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TiO_2 对 Si_3N_4–SiC_w 复合材料致密化和力学性能的影响

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摘 要：以 Yb_2O_3–Al_2O_3 作为烧结助剂，采用烧结–热等静压工艺制备了具有高致密度和优异力学性能的 Si_3N_4–SiC_w 复合材料，研究了 TiO_2 含量对 Si_3N_4–SiC_w 复合材料致密化和力学性能的影响。结果表明：TiO_2 的加入促进了 Si_3N_4–SiC_w 复合材料的致密化。随着 TiO_2 含量的增加，Si_3N_4–8%SiC_w 复合材料的抗弯强度、断裂韧性和 Vickers 硬度均呈现出先提高后降低的变化趋势。当 TiO_2 含量(质量分数)为 3%时，Si_3N_4–8%SiC_w 复合材料的相对密度和综合力学性能最佳，其相对密度、抗弯强度、断裂韧性和 Vickers 硬度分别为(99.5±0.1)%、(1 301±87) MPa、(7.8±0.1) MPa·$m^{1/2}$、(16.2±0.1) GPa。TiO_2 和 Si_3N_4 之间的原位反应生成的 SiO_2 和 TiN 对 Si_3N_4–SiC_w 复合材料的界面结合强度及力学性能产生了重要影响。

关键词：氮化硅；碳化硅晶须；致密化；力学性能；烧结–热等静压
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Effect of Titania Additives on Densification and Mechanical Properties of Si_3N_4–SiC_w Composites

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Abstract: Si_3N_4–SiC_w composites were prepared *via* a sinter–hot isostatic pressing (sinter–HIP) process with Yb_2O_3–Al_2O_3 as sintering additives. The effect of titania (TiO_2) addition on the densification and mechanical properties of Si_3N_4–SiC_w composites was investigated. The results show that the addition of titania enhances the densification of Si_3N_4–SiC_w composites. The flexural strength, fracture toughness and Vickers hardness of Si_3N_4–8%SiC_w composites firstly increase and then decrease with increasing titania content. Si_3N_4–8%SiC_w composites containing 3% TiO_2 have a near-theoretical density and optimal mechanical properties (*i.e.*, the relative density of (99.5±0.1)%, the flexural strength of (1 301±87) MPa, the fracture toughness of (7.8±0.1) MPa·$m^{1/2}$, and the Vickers hardness of (16.2±0.1) GPa). The formation of SiO_2 and TiN based on the *in-situ* reaction between TiO_2 with Si_3N_4 contributes to the improvement of the interfacial strength of bonding between SiC whisker and Si_3N_4 matrix as well as the mechanical behaviors of the composites.

Keywords: silicon nitride; silicon carbide whisker; densification; mechanical properties; sinter–hot isostatic pressing

1 Introduction

Silicon nitride (Si_3N_4) ceramic is one of promising engineering ceramic materials due to its superior properties, such as low specific weight, high strength and hardness, good wear resistance, thermal shock resistance, chemical stability, electrical insulation, and high thermal conductivity[1–4]. Hence, Si_3N_4 materials are widely used as bearing rolling elements, hot section components of automotive engines and micro-sized gas turbines, cutting tools, and high thermal conductivity ceramic substrates[3–5]. However, there exist some problems

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regarding the reliability of Si_3N_4 materials due to the inherent brittleness of ceramics. Subsequently, improving the fracture toughness of Si_3N_4 ceramics has attracted recent attention. The conventional toughening technology for Si_3N_4 ceramic includes whisker/fiber toughening[6–17], particulate toughening[18–23], self-toughening[24–25], *etc*..

SiC whisker is incorporated with Si_3N_4 matrix to reinforce Si_3N_4 based ceramics according to the toughening mechanism of whisker pullout, bridging, and crack deflection[12,14]. However, the addition of a large amount of SiC whisker could retard the densification of Si_3N_4 based ceramics[11,17]. In addition, SiC whisker is expensive, which can remarkably increase the production cost of Si_3N_4 based ceramics. To obtain the full density, SiC whisker reinforced Si_3N_4 ceramic matrix composites (*i.e.*, Si_3N_4–SiC_w) are conventionally fabricated by hot pressing[9,16] or glass-encapsulated hot isostatic pressing (HIP)[7]. Hot pressing can merely prepare the components with simple shapes. Although glass-encapsulated hot isostatic pressing can fabricate the products with complex structures, the cost is relatively higher. In contrast, sinter–HIP is a more economical route to manufacture Si_3N_4–SiC_w composites, which is more suitable for batch production of complicated-structure components, compared with hot pressing or glass-encapsulated HIP.

