

## **C<sub>0.3</sub>N<sub>0.7</sub>Ti-SiC toughed silicon nitride hybrids with non-oxide additives Ti<sub>3</sub>SiC<sub>2</sub>**

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**Abstract:** *In-situ* grown C<sub>0.3</sub>N<sub>0.7</sub>Ti and SiC, which derived from non-oxide additives Ti<sub>3</sub>SiC<sub>2</sub>, are proposed to densify silicon nitride (Si<sub>3</sub>N<sub>4</sub>) ceramics with enhanced mechanical performance. Remarkable increase of density from 79.20% to 95.48% could be achieved for Si<sub>3</sub>N<sub>4</sub> ceramics with 5vol% Ti<sub>3</sub>SiC<sub>2</sub>. The capillarity of decomposed Si from Ti<sub>3</sub>SiC<sub>2</sub>, and *in-situ* reaction between nonstoichiometric TiC<sub>x</sub> and Si<sub>3</sub>N<sub>4</sub> were believed to be responsible for densification of Si<sub>3</sub>N<sub>4</sub> ceramics. An obvious enhancement of flexural strength and fracture toughness for Ti<sub>3</sub>SiC<sub>2</sub> doped Si<sub>3</sub>N<sub>4</sub> ceramics was observed. The maximum flexural strength of 795 MPa for Si<sub>3</sub>N<sub>4</sub> composites with 5vol% Ti<sub>3</sub>SiC<sub>2</sub> and maximum fracture toughness of 6.97 MPa·m<sup>1/2</sup> for Si<sub>3</sub>N<sub>4</sub> composites with 20vol% Ti<sub>3</sub>SiC<sub>2</sub> are achieved when mixed powders are hot-press sintered at 1700 °C. Pull out of elongated Si<sub>3</sub>N<sub>4</sub> grains, crack bridging, crack branching and crack deflection were demonstrated to dominate enhance fracture toughness of Si<sub>3</sub>N<sub>4</sub> composites.

**Keywords:** Ti<sub>3</sub>SiC<sub>2</sub>; Si<sub>3</sub>N<sub>4</sub>; mechanical properties; fracture toughness

### **1. Introduction**

Although a number of alternatives of structural ceramics have been proposed, silicon nitride (Si<sub>3</sub>N<sub>4</sub>)-based ceramics remain competitive due to their superior properties, involving high strength and hardness at elevated temperatures, high resistance to oxidation and chemical attack, low coefficient of tribological friction and thermal expansion, and low dielectric permittivity, etc. [1–9]. As important multifunctional materials, Si<sub>3</sub>N<sub>4</sub> ceramics have found wide range of successful application towards gas turbine engine components [10–13], cutting tools [10, 14], radomes [2], and even integrated circuit [15, 16], optical devices [17, 18], etc.

However, due to the high degree of covalent bonding, Si<sub>3</sub>N<sub>4</sub>-based ceramics are very difficult to densify through the solid-state sintering process. Therefore, effective approaches to ensure rapid consolidation and high mechanical performance of Si<sub>3</sub>N<sub>4</sub>-based ceramics are actively being explored, including gas pressure sintering (GPS)<sup>[10]</sup>, hot-pressing sintering (HPS)<sup>[19–25]</sup>, hot isostatic pressing sintering (HIP)<sup>[26]</sup>, spark plasma sintering (SPS)<sup>[25, 27, 28]</sup>, and microwave sintering [1, 29], etc. However, considering the requirement of high gas pressures for gas pressure sintering and extra current devices for SPS with a significantly higher furnace costs, HP sintering allows the dense and complex-shaped parts with medium cost. Previous considerable efforts have demonstrated that fully dense Si<sub>3</sub>N<sub>4</sub> ceramics with superior strength could be achieved through liquid phase sintering by addition of rare-earth oxides to promote mass transport and accelerate the rate of  $\alpha$ – $\beta$  transformation, most notably the rare-earth oxides involving Y<sub>2</sub>O<sub>3</sub> [4, 30, 31]. A combination of various rare-earth oxides

