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Effects of whisker-like β-Si_3N_4 seeds on phase transformation and mechanical properties of α/β Si_3N_4 composites using $MgSiN_2$ as additives

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Abstract

α/β Si_3N_4 composites with β-Si_3N_4 content ranging from 26% to 100% were hot-pressed with or without β-Si_3N_4 seeds, using $MgSiN_2$ as additives, and their mechanical properties were investigated. When the α-Si_3N_4 content was over 58%, the microhardness of α/β Si_3N_4 composites was in the range of 23–24 GPa, and then the indentation hardness decreases with decreasing the content of α-Si_3N_4, whether with β-Si_3N_4 seeds or not. The toughness increased with increasing elongated β-Si_3N_4 grains, which improved fracture resistance by crack bridging, pull out or the crack deflection mechanism, and reached the maximum value of 7.0 MPa $m^{1/2}$ with 1 wt% β-seeds. In comparison with α/β Si_3N_4 composite with a similar phase composition, the fracture strength was improved by adding β-Si_3N_4 seeds because of the relatively smaller grain sizes and higher toughness. The α/β Si_3N_4 composite with 5 wt% β-seeds showed a high strength of 1253 MPa, a high hardness of 20.9 GPa and a toughness of 6.9 MPa $m^{1/2}$.

Keywords: A. Phase transformation; C. Mechanical properties; D. Silicon nitride; Seeds

1. Introduction

Silicon nitride based ceramics have been extensively studied and are widely used in numerous structural applications, such as engine components, extrusion dies and cutting tools, due to their superior physical and mechanical properties [1,2]. As we know, the compound Si_3N_4 occurs in four polymorphic crystal structures, α, β, γ and another still-ambiguous phase δ-Si_3N_4, and the former two are hexagonal structure and γ-Si_3N_4 has a cubic spinel structure [3–5]. The hardness of γ-Si_3N_4 (the Vickers hardness is 30–43 GPa) is close to that of stishovite, a high-pressure phase of SiO_2, which is considered to be the hardest oxide, however it is difficult to obtain γ-Si_3N_4, which can be fabricated by static high-pressure synthesis utilizing the technique of laser heating in a diamond cell at pressures above 15 GPa and temperatures exceeding 2000 K or dynamic high-pressure synthesis using a propellant gun, which generates high pressure and high temperature simultaneously [3–5]. Therefore, α-Si_3N_4 and β-Si_3N_4 powders have always been used as starting materials to produce bulk silicon nitride based ceramics. The α-Si_3N_4 and β-Si_3N_4 have a similar structure, containing SiN_4 tetrahedra forming a corner-shared three-dimensional network, but the stacking sequence of the planes along the *z*-axis is different, ABCD in α-Si_3N_4 and AB or CD in β-Si_3N_4, resulting in the different mechanical properties [1,6]. It was estimated that the ideal strength of the α-Si_3N_4 and β-Si_3N_4 single crystals calculated for an applied tensile γ_{11} strain, in the [100] plane, is ~51 and 57 GPa, respectively, and the Vickers indentation hardness is ~23.0 GPa

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and 20.4 GPa, respectively [6]. α-Si_3N_4 always has a equiaxed shape and β-Si_3N_4 can form whisker-reinforced microstructure, which is benefit for improving mechanical properties, such as strength and toughness through crack deflection and crack bridging [7–9]. Therefore, α/β Si_3N_4 composite with a microstructure of rod-like β-Si_3N_4 grains embedded in fine, hard α-Si_3N_4 matrix may be a promising material with good combination of hardness, fracture toughness and strength, which is important for silicon nitride based ceramics used as wear-resistance components.

α/β Si_3N_4 composites have been fabricated at a relatively low temperature or by rapid consolidation methods or using La_2O_3 as a sintering additive to suppress the α-β phase transformation [9]. In our previous work, hard and strong α/β Si_3N_4 composite (the Vickers indentation hardness of 23.1 GPa, the fracture strength of about 1000 MPa, the toughness of 6.3 MPa $m^{1/2}$) could be fabricated by hot pressing α-Si_3N_4 powders at 1600 °C for 6 h, using $MgSiN_2$ as sintering additives [10]. α/β Si_3N_4 composites, showing a hardness of 19.0 GPa and a toughness of 7.7 MPa $m^{1/2}$, were also fabricated by spark plasma sintering with $MgSiN_2$ as additives [11]. The microstructures and mechanical properties of α/β Si_3N_4 composites can be tailored by changing the phase compositions through controlling heating schedule, however this change is limited.