Particulate toughening is a facile way to improve the fracture toughness of Si_3N_4 based ceramics. Micro- or nano-particles with high elastic modulus such as SiC[18–19], TiN[20–22], and TiC[23], uniformly dispersed in Si_3N_4 matrix, can generate residual stress due to the mismatch of thermal expansion coefficient between the particles and Si_3N_4 matrix. When the crack propagates through these particles, the crack is deflected or branched, and the fracture energy is consumed, thereby enhancing the fracture toughness of Si_3N_4 based ceramics. Among these reinforced phases, TiN is considered as one of the most effective candidates for Si_3N_4 based materials[21–22].

In this paper, high-performance SiC whisker reinforced Si_3N_4 ceramic matrix composites were prepared by a sinter–HIP method. The influence of TiO_2 addition in Si_3N_4–SiC_w composites on the densification, phase assemblage, microstructure, and mechanical properties of the composites was investigated.

2 Experimental

2.1 Materials and preparation

Commercial Si_3N_4 powder (SN–E10, UBE Industries, Japan, α-Si_3N_4 content >95%, in mass fraction), SiC whisker (Eno High-Tech Material, China, >99% purity, the diameters of 0.1–1.0 μm and the lengths of 10–30 μm), Yb_2O_3 (Sinopharm Chemical, China, >99.9% purity), Al_2O_3 (Sinopharm Chemical, China, >99.9% purity), and TiO_2 (Anatase type, Sinopharm Chemical, China, >99.9% purity, the average particle size is 30 nm) were selected as raw materials. The raw materials were mixed according to the ratios listed in Table 1. The starting powders except SiC whisker were put in a nylon jar and wet-ground for 16 h with Si_3N_4 balls and ethanol as a medium. After 16 h-grinding, ultrasound-dispersed SiC whisker was added and ground for another 8 h. The slurry after grinding was dried in a water bath at 90 ℃ and then passed through a sieve with 80 mesh. The as-prepared powder mixtures were molded into 55 mm × 55 mm × 8 mm blocks by uniaxial pressing at 20 MPa and followed by cold isostatic pressing at 200 MPa. The green compacts were placed in a boron nitride (BN) crucible, sintered in nitrogen at 1 750 ℃ and 1 MPa for a soaking time of 1 h. After sintering, the blanks were HIPed in nitrogen at 1 750 ℃ and 100 MPa for 1 h.

2.2 Characterizations

The bulk densitis of the obtained samples were measured by Archimedes′ method in distilled water, and the relative density was calculated from the theoretical densities of each raw powder using a linear rule of mixture. The phase compositions were determined by a model D8 X-ray diffractometer (XRD, Bruker Co., Germany). The microstructures were analyzed by amodel SU8010 field-emission scanning electron microscope (FESEM, Hitachi Co., Ltd., Japan). The element distribution of the samples was determined by an energy dispersive X-ray spectrometer (EDS). The Vickers hardness was measured on the polished surface of the samples with a load of 196 N and dwell time of 15 s. The fracture toughness was determined by the indentation fracture method proposed by Evans and Charles[26]. The flexural strength was measured by a three-point bending method on the test bars with a dimension of 3 mm × 4 mm × 40 mm, using a span of 30 mm and a crosshead speed of 0.5 mm/min.

