introduced in Si_3N_4 ceramic matrix. The previous investigations indicated that the addition of h-BN to Si_3N_4 ceramic matrix could yield a number of important consequences such as improving the machinability, fracture toughness, resistance to thermal shock and better frictional and wear properties [3–7].

However, the effect of h-BN on β-Si_3N_4 grain growth has been reported in less extent. Ruigang et al. [4] fabricated functionally graded h-BN/Si_3N_4 ceramic composites by hot-pressing and found that the addition of h-BN retarded the growth of elongated β-Si_3N_4 grains. Nevertheless, this result only derived from SEM micrographs of fracture surface. The mechanism of elongated β-Si_3N_4 grain growth to be affected by h-BN was not given yet.

In this investigation, SEM and TEM were used to analyze the effect of h-BN flake on the β-Si_3N_4 grain growth. In addition, the phase composition of hot-pressed h-BN/Si_3N_4 ceramic composites with Y_2O_3–Al_2O_3 sintering additives was investigated.

2. Experimental

Six compositions were designed as shown in Table 1, the mass ratio of Si_3N_4, Y_2O_3 and Al_2O_3 being 94:4.5:1.5. Powders of Si_3N_4 (85% α-Si_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 24 h. After the slurry was dried, the powders were hot-pressed in flowing N_2 at 1800 °C for 1 h in an h-BN-coated graphite die.

Sintered specimens were polished and chemically etched in molten NaOH at 400 °C for 1 min, and the grain morphology was characterized with a Hitachi S-570 scanning electron microscope. Phase identification was made by X-ray diffraction (D/max-*r*B, Japan). A Philips CM-12 transmission electron

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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

microscope was used for TEM work at 120 kV. The chemical elements of grain boundary phase were identified by energy dispersive X-ray spectroscopy (EDS). TEM specimens were prepared in the usual way by cutting, grinding and finally ion beam thinning. Since the Si_3N_4 ceramic under investigation was non-conducting, it was necessary to coat it with a thin layer of gold to prevent surface charging during examination.

3. Results and discussion

3.1. Microstructural analysis

3.1.1. Microstructural development

Fig. 1 shows SEM micrographs of the etched surface of monolithic Si_3N_4 and h-BN/Si_3N_4 ceramic composites with different h-BN content. Besides some fine and equiaxed β-Si_3N_4 grains and intergranular phases, the monolithic Si_3N_4 primarily consists of coarse elongated β-Si_3N_4 grains with high aspect ratios as shown in Fig. 1a. It can be found that the dominant morphology of β-Si_3N_4 grains in SN10 specimen is short rod-like as shown in Fig. 1f.

The formation of elongated β-Si_3N_4 grains can be explained by anisotropic grain growth. Due to the lower boundary energy in the *c*-direction than in *a*-direction of hexagonal crystal [8,9], the energetically more favorable nucleation takes place on the