On the other hand, it is now well accepted that the fracture toughness and strength can be simultaneously improved by controlling the content and size distribution of β-Si_3N_4 seeds in the starting material [12–14]. Hirao et al. reported that by seeding morphologically regulated β-Si_3N_4 particles, the fracture toughness was improved from 6.3 to 8.4–8.7 MPa $m^{1/2}$, retaining high strength of about 1 GPa [13]. High hardness α-Si_3N_4 ceramics reinforced by rod-like β-Si_3N_4 seed particles were fabricated by the tape casting technique using La_2O_3 as a sintering additive [7]. The fracture toughness and strength could be significantly improved from about 2 to 6 MPa $m^{1/2}$ and 387–798 MPa, respectively [7]. In the present work, α/β Si_3N_4 composites were hot-pressed with or without whisker-like β-Si_3N_4 seeds, using $MgSiN_2$ as additives and effects of β-seeds on phase transformation and mechanical properties of α/β Si_3N_4 composites were investigated.

2. Experimental procedures

α-Si_3N_4 powders (SN-E10, UBE Industries, Tokyo, Japan), $MgSiN_2$ powders (purity > 99%, prepared by combustion synthesis in our laboratory [15]) and whisker-like β-Si_3N_4 particles were used as the starting raw materials. The whisker-like β-Si_3N_4 particles were prepared by combustion synthesis using $MgSiN_2$ powders as additives [16], and then were immersed in hydrofluoric acid for 24 h to remove the residual glass phase. Fig. 1 shows the microstructure of β-Si_3N_4 seeds. The raw materials, according to the required mass ratios, were planetary ball milled for 3 h with Si_3N_4 balls and container, using absolute ethanol as a mixing medium. The homogenized slurry was dried in a vacuum oven followed by passing through 40-mesh sieve to obtain agglomerate-free powder mixture. In order to understand the influences of β-seeds on phase transformation and mechanical properties, α/β Si_3N_4 composites with different α/β ratios were also prepared without β-seeds. All samples were hot-pressed under 20 MPa uniaxial pressure in a flowing nitrogen atmosphere. The details of different sintering conditions for all samples are presented in Table 1.

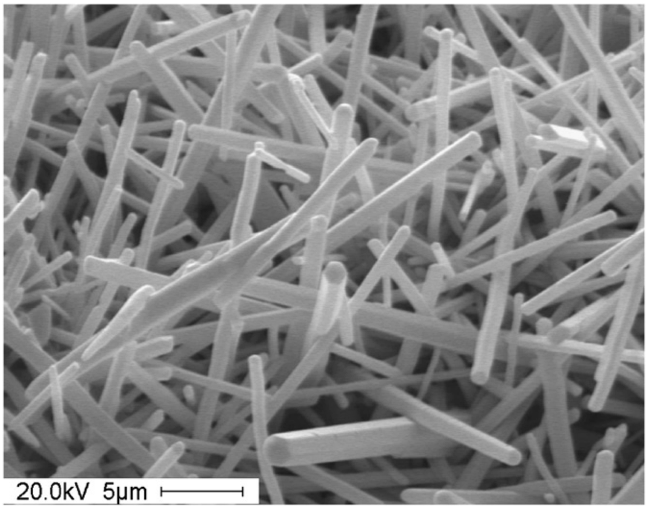

Fig. 1. SEM micrograph of whisker-like β-Si_3N_4 seeds.

Bulk densities were measured by the Archimedes method in distilled water. The phase compositions of the specimens were determined by X-ray diffraction analysis (XRD, Rigaku D/max 2550V, Japan) with *CuKα* radiation, operating at 40 kV and 100 mA. Scanning electron microscopy (SEM, JSM-6700F, Joel, Tokyo, Japan) was used to analyze the microstructure of the specimens, which were finished using a 2.5 μm diamond slurry and etched by molten NaOH for 30–60 s. The Vickers microhardness and fracture toughness were determined by Vickers indentation with a load of 49 N for duration of 10 s on polished surfaces perpendicular to the hot-pressing direction. The fracture toughness was calculated as [17,18]:

$$\frac{K_{IC}\Phi}{(Ha^{1/2})} = 0.15k\left(\frac{c}{a}\right)^{-3/2} \tag{1}$$

where $\Phi(=3)$ and $k(=3.2)$ are two dimensionless constants, H is the hardness, a is the half-diagonal of the Vickers indent and c is the radius of the surface crack. The fracture strength of sintered Si_3N_4 composites, which were ground to a sample size of 4 mm × 3 mm × 35 mm, was measured by a three-point bending test with a 30 mm span at a crosshead speed of 0.5 mm/min at room temperature. All the mechanical tests were performed 5 times.

3. Results and discussion

3.1. Phase transformation

All of the specimens, in the presence of $MgSiN_2$ powders as sintering additives, could be sintered to nearly full

Table 1
Experimental conditions of different samples.