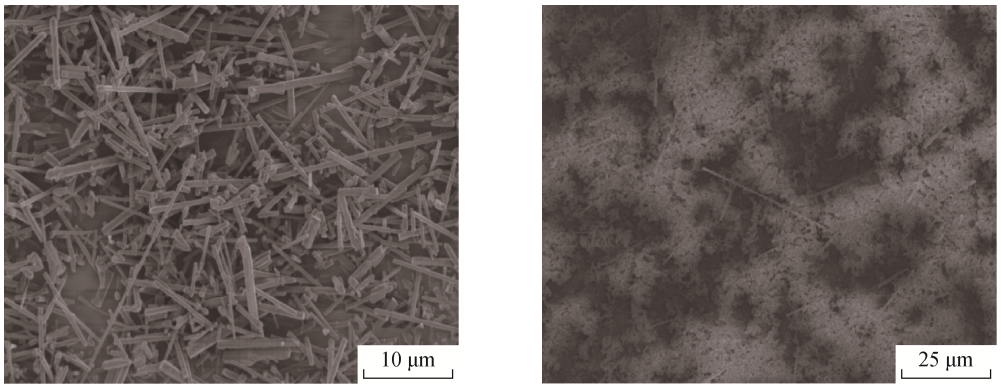
3 Results and discussion

3.1 Effect of SiC whisker content

Figure 1 shows the SEM images of morphologies of SiC whisker and ground powder mixtures containing 8% SiC whisker. Clearly, SiC whisker with a length of approximately 10 μm after grinding is homogeneously dispersed in the powder mixtures.

Table 1 shows the relative densities of the samples with different portions of SiC whisker. The relative density of Si_3N_4–SiC_w composites gradually decreases from (99.6±0.1)% to (92.8±0.3)% as SiC whisker content increases from 0 to 12%, indicating that the addition of SiC whisker inhibits the densification of Si_3N_4 matrix composites [11,17].

Figure 2 shows the effect of SiC whisker content on the mechanical behavior of the samples. Clearly, the Vickers hardness decreases from (16.1±0.2) GPa to (12.9±0.2) GPa, and the fracture toughness increases from (5.8±0.1) MPa·$m^{1/2}$ to (7.1±0.1) MPa·$m^{1/2}$ when SiC whisker content increases from 0 to 12%. The flexural strength increases from (1 066±65) MPa to (1 122±96) MPa with the increase of SiC whisker content from 0 to 4%, but it decreases with the further addition of SiC whisker.



(a) SiC whisker (b) Powder mixtures containing 8% SiC whisker

Fig. 1 SEM images of the morphologies of SiC whisker and ground powder mixtures containing 8% SiC whisker

Table 1 Batch compositions and relative densities of the samples prepared at the same process parameters

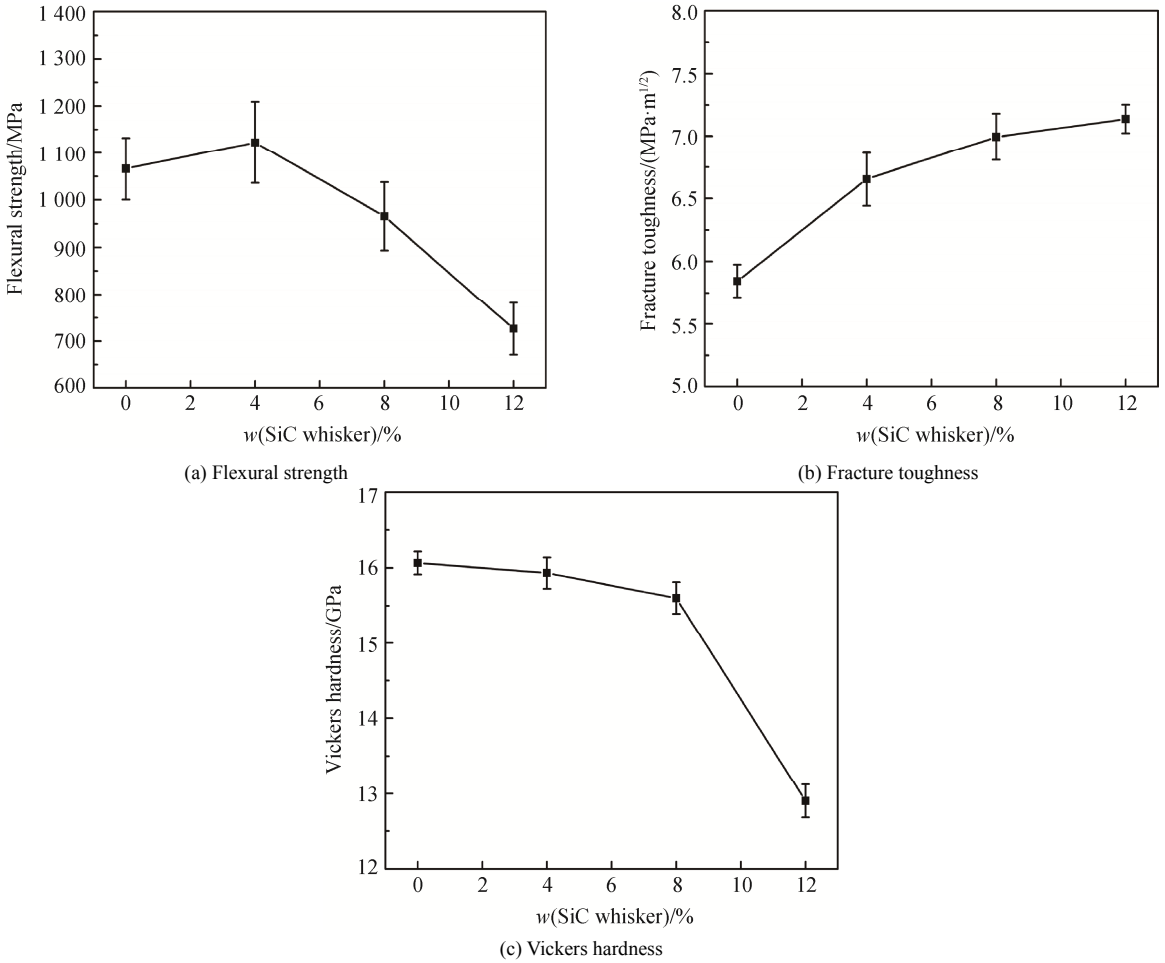
Sample No.	*w*/%					Relative density/%
	Si_3N_4	Yb_2O_3	Al_2O_3	SiCw	TiO_2	
0T0W	92	6	2	0	0	99.6±0.1
0T4W	88	6	2	4	0	98.9±0.2
0T8W	84	6	2	8	0	97.8±0.2
0T12W	80	6	2	12	0	92.8±0.3
1T8W	84	6	2	8	1	98.7±0.2
3T8W	84	6	2	8	3	99.5±0.1
5T8W	84	6	2	8	5	99.7±0.1