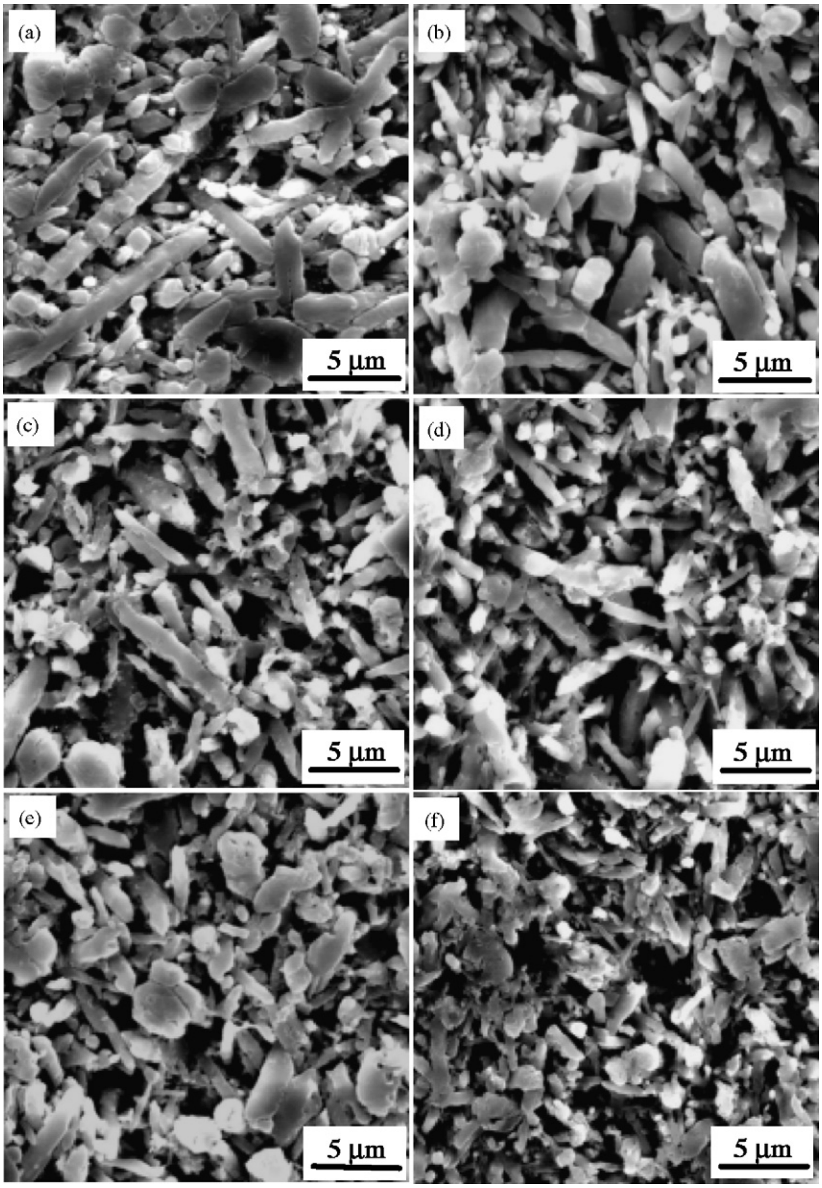

Fig. 1. SEM micrographs of etched surface of monolithic Si_3N_4 and h-BN/Si_3N_4 ceramic composites: (a) SN0, (b) SN2, (c) SN4, (d) SN6, (e) SN8 and (f) SN10.

surface of the basal plane. That results in a higher growth rate in the *c*-direction.

The formation of fine and equiaxed β-Si_3N_4 grains is related to nucleation during the transformation of α- to β-Si_3N_4. The β-nuclei, generated at the terminal stage of phase transformation from α- to β-Si_3N_4, develop insufficiently due to the remainder space limitations in polycrystalline Si_3N_4. Eventually fine and equiaxed β-Si_3N_4 grains are observed. Therefore, the Si_3N_4 matrix consists of some coarse elongated grains with high aspect ratios and other fine and equiaxed β-Si_3N_4 grains.

It can be found that the diameter and aspect ratio of β-Si_3N_4 grains decrease with increasing h-BN content as shown in Fig. 1. The result indicates that h-BN flakes hinder the growth of elongated β-Si_3N_4 grains. In order to further investigate the effect of h-BN flakes on the growth of β-Si_3N_4 grains, TEM examination was conducted.

3.1.2. Effect of h-BN flake on the growth of β-Si_3N_4 grain

Fig. 2 shows the typical morphology of β-Si_3N_4 grains in SN0 and SN10 specimens and the distribution of h-BN flakes in h-BN/Si_3N_4 ceramic composite. TEM examination reveals that h-BN flakes are primarily present at the grain pockets and some fine h-BN flakes are also present within β-Si_3N_4 grains as shown in Fig. 2c–e.