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and other metallic oxides, such as  $\text{Y}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ,  $\text{Lu}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ , also are effective sintering aids to densify  $\text{Si}_3\text{N}_4$  [24, 29, 31-34]. Nevertheless, these oxides additives crystallized to intergranular glassy phase in the cooling stage [30], which deteriorate the high-temperature performance of the ceramics such as creep and high-temperature strength due to the relative low eutectic temperature [31, 35]. As a result of the early interest in hot-pressed  $\text{Si}_3\text{N}_4$  ceramics as a high-temperature gas-turbine material, attention was directed to high-temperature strength and creep resistance. Therefore, it is quite essential to explore novel heat-resistant sintering aids for high-performance  $\text{Si}_3\text{N}_4$  ceramics from new view point. The last two decades have been witness to the dramatic development on MAX phase cermet with the hexagonal symmetry due to their unique combination of characteristics of both ceramics and metals (M is an early transition metal, A is a group A element, X is either carbon and/or nitrogen), especially the layered ternary carbide titanium aluminum carbide ( $\text{Ti}_3\text{AlC}_2$ ) and titanium silicon carbide ( $\text{Ti}_3\text{SiC}_2$ ) [36-38]. The crystal structure of these MAX cermets can be described by alternately stacking of  $\text{TiC}_6$  and Al/Si atomic planes. The unique combination of excellent properties of  $\text{Ti}_3\text{AlC}_2$  or  $\text{Ti}_3\text{SiC}_2$ , including high melting point, high hardness, high elastic modulus, good thermal and electrical conductivity, and considerable chemical stability, make them to be fascinating candidates for various application. Moreover, elemental metal powder-derived MAX materials have demonstrated to be effective reinforcement in  $\text{TiB}_2$  [39-41],  $\text{Al}_2\text{O}_3$  [42-44] composites with enhanced mechanical properties by *in situ* reaction. More recently, as explicated in our previous work [45-49], titanium aluminum carbide ( $\text{Ti}_3\text{AlC}_2$ ) was chosen as an effective sintering aid to effectively densify  $\text{B}_4\text{C}$  ceramics with enhanced sintering ability and mechanical performance simultaneously. High hardness and toughness values of 28.5 GPa and 7.02  $\text{MPa}\cdot\text{m}^{1/2}$  respectively were achieved for  $\text{B}_4\text{C}$  composites sintered with 20vol%  $\text{Ti}_3\text{AlC}_2$  at 1900 °C. The mechanisms of the enhanced sinterability of high-performance ceramics in previous works could be classified into two aspects: Firstly, the decomposed metals from  $\text{Ti}_3\text{SiC}_2$  or  $\text{Ti}_3\text{AlC}_2$  at high temperature can form liquid phase which promote sintering effectively. Secondly, *in situ* reaction sintering between matrix and titanium carbon compound would also promote densification and mechanical performance. The main competitive advantage of MAX aids is considered to be formation of reaction bonding between  $\text{Si}_3\text{N}_4$  matrix and aids, rather than intergranular glassy phase. Motivated by such an idea, these non-oxides cermets are highly expected to play a multifunctional role in densification and enhancement of mechanical properties of  $\text{Si}_3\text{N}_4$  ceramics. It is also noteworthy that Al decomposed from  $\text{Ti}_3\text{AlC}_2$  and residual O originated from raw  $\text{Si}_3\text{N}_4$  powders would be dissolved into  $\text{Si}_3\text{N}_4$  grains during high-temperature sintering procedure, which is harmful to the purity and thermal performance of  $\text{Si}_3\text{N}_4$ -based ceramics. As Y. Zhou illustrated [50], a tendency of decreasing fracture toughness with increasing Al dopant could be observed. Moreover, even the 0.4wt% concentration of Al would lead to a drastically reduce of thermal conductivity by 36.9% (from  $91.9\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  to  $58.0\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) for  $\text{Si}_3\text{N}_4$  ceramics. Therefore in this work,  $\text{Ti}_3\text{SiC}_2$  were introduced to densify  $\text{Si}_3\text{N}_4$  ceramics in order to demonstrate that it provided any advantages over the rare-earth oxide system. Besides, the effect of

Ti<sub>3</sub>SiC<sub>2</sub> volume fraction on the microstructure, hardness, flexural strength and fracture toughness was also studied. It is believed that Ti<sub>3</sub>SiC<sub>2</sub> or other members of MAX family would lead to new scientific and technological data providing new insight into functionalization of Si<sub>3</sub>N<sub>4</sub> ceramics.