w—Mass fraction.

The results above indicate that the optimal mechanical properties of Si_3N_4–SiC_w composites are obtained by addition of 8% SiC whisker. Consequently, Si_3N_4–SiC_w composites containing 8% SiC whisker (*i.e.*, Si_3N_4–8%SiC_w) are chosen to investigate the effect of TiO_2 content on the densification, phase compositions, microstructure, and mechanical properties of the composites.

3.2 Effect of TiO_2 content

Figure 3 shows the XRD patterns of Si_3N_4–8%SiC_w composites with different TiO_2 contents sintered in nitrogen gas at 1 750 ℃ and 1 MPa for 1 h and HIPed in



(a) Flexural strength (b) Fracture toughness

(c) Vickers hardness

Fig. 2 Effect of SiC whisker content on mechanical properties of the samples

nitrogen gas at 1 750 ℃ and 100 MPa for 1 h, respectively. Clearly, the diffraction peaks of β-Si_3N_4, $Yb_4Si_2O_7N_2$ and 3C-SiC appear for all the samples, and the diffraction peak of TiN occurs for the samples with the addition of TiO_2. Moreover, the intensity of TiN peak becomes more intense gradually with the increase of TiO_2 content. Previous work confirmed that TiN is formed by the *in-situ* reaction of TiO_2 with Si_3N_4[20–21], as shown in the reactions (1) and (2). The corresponding thermodynamic calculations indicated that the reaction could proceed at 1 700 ℃ if $P(N_2)$ <1.1×10^{23} Pa for reaction (1) and $P(O_2)$ <3.6 Pa for reaction (2). As the samples were sintered in N_2 atmosphere at 1 750 ℃ and 1 MPa in a carbon heater furnace, the conditions required for both the reactions could be satisfied. In sintering, Yb_2O_3–Al_2O_3 additives can react with native SiO_2 on the surface of Si_3N_4 to form Yb—Si—Al—O—N liquid phase, thus accelerating the densification and microstructure evolution of the composites through particle rearrangement and dissolution-reprecipitation mechanisms. In the final stage of sintering, a certain proportion of Si and N in β-Si_3N_4 lattice can be substituted by Al and O to form β-SiAlON solid solution, and the remaining Al and O still coexist as an amorphous phase in the samples. Therefore, the diffraction peak of the crystalline phase containing Al does not appear in the XRD patterns. Furthermore, $Yb_4Si_2O_7N_2$ can be generated from the partial crystallization of Yb—Si—Al—O—N glass during cooling. Figure 4 shows the elements distributions of polished surface of the sample 3T8W. The elements Yb, Al, and Ti are evenly distributed in the composites.