It can be observed from Fig. 2a that the growth of β-Si_3N_4 grains in SN0 specimen is unlimited in the *a*-direction and the β-Si_3N_4 grains develop sufficiently and integrally; eventually the regular hexagon of β-Si_3N_4 grain section morphology is observed in SN0 specimen. After h-BN flakes are introduced into Si_3N_4 ceramic matrix, the β-Si_3N_4 grain (grain A shown in Fig. 2c) can enwrap the small-size h-BN flake and develop incessantly during growth of β-Si_3N_4 grain. When the β-Si_3N_4 grains (grains B and C shown in Fig. 2c) contact a large h-BN flake in the *c*-direction shown in Fig. 2c, then the β-Si_3N_4 grain

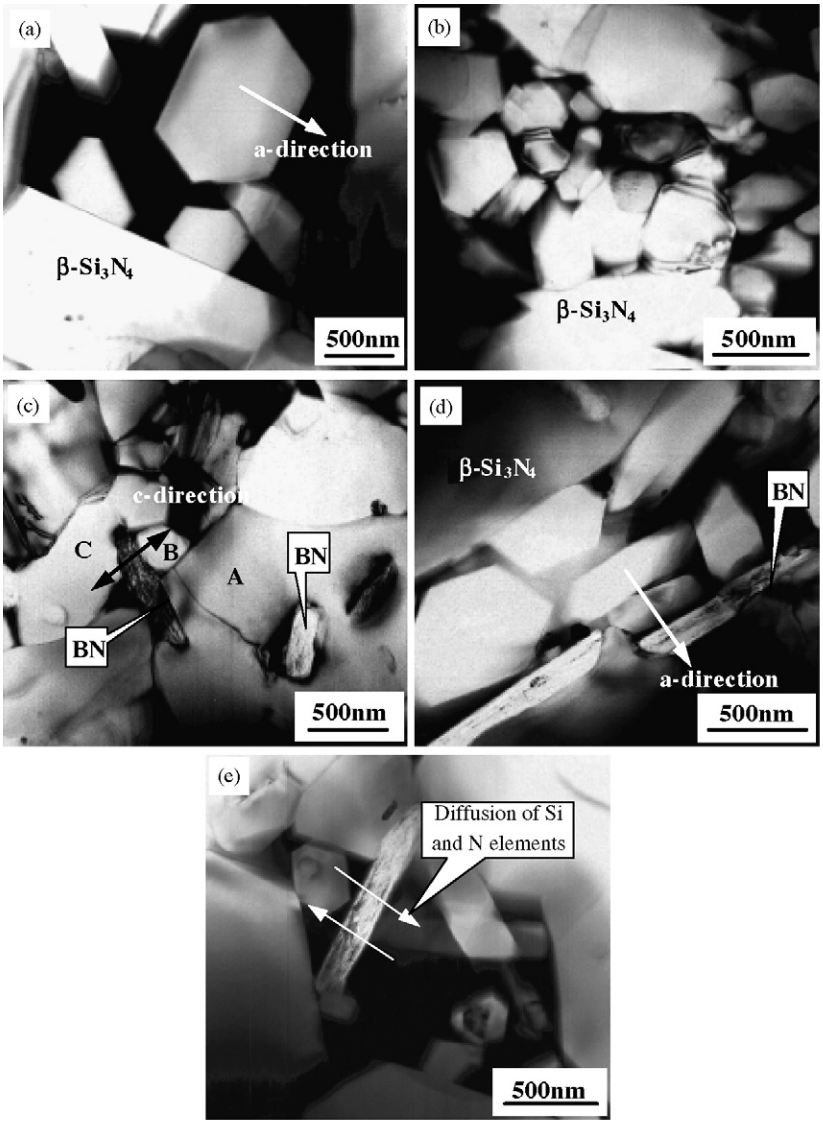

Fig. 2. TEM observation of the effect of h-BN flakes on the growth of β-Si_3N_4 grains: (a) typical morphology of β-Si_3N_4 grains in monolithic Si_3N_4; (b) typical morphology of β-Si_3N_4 grains in SN10; (c, d) distribution of h-BN flakes in SN6; and (e) diffusion of Si and N elements in SN6.

growth in that direction either stops or proceeds incessantly around one end of the h-BN flake. When h-BN flakes are arranged in a line as one barrier, β-Si_3N_4 grain growth takes place in a limited space and the β-Si_3N_4 grains are unable to develop sufficiently along the *a*-direction, but they develop along other unlimited directions as shown in Fig. 2d. With increasing h-BN content, the limitation of h-BN flakes on the growth space of β-Si_3N_4 grains is more significant, which is confirmed by the microstructure of SN10 specimen as shown Fig. 2b. The section morphology of β-Si_3N_4 grains in SN10 specimen is more irregular compared with that of SN6 specimen.