## 2. Experimental procedure

### 2.1 Preparation of samples

Commercially available  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder (purity>93%, d<sub>50</sub>=0.7 $\mu$ m, Jinshenghao New Materials Co. Ltd., China) was used as a starting material. As a novel sintering aid, Ti<sub>3</sub>SiC<sub>2</sub> powders (d<sub>50</sub>=5 $\mu$ m, purity>98%) were kindly provided by Forsman Scientific Co., Ltd., Beijing, China. In order to investigate the effect of Ti<sub>3</sub>SiC<sub>2</sub> content on the mechanical properties, experiments were conducted with various amounts of Ti<sub>3</sub>SiC<sub>2</sub> powders (1 to 20 vol.%) embedded in  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powders. To ensure the homogeneity of the mixed powders,  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>-*x* vol.% Ti<sub>3</sub>SiC<sub>2</sub> powders (*x*=1~20) were wet ball-milled for 10h by using ethanol as ball-milling media. The substance was dried at 80°C, and sieved with a filter with a mesh size of 63 $\mu$ m, then placed in a graphite die coated with BN powder to avoid reaction between the powder and graphite die. Hot-press (HP) sintering was performed with ramp of 10°C/min 1600°C and 1700°C for 90min in flowing nitrogen under 30MPa uniaxial pressure during the whole cycle. After natural cooling to room temperature inside furnace, samples were polished and ultrasonic cleaned before characterization. For comparison,  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powders with 2wt.% Alumina (Al<sub>2</sub>O<sub>3</sub>, AR, Sinopharm Chemical Reagent Co., Ltd., China) and 5wt.% yttria (Y<sub>2</sub>O<sub>3</sub>, AR, Sinopharm Chemical Reagent Co., Ltd., China) were hot-pressed at the same sintering condition.

### 2.2 Characterizations

The bulk density of each sample was determined according to the Archimedes principle in distilled water. XRD patterns were recorded on X'pert PRO (PANalytical B.V., Netherlands) for phase identification. The microstructures of polished surfaces and fracture surfaces were observed using scanning electron microscopy (SEM, Nova NanoSEM230) with an energy-dispersive X-ray (EDX) analyzer. The Vickers hardness was performed on micro hardness tester (VTD 512) under load of 9.8 N with a dwell time of 10 seconds, and determined by the Vickers diamond indentation method using the following equation:

$$H_v = 0.102 \frac{F}{S} = 0.102 \frac{2F \sin \frac{136^\circ}{2}}{d^2} = 0.1891 \frac{F}{d^2} \quad (1)$$

where *P* is the indentation load on the polished surface and *d* is the average diagonal length of the Vickers indentation. For accuracy, 11 Vickers indentations on each specimen were applied. After indentation, the microstructures were immediately observed by optical microscopy (ECLISPE LV150N, Japan). As a simple way of estimating toughness, indentation techniques were applied from observed corner cracks and calculated Vickers hardness using the Anstis equation:

$$K_{IC} = 0.016 \left( \frac{E}{H_v} \right)^{\frac{1}{2}} \left( \frac{P}{c^{\frac{3}{2}}} \right) \quad (2)$$

where *E* is the Young's modulus and *c* is the half-length of cracks formed by the indentation. Three-point flexural strength of specimens with size of 3mm×4mm×36mm

was performed on the mechanical testing machine (Instron3369, USA) at a cross head speed of 0.5mm/min.

### 3. Results and discussion

Fig. 1 illustrates the density of  $\text{Ti}_3\text{SiC}_2$  filled  $\text{Si}_3\text{N}_4$  ceramics as a function of  $\text{Ti}_3\text{SiC}_2$  volume fraction. For  $\text{Si}_3\text{N}_4$  ceramics which HP sintered at  $1600^\circ\text{C}$  without aids, the density is only  $2.58 \text{ g cm}^{-3}$ . Partial densification may be attributed to the residual  $\text{SiO}_2$  liquid phase during firing at high temperature which always present on  $\text{Si}_3\text{N}_4$  powder particles. A remarkable increase to  $3.11 \text{ g cm}^{-3}$  could be observed for  $\text{Si}_3\text{N}_4$  ceramics filled with only 5vol%  $\text{Ti}_3\text{SiC}_2$  when sintered at the same temperature. The enhanced density is even more noticeable than the  $\text{Si}_3\text{N}_4$  ceramics with 7wt%  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  aids. These observed results demonstrate  $\text{Ti}_3\text{SiC}_2$  to be a effective sintering aid to densify  $\text{Si}_3\text{N}_4$  ceramics. However, further increase in  $\text{Ti}_3\text{SiC}_2$  content dose not bring any appreciable consolidation.