Sample	Mass ratio			Temperature (°C)	Hold time (h)
	α-Si_3N_4	$MgSiN_2$	β-seeds		
S1	100	5	0	1600	6
S2	100	5	1	1600	6
S3	100	5	5	1600	6
S4	100	5	10	1600	6
S5	100	5	0	1600	1
S6	100	5	0	1600	3
S7	100	5	0	1600	10
S8	100	5	0	1650	1
S9	100	5	0	1700	1
S10	100	5	0	1750	1

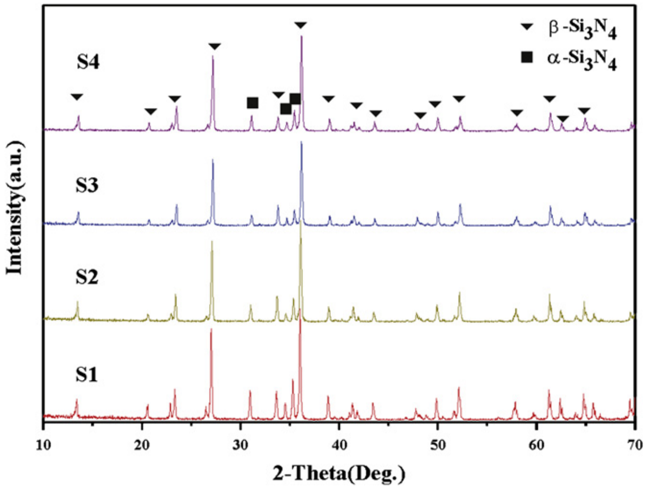

Fig. 2. XRD patterns of samples S1, S2, S3 and S4.

density (>99% of theoretical density) with or without whisker-like β-Si_3N_4 seeds and almost no open porosities were observed on the polished surfaces of all sintered materials, examined by an optic microscope. These results indicate that when the β-Si_3N_4 seeds content is less than or equal to 10 wt% of α-Si_3N_4 starting materials, the influence of β-Si_3N_4 seeds on the sintering activity of starting materials is negligible in the present investigation, which is consistent with other previous studies [19].

The X-ray diffraction patterns of sample S1, S2, S3 and S4, which were all hot-pressed at 1600 °C for 6 h besides with the different β-Si_3N_4 seeds content, are presented in Fig. 2. It is clear that all four specimens were composed of α-Si_3N_4 and β-Si_3N_4 phases and no other crystal phases were detected. The reason of the disappearance of $MgSiN_2$ phase in the resultant silicon nitride ceramics was considered that $MgSiN_2$ reacted with surface silica and Si_3N_4 to form low-viscosity Mg–Si–O–N liquid phase, which would effectively promote the densification of α-Si_3N_4 powders [10,11]. The α-Si_3N_4 content of specimen S5, which was fully densified at 1600 °C for 1 h, is as high as 74 wt%, thus, it is reasonable to speculate that high density α/β Si_3N_4 composites can be obtained by densifying through not only the solution-precipitation process but also by diffusion and material transfer.

The amount of α- and β-phases in all α/β Si_3N_4 composites were quantitatively analyzed by the method, proposed by Käll, based on the determination of the intensity ratios of the reflections (101) and (210) in the β-phase and (102) and (201) in the α-phase [20], and the results are listed in Table 2. The β-Si_3N_4 content increased along with the extension of hold time or the increasing of the sintering temperature. Noted that if the starting β-Si_3N_4, containing β-Si_3N_4 in the starting α-Si_3N_4 powders (SN-E10) and whisker-like β-Si_3N_4 seeds, is subtracted from the final β-Si_3N_4 content in the composites, the net β-Si_3N_4 formed during the hot-pressing processes of sample S1, S2, S3 and S4, are 37, 75, 75 and 69%, respectively. It can be seen that the phase transformation rate of α to β phase was significant elevated by adding β-Si_3N_4 seeds, even though the amount of β-Si_3N_4 seeds was as little as 1 wt% with respect to α-Si_3N_4 starting powders. The α to β phase transformation, driven by a solubility difference between α-Si_3N_4 and β-Si_3N_4 crystals, takes place by (a) dissolution of the α-Si_3N_4 and saturation of the liquid phase, (b) transport of Si and N ions through the liquid phase, and (c) attachment onto exiting β-Si_3N_4 grains [21]. The effect of volume fraction of β-Si_3N_4 crystal on the α–β transformation rate was simulated by Kitayama et al. adopting the anisotropic Ostwald ripening theory, and the results showed that if the phase transformation is controlled primarily by the interfacial reaction of β-Si_3N_4 crystals and the liquid phase, the α–β transformation rate increased with the increasing of the fraction of the β-Si_3N_4 [22]. Kitayama et al. also found that the α–β transformation rate significantly increased by adding β-Si_3N_4 seeds and they believed that the phase transformation is controlled primarily by the interfacial reaction of β-Si_3N_4 crystal [7]. In the present instance, the phase transformation, therefore, might also be interfacial reaction controlled. Thus, the α–β transformation rate increased with β-Si_3N_4 addition, which increased the interface of the β-Si_3N_4 crystal. It should be also noted that the α–β transformation rate with 5 wt% β-Si_3N_4 seeds was the

Table 2
Phase compositions and mechanical properties of α/β Si_3N_4 composites.