In addition, h-BN flakes affect the diffusion of Si and N elements in the liquid glass phase. It is known that the transformation of α- to β-Si_3N_4 occurs by solution–diffusion–precipitation of α-Si_3N_4. This transformation takes place at elevated temperature. During the transformation process, diffusion of Si and N elements is a key factor to control the growth rate of β-Si_3N_4 grains. When no h-BN flakes are in the liquid glass phase, the diffusion rate of Si and N elements mainly depends on the compositions and characteristics of liquid glass phase. However, after the h-BN flakes are introduced into the Si_3N_4 ceramic matrix, the h-BN flakes affect the viscous flow and mass transport of liquid glass phase since h-BN flakes are mainly present at the grain pockets. For instance, the diffusion rate of Si and N elements reduces when the Si and N elements diffuse from one side of h-BN flake to the other side as shown in Fig. 2e.

These results indicate that h-BN flake limits the growth space for β-Si_3N_4 grains and reduces the diffusion rate of Si and N elements in the liquid glass phase. However, the growth space for β-Si_3N_4 grains and the diffusion of Si and N elements are necessary and important for the β-Si_3N_4 grain growth. According to the above, when a β-Si_3N_4 nucleus contacts an h-BN flake in its growth direction, the growth space for the β-Si_3N_4 nucleus will be limited by the h-BN flake. In this instance, the β-Si_3N_4 nucleus is unable to develop sufficiently and integrally. In addition, the incorporation of h-BN decreases the diffusion rate of Si and N in the liquid glass phase, which causes the reduction in growth rate of β-Si_3N_4 grains. Therefore, the addition of h-BN retards the growth of elongated β-Si_3N_4 grains. Consequently, the diameter and aspect ratio of β-Si_3N_4 grains decrease with increasing h-BN content.

3.2. Phase composition analysis

3.2.1. General phase composition

Fig. 3 shows the XRD patterns of monolithic Si_3N_4 and h-BN/Si_3N_4 ceramic composites with different h-BN content. The XRD results show that monolithic Si_3N_4 consists of β-Si_3N_4 and a small amount of $Y_2Si_3O_3N_4$ and h-BN/Si_3N_4 ceramic composites consist of β-Si_3N_4, h-BN and $Y_2Si_3O_3N_4$. The XRD patterns indicate complete transformation from α- to β-Si_3N_4 to be achieved in all specimens. In addition, the Al_2O_3 phase was unidentified in hot-pressed specimens by XRD, which is possibly caused by the less Al_2O_3 content.

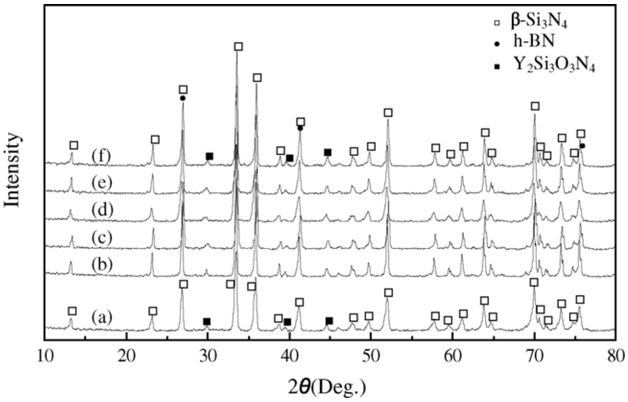

Fig. 3. XRD patterns of monolithic Si_3N_4 and h-BN/Si_3N_4 ceramic composites: (a) SN0, (b) SN2, (c) SN4, (d) SN6, (e) SN8 and (f) SN10.

Fig. 4 shows a TEM micrograph of the interface of h-BN flake between β-Si_3N_4 grains. No second phase is found at the interface between β-Si_3N_4 grain and h-BN flake, which implies that the chemical stability of h-BN in h-BN/Si_3N_4 ceramic composites is quite good.

3.2.2. Grain boundary phase

The formation and character of the grain boundary phase are related to sintering additives. In order to achieve high dense h-BN/Si_3N_4 ceramic composites, a liquid phase is introduced into this system during sintering. This liquid phase is formed by the reaction of Y_2O_3–Al_2O_3 sintering additives with SiO_2 present on the surface of the Si_3N_4 particles at elevated temperature. After sintering, this liquid phase is usually retained at the grain pockets and at the two-grain boundaries.