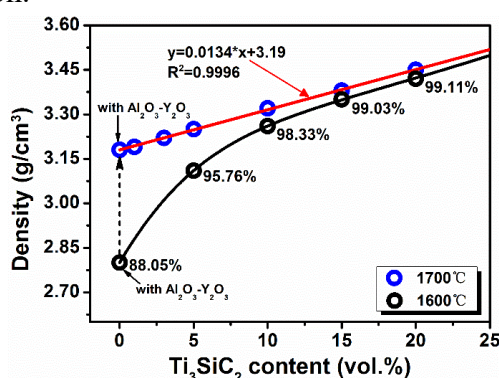


Fig. 1 Density of  $\text{Si}_3\text{N}_4$  ceramics as a function of  $\text{Ti}_3\text{SiC}_2$  content

As expected, higher sintering temperature  $1700^\circ\text{C}$  could further promote densification of  $\text{Si}_3\text{N}_4$  ceramics filled with  $\text{Ti}_3\text{SiC}_2$ . Besides, experimental points are inclined to distribute on a straight line with coefficient of determination ( $R^2$ ) above 0.99, which is accordant with mix law. Due to the complex reaction between  $\text{Si}_3\text{N}_4$  and  $\text{Ti}_3\text{SiC}_2$  which will discuss later, it is difficult to determine the theoretical density of the  $\text{Ti}_3\text{SiC}_2\text{-Si}_3\text{N}_4$  composites accurately. However, an approximation method could be applied by assuming a nearly full densification for 20vol%  $\text{Ti}_3\text{SiC}_2\text{-Si}_3\text{N}_4$  ceramics sintered at  $1700^\circ\text{C}$  according to this linear behavior.

Fig. 2 shows the XRD patterns of  $\text{Si}_3\text{N}_4$  ceramics filled with different volume fraction of  $\text{Ti}_3\text{SiC}_2$  sintered at  $1600^\circ\text{C}$  and  $1700^\circ\text{C}$ , as well as 7wt% ( $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ ) densified  $\text{Si}_3\text{N}_4$  ceramics. As seen in Fig. 2(a), both  $\alpha$  and  $\beta$  phase of  $\text{Si}_3\text{N}_4$  could be detected when sintering temperature is  $1600^\circ\text{C}$ , which suggests only a partial transformation of  $\alpha$  phase to the more stable  $\beta$  phase. In contrast, when further improving sintering temperature to  $1700^\circ\text{C}$ , all diffraction peaks of  $\alpha\text{-Si}_3\text{N}_4$  phase disappear (see in Fig. 2(b)). This completely transformation of  $\alpha$  to  $\beta\text{-Si}_3\text{N}_4$  phase is believed to be essential to the enhancement of densification and mechanical performance.

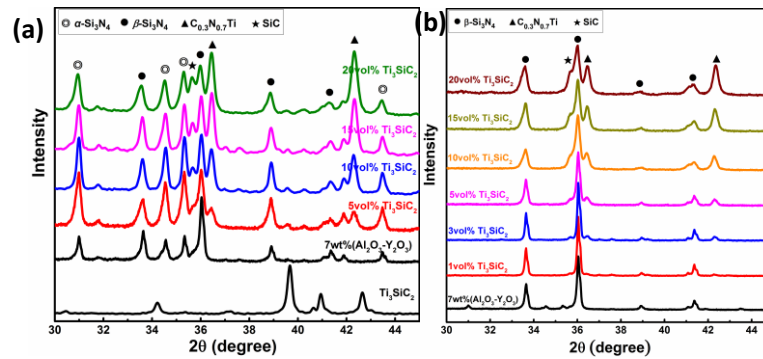
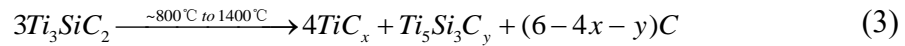


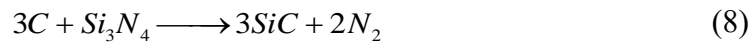
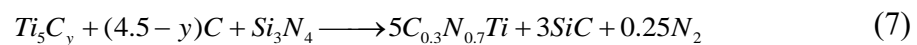
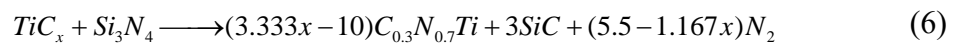
Fig. 2 XRD patterns of  $\text{Ti}_3\text{SiC}_2$  doped  $\text{Si}_3\text{N}_4$  ceramics sintered at (a)  $1600^\circ\text{C}$  and (b)  $1700^\circ\text{C}$ . Another important feature should be noted here is that the characteristic diffraction peaks of the raw  $\text{Ti}_3\text{SiC}_2$  powder nearly disappear completely after sintering. This could be ascribed to the fact that  $\text{Ti}_3\text{SiC}_2$  powder is thermal stable up to  $\sim 800^\circ\text{C}$ , and the following reaction can be responsible for the decomposition of  $\text{Ti}_3\text{SiC}_2$  [51]:



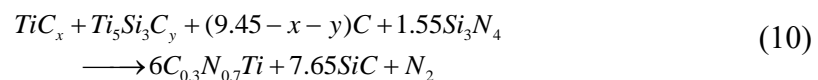
where the value of  $x$  ranges from 0.6 to 0.8 and  $y \leq 1$ . Besides, the  $\text{TiC}_x$  phase appears to result in more rapid deterioration of the  $\text{Ti}_3\text{SiC}_2$  phase. Also noted that the decomposition usually accomplished with decomposition of  $\text{Ti}_3\text{SiC}_2$  to form nonstoichiometric  $\text{TiC}_x$  and gaseous Si, as demonstrated previously [52]:



The Si is believed to be act as lubricating phase between  $\text{Si}_3\text{N}_4$  grains to promote densification of  $\text{Si}_3\text{N}_4$  ceramics through capillarity. Meanwhile, the residual Si would further react with nitrogen to form  $\text{Si}_3\text{N}_4$ . On the other hand, further heating during insulation stage will result in the likely loss of gaseous silicon. Furthermore, the decomposition products of  $\text{Ti}_3\text{SiC}_2$  would further react with  $\text{Si}_3\text{N}_4$  through diffusion of C and N according to the following reactions:



or



It is reasonable to claim that the *in situ* reaction is responsible for the additional characteristic diffraction peaks of  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$  and SiC in XRD patterns.

Fig.3 shows the micro-morphology of polished surface of  $\text{Si}_3\text{N}_4$  with different volume fractions of  $\text{Ti}_3\text{SiC}_2$  sintered at  $1700^\circ\text{C}$ . Due to the lack of sufficient sintering aids, lots of pores could be observed, and grain growth of  $\beta$ - $\text{Si}_3\text{N}_4$  is not complete for monolithic  $\text{Si}_3\text{N}_4$  ceramic (see Fig.3(a)). However, the microstructures of  $\text{Ti}_3\text{SiC}_2$ - $\text{Si}_3\text{N}_4$  ceramics (see Fig.3(b) to Fig.3(g)) exhibit much more close-grain

structure, and consist of randomly oriented elongated  $\text{Si}_3\text{N}_4$  grains which is accordant with XRD results in Fig.2. The average diameters of grains present slight increasing trend from  $0.6771\ \mu\text{m}$  to  $0.9802\ \mu\text{m}$  by quantitative image analysis as the amount of  $\text{Ti}_3\text{SiC}_2$  increased. Besides, the bright contrasted phase which uniformly embedded in  $\text{Si}_3\text{N}_4$  matrix could be observed, and are inclined to aggregate especially when  $\text{Ti}_3\text{SiC}_2$  content exceeds 15vol%. Furthermore, as shown in Table 1, energy dispersive spectrometer (EDS) at spot A in Fig. 3(e) suggests dominant phase of  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$ , which is associated with reaction described by Eq.(10). Additional O element may be originated from surface of raw  $\alpha\text{-Si}_3\text{N}_4$  powders. Meanwhile, the bright region at spot B is proved to be enriched by Ti according to the EDS results in Table 1. Combined with the results of XRD analysis, it is reasonable to claim that the dispersive bright regions consist of  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$  and  $\text{SiC}$ , which are believed to affect the mechanical performance of reaction bonded  $\text{Si}_3\text{N}_4$  ceramics.