Sample	Phase composition (%)		Hv (GPa)	σ_f (MPa)	K_{IC} (MPa $m^{1/2}$)
	α-Si3N4	β-Si3N4			
S1	58	42	23.1 ± 0.1	988 ± 25	6.3 ± 0.1
S2	19	81	19.9 ± 0.1	1249 ± 29	7.0 ± 0.1
S3	16	84	20.9 ± 0.1	1253 ± 34	6.9 ± 0.1
S4	18	82	19.3 ± 0.2	1149 ± 27	6.5 ± 0.1
S5	74	26	23.5 ± 0.2	607 ± 25	4.6 ± 0.1
S6	60	40	23.7 ± 0.6	750 ± 15	5.2 ± 0.1
S7	29	71	20.0 ± 0.3	1051 ± 52	6.9 ± 0.1
S8	32	68	21.8 ± 0.2	1058 ± 37	6.4 ± 0.2
S9	15	85	19.7 ± 0.4	1028 ± 29	6.7 ± 0.1
S10	0	0	17.7 ± 0.4	1121 ± 44	5.5 ± 0.2

same as that with 1 wt% β-seeds and then the transformation rate decreased when the amount of β-seeds increased to 10 wt%. Besides of the α:β ratio in starting materials, the amount of liquid phase, formed during the α–β transformation process at high temperature, likewise decreased with the rise of β-seeds content from 1 wt% to 10 wt% and subsequently the interface between Si_3N_4 crystals (both α-Si_3N_4 and β-Si_3N_4) and liquid phase was correspondingly reduced, resulting in the speed of the dissolution of α-Si_3N_4 in liquid phase and the formation of β-Si_3N_4 decreased.

3.2. Hardness

The mechanical properties, i. e. the Vickers hardness, fracture toughness and fracture strength of all samples in the present study are listed in Table 2. The dependencies of the microhardness on the β-Si_3N_4 content are illustrated in Fig. 3. When the α-Si_3N_4 content of sintered α/β Si_3N_4 composite S6 is 60%, the microhardness is highest, 23.7 GPa, and the microhardness value is almost constant, in the range of 23–24 GPa, while the α-Si_3N_4 amount is higher than 58%. This result is similar to that finding by Kitayama et al., and in that case, the hardness (about 19 GPa) is independent of the α-contents, which is higher than 57.1% [7]. They thought that the reason was probably related to the alignment of the elongated β-Si_3N_4 grains, due to both tape casting and hot-pressing, because the prismatic plane of the β-Si_3N_4 crystal has much higher hardness than the basal plane [7]. Fig. 4 shows the SEM micrographs of the polished and etched surfaces of samples S5 and S6, containing 74% and 60% α-Si_3N_4, respectively. The needle-like β-Si_3N_4 grains with the length of about 1 μm (Fig. 4a and b) and a small amount of rod-like β-Si_3N_4 grains with the length of about 2.5 μm (Fig. 4b) embedded in a large quantity of equiaxed α-Si_3N_4 grain matrix, and the total amount of β-Si_3N_4 grains is so small that the β-Si_3N_4 grains cannot contact each other. This microstructure is may be another reason for the microhardness of α/β Si_3N_4 composites with high α-Si_3N_4 content is independent of the β-contents and close to the Vickers indentation hardness of the α-Si_3N_4 single crystal, which was estimated to be ~23 GPa using a reported empirical method [6].

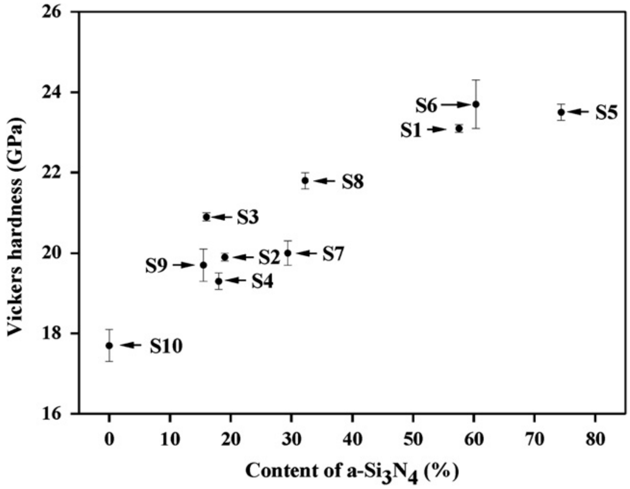

Fig. 3. Relationship between the Vickers hardness and α-Si_3N_4 content of the α/β Si_3N_4 composites.