$$2Si_3N_4(s)+6TiO_2(s)\rightarrow 6SiO_2(s)+6TiN(s)+N_2(g) \quad (1)$$

$$\Delta G=\Delta G^{\ominus}+RT\ln P(N_2)$$

$$Si_3N_4(s)+4TiO_2(s)\rightarrow 3SiO_2(s)+4TiN(s)+O_2(g) \quad (2)$$

$$\Delta G=\Delta G^{\ominus}+RT\ln P(O_2)$$

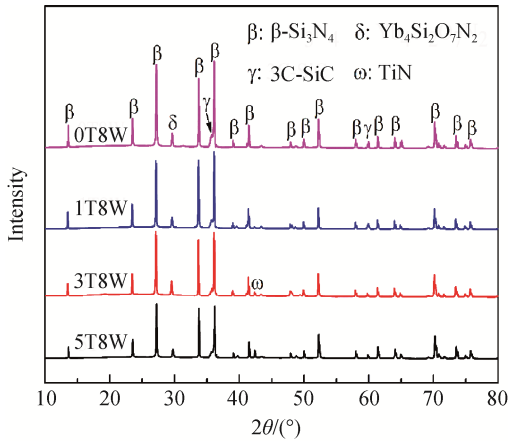
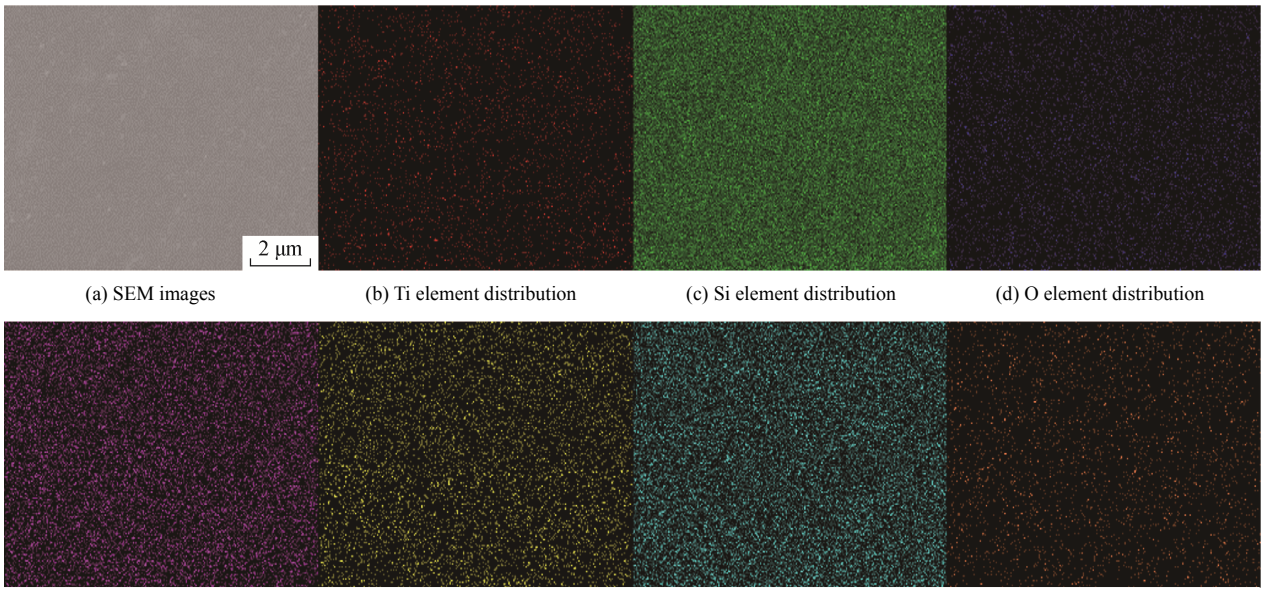


Fig. 3　XRD patterns of the samples containing 8% SiC whisker with different TiO_2 contents

Table 1 also shows the relative densities of the samples with different TiO_2 contents. The relative density of Si_3N_4–8%SiC_w composites gradually increases from (97.8±0.2)% to (99.7±0.1)% when TiO_2 content increases from 0 to 5%, indicating that the addition of TiO_2 promotes the densification of the composites. The formation of SiO_2 through the *in-situ* reaction of TiO_2 with Si_3N_4, can be used as sintering additives to create the more amounts of liquid phases during sintering. As a result, the particle rearrangement and dissolution-reprecipitation are enhanced.