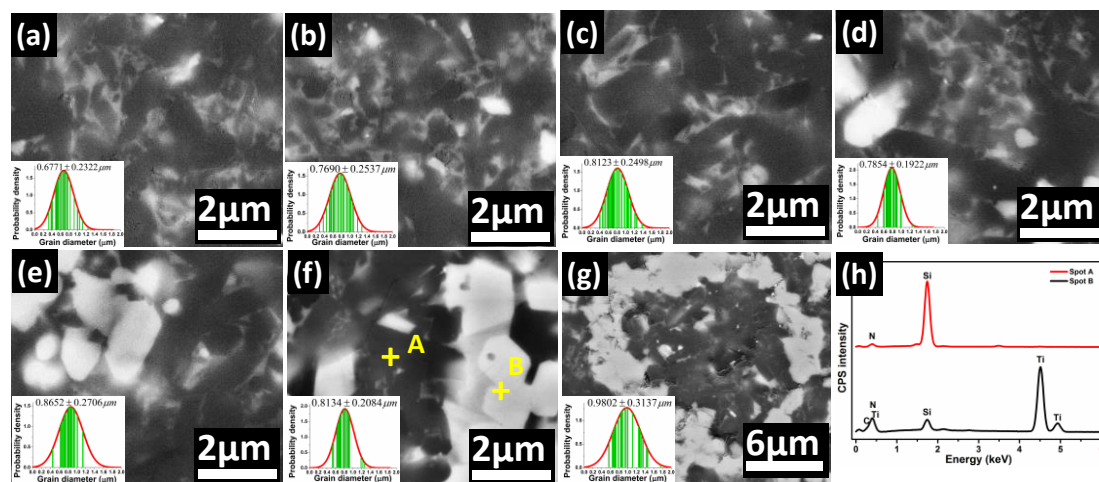


Fig. 3 Polished surface of  $\text{Si}_3\text{N}_4$  ceramics with different content of  $\text{Ti}_3\text{SiC}_2$  sintered at  $1700\ ^\circ\text{C}$ : (a) 5wt%  $\text{Y}_2\text{O}_3$ -2wt%  $\text{Al}_2\text{O}_3$ , (b) 1vol%  $\text{Ti}_3\text{SiC}_2$ , (c) 3vol%  $\text{Ti}_3\text{SiC}_2$ , (d) 5vol%  $\text{Ti}_3\text{SiC}_2$ , (e) 10vol%  $\text{Ti}_3\text{SiC}_2$ , (f) 15vol%  $\text{Ti}_3\text{SiC}_2$ , (g) 20vol%  $\text{Ti}_3\text{SiC}_2$ , (h) EDS spectra at spot A and B  
Table 1 EDS chemical analysis (at.%) at different positions in Fig. 3(g)

	Si	N	O	Ti	C	Possible phases
Spot A	52.21	35.43	2.04	1.29	9.03	$\text{Si}_3\text{N}_4$ , $\text{SiC}$
Spot B	5.10	27.18	-	50.13	17.59	$\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$ , $\text{SiC}$

The mechanical properties, including Vickers hardness, flexural strength and fracture toughness, of dense  $\text{Si}_3\text{N}_4$  ceramics with different  $\text{Ti}_3\text{SiC}_2$  content sintered at  $1700\ ^\circ\text{C}$  are illustrated in Fig. 4. Clearly, the Vickers hardness of  $\text{Si}_3\text{N}_4$  ceramics has been upgraded after modification of  $\text{Ti}_3\text{SiC}_2$ , and presents slight increase compared with that of  $\text{Si}_3\text{N}_4$  ceramics containing conventional oxides aids. Besides, an obvious enhancement of flexural strength and fracture toughness could be observed. A maximum flexural strength of 795 MPa could be achieved for 5vol% $\text{Ti}_3\text{SiC}_2$ doped  $\text{Si}_3\text{N}_4$  composites, which is almost twice that of 7wt% ( $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ )- $\text{Si}_3\text{N}_4$  ceramics prepared at the same condition. This enhancement of flexural strength could be attributed to the  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$  and  $\text{SiC}$  which originated from reaction bonding between  $\text{Ti}_3\text{SiC}_2$  and  $\text{Si}_3\text{N}_4$ . However, further increment of  $\text{Ti}_3\text{SiC}_2$  content reduces the flexural strength of  $\text{Si}_3\text{N}_4$  ceramics which may be ascribed to the enhanced residual stresses around grain boundary. Note that this residual stress is believed to result in

microcracks and intergranular fracture mode which will be discussed later. Moreover, the fracture toughness of  $\text{Si}_3\text{N}_4$  composites is also effectively boosted after  $\text{Ti}_3\text{SiC}_2$  decoration, and reaches maximum value of  $6.97 \text{ MPa}\cdot\text{m}^{1/2}$  for 20vol% $\text{Ti}_3\text{SiC}_2$ - $\text{Si}_3\text{N}_4$  ceramics which is 37% higher than that of 7wt% ( $\text{Y}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ )- $\text{Si}_3\text{N}_4$  ceramics.