Note also that the microhardness of α/β Si_3N_4 composites in the present work is higher than that of α/β Si_3N_4 composites with the similar phase compositions, hot-pressed with La_2O_3 [7]. In addition to α-Si_3N_4 and β-Si_3N_4, there is a small amount of the amorphous grain boundary phase in Si_3N_4 ceramics, and the amount of glass boundary phase, existing in the result ceramics, with $MgSiN_2$ as an addition should be much less than that with 5 vol% La_2O_3 additives because of the much less oxygen content in the former. It is obvious that reducing the amount of the glassy phase is benefit for improving the hardness, owing to the much lower hardness of the vitreous materials than that of both α-Si_3N_4 and β-Si_3N_4, and this is also the reason that Sialon is always harder than Si_3N_4 ceramic. This can also be proved by the fact that the microhardness (23.1 GPa) of sample S1 was much higher than that (19.5 GPa, using the identical measuring method with sample S1) of the α/β Si_3N_4 ceramic with 5 wt% MgO as additives, although both have nearly the same phase

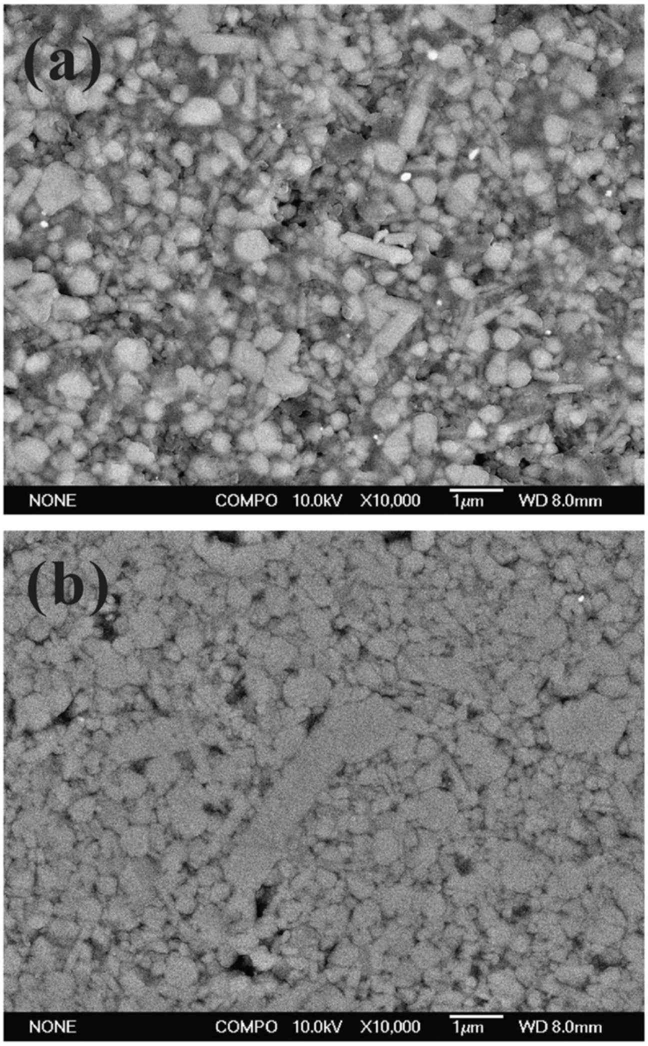

Fig. 4. SEM micrographs of the polished and etched surfaces of the α/β Si_3N_4 composites: (a) S5; and (b) S6.

compositions, as shown in Fig. 5. What's more, the microhardness of α/β Si_3N_4 composites, with more than 58% α-Si_3N_4, in the present work, is slight higher than that of α-Sialon or α/β Sialon. The hardness improvement is probably due to the harder crystal lattice of α-Si_3N_4 than that of α-Sialon and the smaller amount of glass boundary phase by using $MgSiN_2$ as additives.

The microhardness of β-Si_3N_4 ceramic with no α-Si_3N_4 is lowest, 17.7 GPa, and then the Vickers indentation hardness increases with increasing the content of α-Si_3N_4, whether with or without β-Si_3N_4 seeds. It is well accepted that α-Si_3N_4 is harder than β-Si_3N_4, due to the longer stacking sequence in α-Si_3N_4 and the longer Burgers vector required for slip dislocation [23,24]. Since the α/β Si_3N_4 ceramics were regarded as two-phase composites of α-Si_3N_4 and β-Si_3N_4, the elevation of Vickers indentation hardness with increasing of the α-Si_3N_4 content was easily understood based the rule of mixture. The variations of Vickers hardness of α/β Si_3N_4 composites after adding β-Si_3N_4 seeds are, therefore, an expected result.

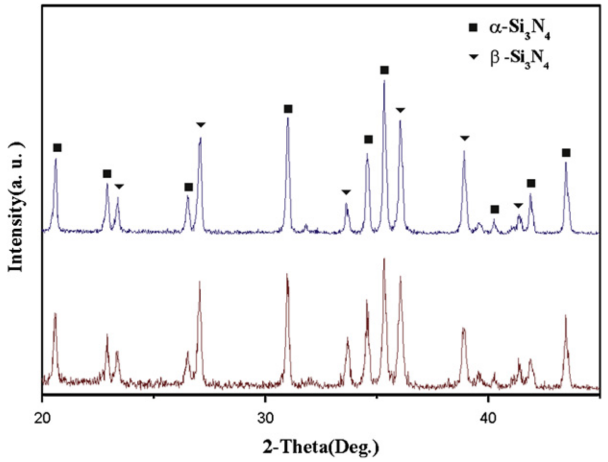

Fig. 5. XRD patterns of the α/β Si_3N_4 composites with $MgSiN_2$ or MgO additives.