Figure 5 shows the effect of TiO_2 content on the mechanical properties of Si_3N_4–8%SiC_w composites. The flexural strength increases from (965±72) MPa to (1 301±87) MPa, the Vickers hardness increases from (15.6±0.2) GPa to (16.2±0.1) GPa, and the fracture toughness increases from (7.0±0.2) MPa·$m^{1/2}$ to (7.8±0.1) MPa·$m^{1/2}$ as TiO_2 content increases from 0 to 3%. However, when TiO_2 content further increases to 5%, the flexural strength, the Vickers hardness and the fracture

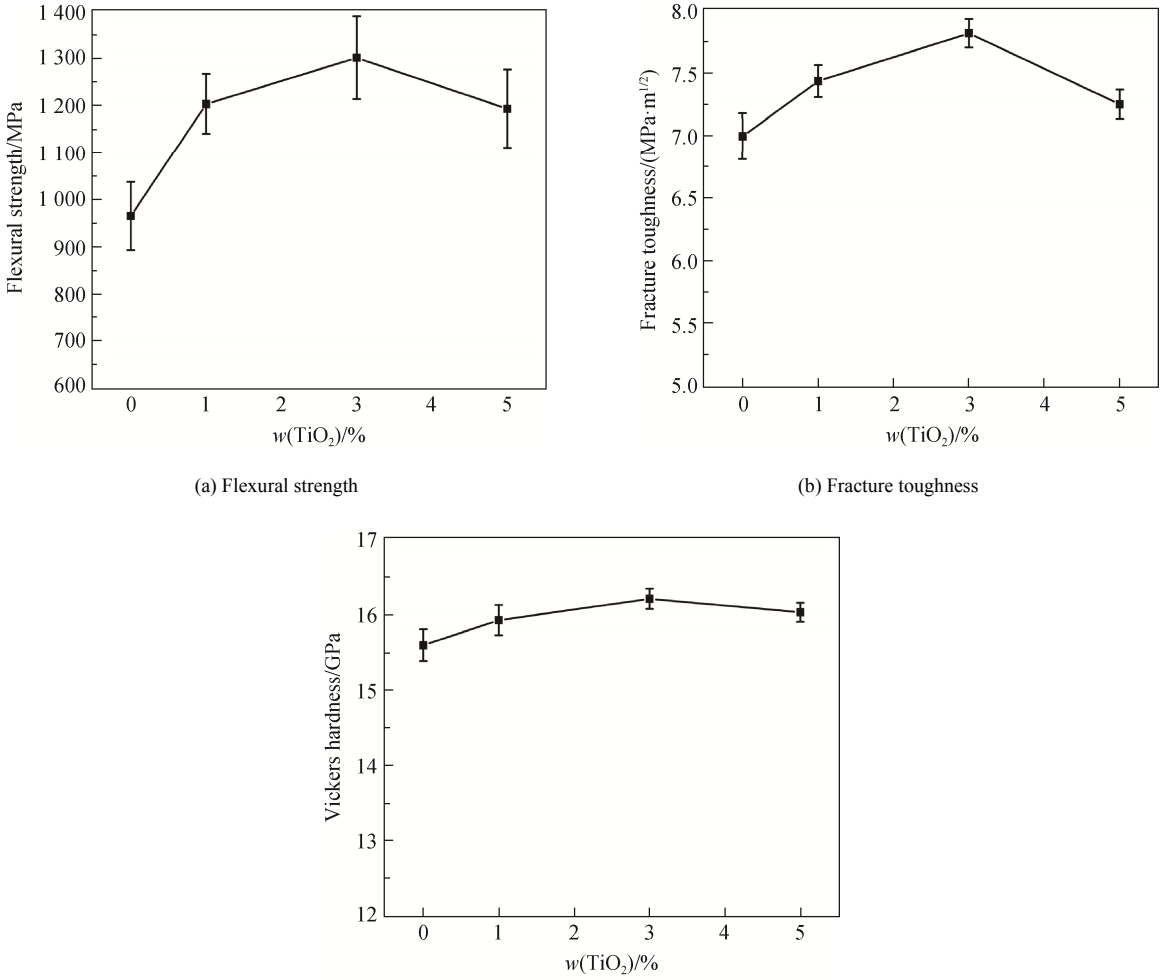


(a) SEM images　(b) Ti element distribution　(c) Si element distribution　(d) O element distribution