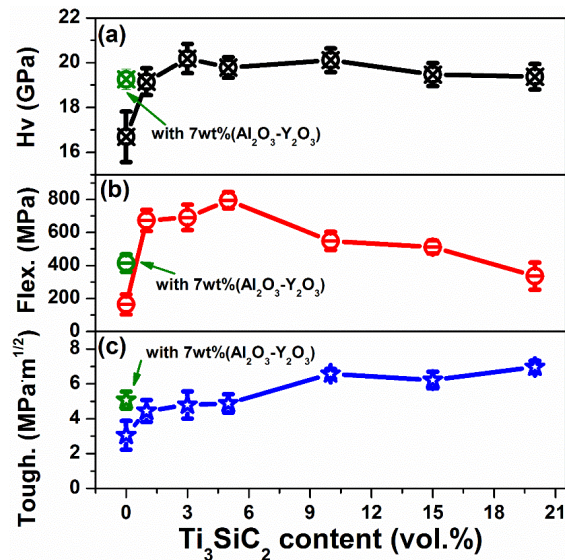


Fig. 4 Mechanical properties of  $\text{Ti}_3\text{SiC}_2$  doped  $\text{Si}_3\text{N}_4$  ceramics: (a) Vickers hardness, (b) flexural strength and fracture toughness

Fig. 5 illustrates the typical optical micrographs of the Vickers hardness indents and the induced cracks of  $\text{Si}_3\text{N}_4$  ceramics with different  $\text{Ti}_3\text{SiC}_2$  contents, as well as 7wt% ( $\text{Y}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ ). Clearly, the polished surfaces of  $\text{Ti}_3\text{SiC}_2$  doped  $\text{Si}_3\text{N}_4$  ceramics become much smoother than the monolithic  $\text{Si}_3\text{N}_4$  ceramic which HP sintered at  $1700^\circ\text{C}$ , corresponding to the enhancement of densification. Besides, it can be seen that the area of indentation presents no obvious change for  $\text{Ti}_3\text{SiC}_2$  doped  $\text{Si}_3\text{N}_4$  ceramics, which is consistent with the stable Vickers hardness. However, the cracks obviously become shorter especially when the  $\text{Ti}_3\text{SiC}_2$  contents exceed 10vol%, which is responsible for the enhancement of fracture toughness.

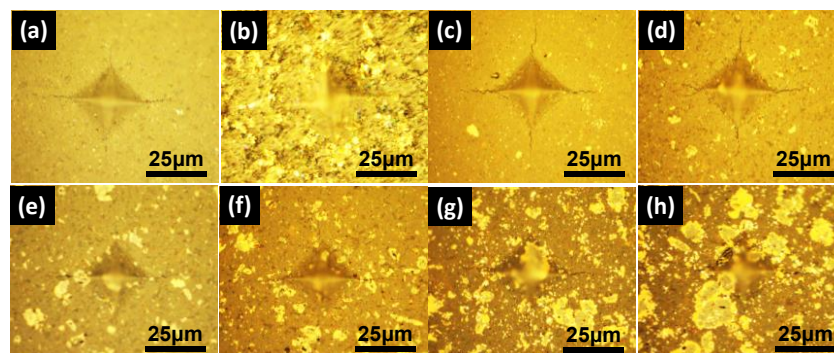


Fig. 5 Optical micrographs of the Vickers hardness indents and the induced cracks in (a)  $\text{Si}_3\text{N}_4$ -7wt% ( $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$ ), (b)  $\text{Si}_3\text{N}_4$ -3vol%  $\text{Ti}_3\text{SiC}_2$ , (c)  $\text{Si}_3\text{N}_4$ -5vol%  $\text{Ti}_3\text{SiC}_2$ , (d)  $\text{Si}_3\text{N}_4$ -10vol%  $\text{Ti}_3\text{SiC}_2$ , (e)  $\text{Si}_3\text{N}_4$ -15vol%  $\text{Ti}_3\text{SiC}_2$ , (f)  $\text{Si}_3\text{N}_4$ -20vol%  $\text{Ti}_3\text{SiC}_2$ , (g)  $\text{Si}_3\text{N}_4$ -20vol%  $\text{Ti}_3\text{SiC}_2$ , (h)  $\text{Si}_3\text{N}_4$ -20vol%  $\text{Ti}_3\text{SiC}_2$

To illustrate the fracture behaviors and activated toughening mechanisms, micromorphology and crack paths are investigated on cross-sectional fracture surfaces and polished surfaces, respectively. Comparison of typical fracture surfaces between