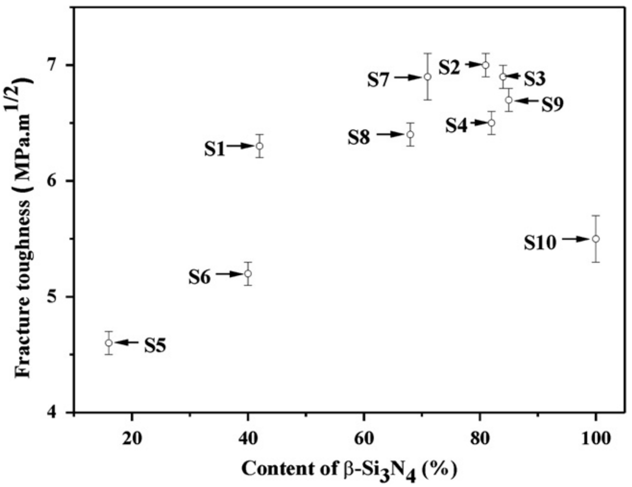

Fig. 6. Relationship between the fracture toughness and β-Si_3N_4 content.

3.3. Fracture toughness

Fig. 6 illustrates the indentation toughness as a function of β-phase content. Without β-seeds, the toughness increased from 4.6 MPa m$^{1/2}$ for S5 with 26% β-Si_3N_4 to a maximum value 6.9 MPa m$^{1/2}$ for S7 with 71% β-Si_3N_4, and then decreased to 5.5 MPa m$^{1/2}$ for S10 with 100% β-phase, which is analogical with the toughness variation of α/β Si_3N_4 ceramics prepared by SPS with $MgSiN_2$ additives or hot-pressed at 1450–1700 °C with MgO as sintering additions [9,11]. Since α-Si_3N_4 is always equiaxed and β-Si_3N_4 can form rod-like grains, the elongated β-Si_3N_4 grain amount increased with the increasing of the β-Si_3N_4 content, as shown in Figs.4a, b and 7a. The presence of elongated β-Si_3N_4 grains is a prerequisite for triggering respective toughening mechanisms, such as crack bridging, pull out and crack deflection, which contribute to an enhanced energy dissipation upon crack propagation and hence can effectively improve fracture toughness [25–27]. In general, the fracture toughness of silicon nitride increases with the diameter and the amount of the

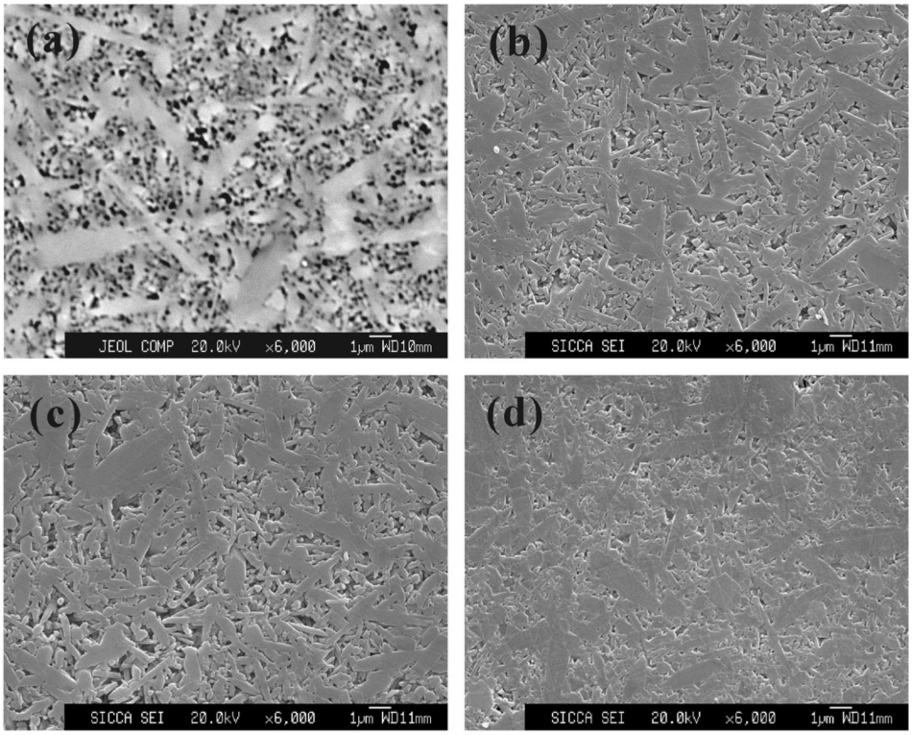

Fig. 7. SEM micrographs of the polished and etched surfaces of the α/β Si_3N_4 composites: (a) S9; (b) S2; (c) S3; and (d) S4.