Fig. 5 shows TEM micrographs and EDS spectrum of the grain boundary phase in 6 vol.% h-BN/Si_3N_4 ceramic composite. Grain boundary phases are usually present at the grain pockets and at the two-grain boundaries as shown in

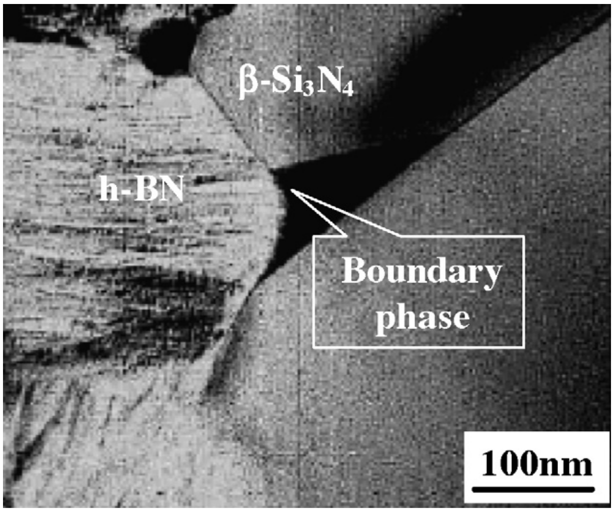

Fig. 4. TEM micrograph of the interface of h-BN flakes between β-Si_3N_4 grains.

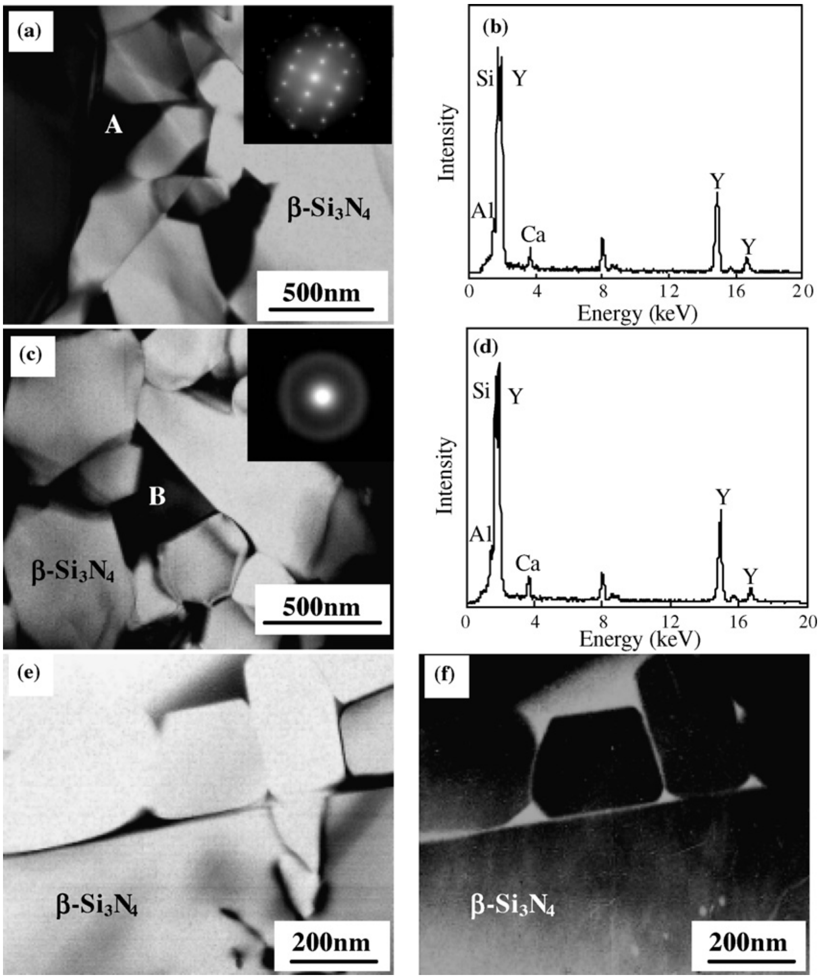

Fig. 5. TEM micrographs and EDS spectrum of grain boundary phases in 6 vol.% h-BN/Si_3N_4 ceramic composite: (a) crystalline phase at grain pockets; (b) EDS spectrum of the crystalline phase corresponding to A point; (c) glass phase at grain pockets; (d) EDS spectrum of the glass phase corresponding to B point; (e) bright field imaging of the grain boundary phase; and (f) dark field imaging of grain boundary phase.