(e) N element distribution　(f) C element distribution　(g) Al element distribution　(h) Yb element distribution

Fig. 4　EDS element maps for the element distributions on the polished surface of the sample 3T8W

toughness of the composites simultaneously decrease. Consequently, the optimal mechanical properties of Si_3N_4–8%SiC_w composites are obtained at the addition of 3% TiO_2.



(a) Flexural strength

(b) Fracture toughness

(c) Vickers hardness

Fig. 5 Effect of TiO_2 content on mechanical properties of the samples containing 8% SiC whisker

Figure 6 shows the SEM images of the fracture surface of the samples containing different TiO_2 contents. More elongated β-Si_3N_4 grains appear in the microstructure as TiO_2 content increases, indicating that the addition of TiO_2 is beneficial for the anisotropic growth of β-Si_3N_4 grains. An increase in the aspect ratio of β-Si_3N_4 grains is conducive to the improvement of the fracture toughness[24–25]. Moreover, the mismatch of thermal expansion coefficient between TiN (converted from TiO_2) particles and Si_3N_4 grains can generate the tensile stress on Si_3N_4 matrix to cause the cracks deflection[21–22]. The crack length that is defined as the distance from the tip of Vickers indentation to the tip of crack for the samples 0T0W, 0T8W, and 3T8W is (143.5±2.9) μm, (117.1±3.7) μm, and (104.6±1.4) μm, respectively, indicating that the *in-situ* TiN formation is able to be resistant to the crack propagation. Furthermore, a previous work [8] showed that the Si_3N_4 matrix composites reinforced with SiC whisker with TiO_2 coating exhibited greater interfacial bonding strength and fracture toughness. In Fig. 6, there exists an obvious pullout of SiC whisker and β-Si_3N_4 grains (marked with arrows) on the fracture surface of the samples. Therefore, the fracture toughness of the samples with TiO_2 content of 3% or less is improved.

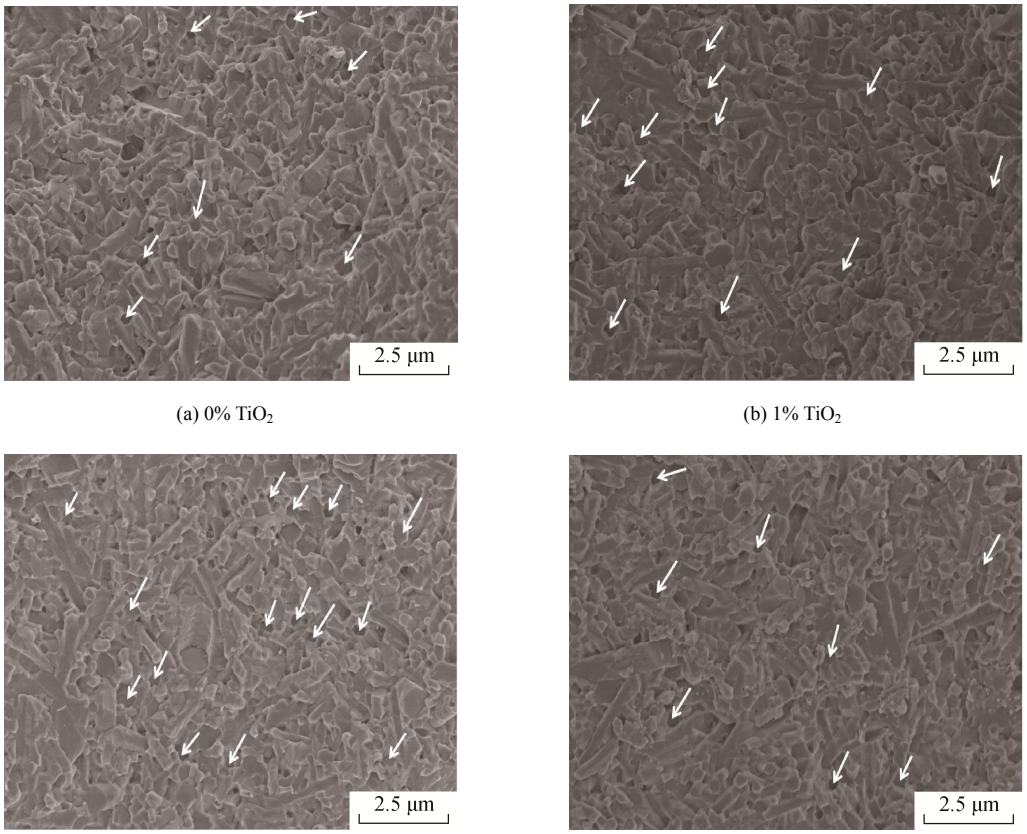
In addition, the flexural strength and the Vickers hardness of the samples containing less than 3% TiO_2 are also enhanced due to the increase of relative density. However, when the content of TiO_2 is 5%, much grain boundary phases generated by excessive liquid phase exist in the composites, resulting in a decrease of the flexural strength as well as the Vickers hardness.