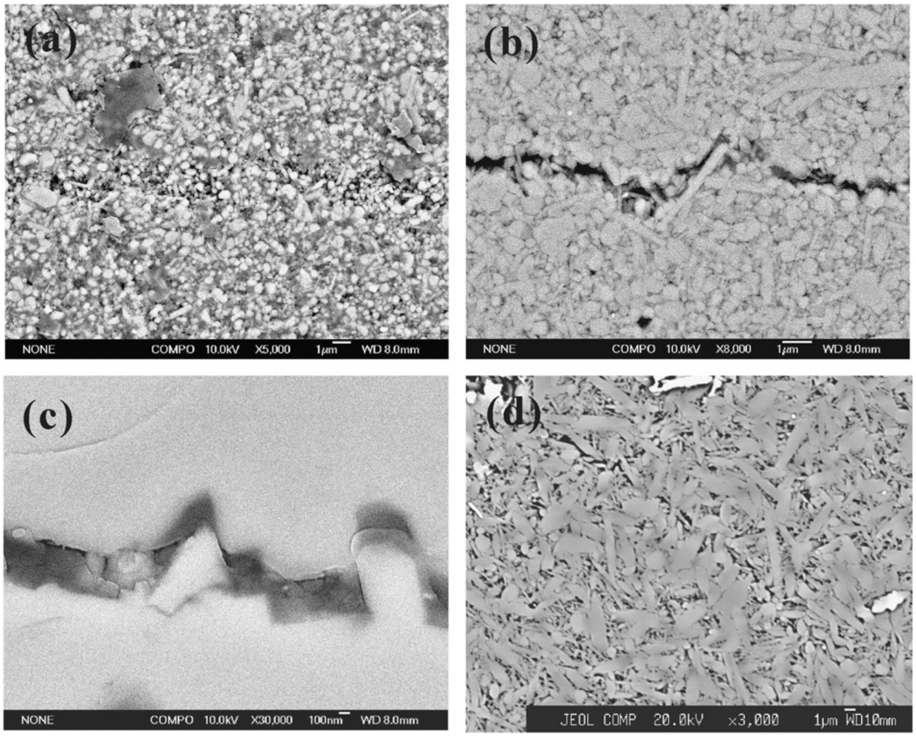

Fig. 8. SEM photographs of the crack propagation paths of the α/β Si_3N_4 composites: (a) S5; (b) S1; (c) S7; and (d) S10.

larger elongated grains, as predicted for frictional bridging and pullout processes [26,27]. Fig. 8 presents crack propagation behaviors of samples S5, S1, S7 and S10, with the β-phase content of 26%, 42%, 71% and 100%, respectively. The crack propagation path of sample S5 is practically straight due to the microstructure composed of equiaxed grains for the most part and small needle-like grains. The crack propagation paths of samples S1 and S7 (Fig. 8b and c) confirmed that crack-deflection and poll out occurred in sintered α/β Si_3N_4 composites with the self-reinforced microstructure with large elongated grains embedded in a fine-grained matrix, which has been considered as an ideal microstructure realizing the toughening mechanism. The crack propagation path of sample S10 (Fig. 8d), nevertheless, is straighter than that of sample S7, resulting in the fracture toughness decreased to 5.5 MPa $m^{1/2}$, although the amount of large elongated grains increased. A number of investigations have verified that interfacial debonding, in addition of the reinforcing elongated grains, is a key step in toughening mechanisms [28,29]. The debonding between the reinforcing grains and the intergranular glass must occur so that the crack tip is deflected along the grain face, rather than cutting through the elongated grain, while leaving intact elongated grains to bridge the crack in its wake, and the key issue for the interfacial debonding is the weak interface strength [28,29]. The decreasing of fracture toughness, in this work, is may be owing to too high bonding strength between the elongated β-Si_3N_4 grain and the glass phase, when most of the glass phase was extruded into the three- or four-grain junction because of the increasing sizes of β-Si_3N_4 grains.

The indentation toughness of samples S2, S3 and S4, with 1 wt%, 5 wt% and 10 wt% β-seeds, respectively, in which the β-Si_3N_4 contents are almost the same ranging between 81% and 84%, is close to each other ranging in 6.5–7.0 MPa $m^{1/2}$. This value is also close to the toughness of samples S7 and S9, with 71% and 85% β-phase, respectively, although both were obtained with no β-seeds, as shown in Fig. 6. These results demonstrated that in the present system, the fracture toughness of α/β Si_3N_4 composite with 70–85% β-phase was primarily controlled by the β-phase content.