Fig. 5. No second phase is observed at β-Si_3N_4 grains and h-BN flakes interface, indicating that all the sintering additives are dissolved in the eutectic liquid during the sintering process.

The diffraction contrast of some grain boundary phases (such as point A shown in Fig. 5a) varies by rotating the specimen during the TEM observation. Fig. 5a shows the electron diffraction patterns of point A. The results indicate that these grain boundary phases are crystalline. The EDS spectrum shows that these grain boundary phases are rich in Y and Si, possibly $Y_2Si_3O_3N_4$ according to the XRD.

However, not all the grain pockets examined are filled with crystalline boundary phases. A glassy phase (such as point B shown in Fig. 5c) is also present at the grain pockets, which can be confirmed directly by its electron diffraction patterns as shown in Fig. 5c. The EDS spectrum indicates that the glass phase also mainly contains Y and Si as shown in Fig. 5d. However, according to the EDS results, the mass ratio of Y and Si in the glass phase is different to that of crystalline $Y_2Si_3O_3N_4$. In addition, an amorphous film is identified between two adjacent β-Si_3N_4 grains by means of bright and dark field imaging of the grain boundary phase, as shown in Fig. 5e and f. In order to full establish the size and the chemistry of the very thin films between two adjacent β-Si_3N_4 grains, some authors have investigated these films by high-resolution electron microscopy (HREM) [10]. The result indicates incomplete crystallization of the grain boundary phases in the h-BN/Si_3N_4 ceramic composites. An incomplete crystallization also was observed in in situ reinforced Si_3N_4 ceramic [10,11].

The grain boundary phases mainly are crystalline $Y_2Si_3O_3N_4$ and a glassy phase containing Y and Si. The EDS spectrum also reveals evidence of existence of Al and other impurity elements such as Ca in the grain boundary phase. However, the mass ratio of Y and Si in the glassy phase is different to that of crystalline $Y_2Si_3O_3N_4$. Thereby, whether the grain boundary phase can fully crystallize is mainly related to the chemical composition of the grain boundary phase. Nevertheless, other factors also can affect the crystallization of grain boundary phase such as the volume of liquid phase at grain pockets, temperature–time history and the cooling rate [12–16].

According to the XRD and TEM results, h-BN/Si_3N_4 ceramic composites are composed of β-Si_3N_4, h-BN, $Y_2Si_3O_3N_4$ and a glassy phase mainly containing Y and Si.

These results reveal that the phase composition of the Si_3N_4 ceramic matrix is unaffected by the addition of h-BN and that the chemical stability of h-BN in h-BN/Si_3N_4 ceramic composites is quite good.

4. Conclusions

1. The diameter and aspect ratio of β-Si_3N_4 grains in the composites decrease with increasing h-BN content. h-BN flake retards the growth of elongated β-Si_3N_4 grains, consequently resulting in microstructure refining.
2. Coarse h-BN flakes are primarily present at the gain pockets and some small-size h-BN flakes are present within the β-Si_3N_4 grains. Some β-Si_3N_4 grains in the composites are unable to develop sufficiently and integrally since h-BN flake limits the growth space for β-Si_3N_4 grain and reduces the diffusion rate of Si and N in the liquid glass phase.
3. The phases present in hot-pressed h-BN/Si_3N_4 ceramic composites with Y_2O_3–Al_2O_3 sintering additives are β-Si_3N_4, h-BN, $Y_2Si_3O_3N_4$ and a glassy phase mainly containing Y and Si. The phase composition of the Si_3N_4 ceramic matrix is noticeably unaffected by the addition of h-BN and the chemical stability of h-BN in h-BN/Si_3N_4 ceramic composites is quite good.

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