The fracture toughness of Si_3N_4–SiC_w composites is closely related to the interfacial strength of bonding between Si_3N_4 matrix and SiC whisker[6,11]. A few of SiC whisker and elongated β-Si_3N_4 grains pull out from Si_3N_4 matrix in the sample containing 5% TiO_2, as shown in Figure 6d. One of the main reasons could be since the bonding strength of the interface between

Si_3N_4 matrix and SiC whisker becomes more intense as TiO_2 content increases, making it difficult to pull out for SiC whisker or rod-like β-Si_3N_4 grains. Another possible reason could be that excessive SiO_2 reacts with SiC whisker if $P_{CO}(P_{SiO})^3$ <3.2×10^{16} Pa at 1 700 ℃, as shown in the reaction (3), leading to the weakening of toughening effect of SiC whisker. As a result, the fracture toughness of the composites with 5% TiO_2 decreases drastically.

$$SiC(s) + 2SiO_2(s) \rightarrow 3SiO(s) + CO(g) \quad (3)$$

$$\Delta G=\Delta G^{O}+RT\ln (P(CO)P(SiO)^3)$$



(a) 0% TiO_2　(b) 1% TiO_2

(c) 3% TiO_2　(d) 5% TiO_2

Fig. 6　SEM images on the fracture surface of the samples containing 8% SiC whisker with different TiO_2 contents

4 Conclusions

Highly-densified Si_3N_4–SiC_w composites with superior mechanical properties were fabricated by a cost-effective sinter–HIP method. The densification, phase compositions, microstructure and mechanical behaviors of the Si_3N_4–SiC_w composites with various portions of SiC whisker and TiO_2 were discussed. The results were summarized as follows:

1) The addition of SiC whisker hindered the densification of Si_3N_4 matrix composites. The flexural strength and the Vickers hardness of the composites with 8% SiC whisker decreased drastically due to an increase in the porosity, compared with that of monolithic Si_3N_4 ceramics. The fracture toughness of the composites increased monotonically with SiC whisker content.

2) TiO_2 additives promoted the densification of Si_3N_4–8%SiC_w composites and the growth of β-Si_3N_4 grains along the length. The composites containing 3% TiO_2 with the flexural strength of (1 301±87) MPa, the Vickers hardness of (16.2±0.1) GPa, and the fracture toughness of (7.8±0.1) MPa·$m^{1/2}$ were obtained, compared with the composites without TiO_2 addition under the same process conditions.

3) TiN and SiO_2 were formed from the reaction of TiO_2 with Si_3N_4 during sintering. The formation of SiO_2 offered the more amounts of liquid phases to enhance the densification. However, the excessive SiO_2 also led to an intense interfacial bonding strength and weakened the toughening effect of SiC whisker, thus resulting in a decrease in the fracture toughness. Besides, *in-situ* TiN formation could further improve the fracture toughness of Si_3N_4–8%SiC_w composites through the particulate toughening mechanism.

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