3.4. Fracture strength

The fracture strength,σ_f, can be expressed as:

$$\sigma_f = \frac{K_{IC}}{Y} \times c^{1/2} \tag{2}$$

where K_{IC}, Y and c are the fracture toughness, geometry coefficient determined by a shape of the defect and critical flaw size, respectively [30]. Obviously, in order to enhance the fracture strength of silicon nitride ceramic, it is necessary to elevate the fracture toughness, K_{IC}, and to minimize the size and distribution of defects as small as possible. Fig. 9 exhibits the correlation of fracture strength of all specimens, either with β-seeds or without, and the β-phase content. Without β-seeds, the fracture strength increased with increasing of the β-phase content and reached the value of 1058 MPa at the β-phase content of 68%. The improvement of the fracture strength of α/β Si_3N_4 composites is due to increasing the fracture toughness value, as a result of the formation of reinforcing β-Si_3N_4 particles along with the α–β phase transformation. When the β-phase content further increased to 85%, the fracture strength slightly dropped to 1028 MPa and the fracture strength increased again to 1121 MPa when α-Si_3N_4 completely transformed to β-Si_3N_4. The reason of the decreasing of strength with the further increasing of β-phase contents should be the increasing the critical flaw size because of the coarsening of β-Si_3N_4 grains. Kawaoka et al. reported that the analogous phenomenon was also observed in α/β Si_3N_4 composites, prepared by pulse electric current sintering process with 6 mol% Y_2O_3 and 2 mol% Al_2O_3 additives at 1650–1700 °C for 1–10 min, and they found out that the fracture in the specimen with 89 wt% β-phase was initiated from an agglomerated grain whose size was about 25 μm, while the specimen with 56 wt% of β-phase was fractured from a void with 10 μm size [8]. The cause of the increasing of fracture strength of sintered α/β Si_3N_4 composite with 100% β-Si_3N_4 is unclear, and need to be further explored. After adding whisk-like β-Si_3N_4 particles as seeds, the fracture strength was improved and the maximum value of 1253 MPa was achieved while the content of β-Si_3N_4 seeds was 5 wt%. Since the fracture toughness of sample S2 is practically close to that of sample S9, the elevation of the strength of sample S2 is attributed to the relatively small sizes of rod-like β-Si_3N_4 grains, as shown in Fig. 7a and b, although the β-Si_3N_4 content of sample S2 is almost equal to that of sample S7. As shown in Fig. 7, the grain sizes of α/β Si_3N_4 composites with 1 wt%, 5 wt% or 10 wt% β-seeds were relatively small, and this microstructure should attribute to the improvement of strength. A very high strength of about 2.0 GPa, reported by Yoshimura et al. [31], could be achieved by controlling the grain sizes, which is an effective method to improve the fracture strength of silicon nitride based ceramics [31–33].

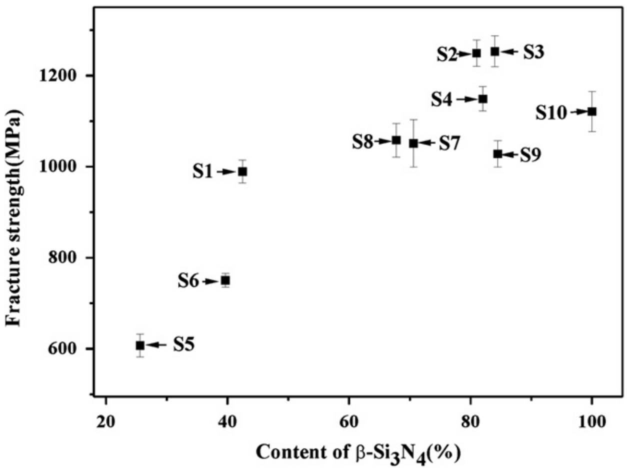

Fig. 9. Relationship between the fracture strength and β-Si_3N_4 content.

4. Conclusion

α/β Si_3N_4 composites with various α/β ratios were fabricated by hot-pressing at 1600¯750 °C with or without whisker-like β-Si_3N_4 seeds, using $MgSiN_2$ as additives. α-Si_3N_4 powders could be fully sintered with $MgSiN_2$ additives while the content of β-seeds was below 10 wt%. The phase transformation rate of α to β phase was significant elevated by adding β-Si_3N_4 seeds. The microhardness value is almost constant, in the range of 23–24 GPa while the α-Si_3N_4 amount is higher than 58%, and then the Vickers indentation hardness decreases with decreasing the content of α-Si_3N_4, whether with β-Si_3N_4 seeds or not. Without β-seeds, the toughness increased from 4.6 MPa with 26% β-Si_3N_4 to a maximum value 6.9 MPa with 71% β-Si_3N_4, and the increasing is primarily attributed to the formation of the elongated β-Si_3N_4 grains, which can effectively improve fracture resistance by crack bridging, pull out or the crack deflection mechanism. The indentation toughness of samples S2, S3 and S4, with 1 wt%, 5 wt% and 10 wt% β-seeds, respectively, is close to each other ranging in 6.5–7.0 MPa, owing to the similar content of β-phase. The maximum fracture strength of 1253 MPa with 5 wt% β-Si_3N_4 seeds was achieved while the strength of α/β Si_3N_4 composite with a similar phase composition but without β-seeds was 1028 MPa, and the relatively smaller grain sizes and higher toughness for the former is responsible for the improvement of the strength.

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