$\text{Si}_3\text{N}_4$  doped with  $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$  and  $\text{Ti}_3\text{SiC}_2$  is illustrated in Fig. 6. As can be seen from Fig. 6(a), a small amount of pores occur in the  $\text{Si}_3\text{N}_4\text{-7wt\% (Al}_2\text{O}_3\text{-Y}_2\text{O}_3)$  composites, which is harmful for the mechanical performances. In contrast, the  $\text{Si}_3\text{N}_4\text{-Ti}_3\text{SiC}_2$  specimen presents a much more close-grain fracture surface owing to the higher density. As marked by red arrows in Fig. 6(b), large amounts of dimples corresponding to the transgranular fracture could be observed. And this fracture mode is considered to make a dominate contribution to the superior flexural strength of  $\text{Si}_3\text{N}_4\text{-Ti}_3\text{SiC}_2$  composites. Besides, as marked by yellow arrows, lots of interface debonding between the  $\text{Si}_3\text{N}_4$  grains and grain boundary phase could be observed. This intergranular fracture mode may result from the pullout of elongated  $\beta\text{-Si}_3\text{N}_4$  grains, which is believed to make a contribution to the enhancement of overall fracture toughness.

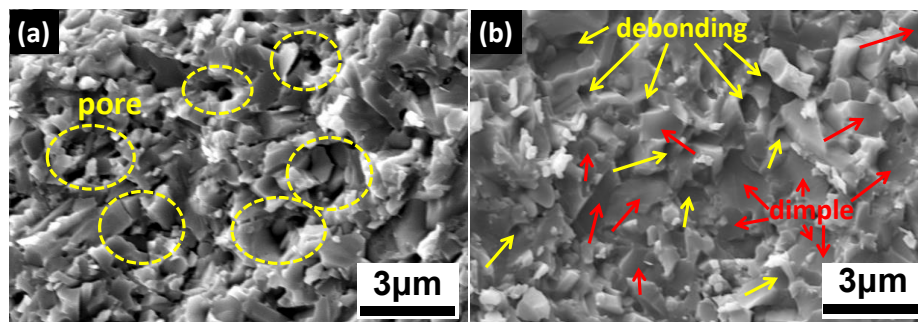


Fig. 6 Typical fracture surfaces of  $\text{Si}_3\text{N}_4$  with (a) 7wt%  $(\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3)$ , (b) 10vol%  $\text{Ti}_3\text{SiC}_2$

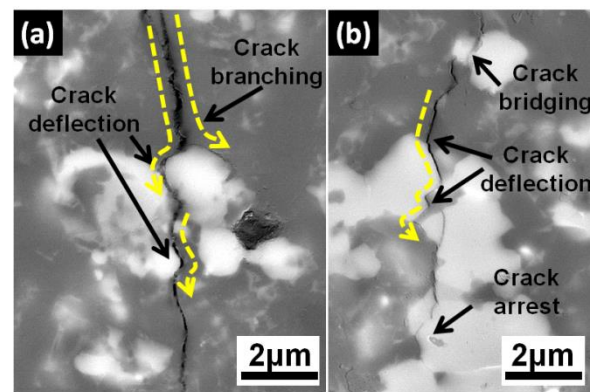


Fig. 7 Typical SEM images of crack deflection in  $\text{Ti}_3\text{SiC}_2$  densified  $\text{Si}_3\text{N}_4$  composites

Another mechanism of the enhanced fracture toughness of  $\text{Si}_3\text{N}_4\text{-Ti}_3\text{SiC}_2$  composites could be ascribed to the crack branching, deflection and grain bridging by *in-situ* derived  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$  and  $\text{SiC}$  grains embedded in  $\text{Si}_3\text{N}_4$  matrix, which illustrated in Fig. 7. Due to the superior hardness of  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$  and the thermal mismatch between  $\text{Si}_3\text{N}_4$  and  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$ , there exists residual stress around  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$  grains during cooling, giving rise to the microcracks inside composites. When subjected to the external mechanical stress, these microcracks tend to be activated and the propagation path of cracks tends to be splitted by  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$  hard-phase and deflected along the interface. Such mechanisms consumed more fracture energy during the crack propagation which leads to crack arrest.

A comparison of mechanical properties of  $\text{Si}_3\text{N}_4$ -based ceramics obtained in the present work and selected previous works with conventional oxide aids is shown in Table 2.

Clearly, the Vickers , flexural strength and toughness of  $\text{Ti}_3\text{SiC}_2$  doped  $\text{Si}_3\text{N}_4$  ceramics present the same level or even better compared with  $\text{Si}_3\text{N}_4$  ceramics sintered with oxide aids. Moreover, due to the superior mechanical and thermal properties of *in situ* formed  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$  and  $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$  ceramics obtained in this work are believed to have a significant competitive advantage and to promote the development of  $\text{Si}_3\text{N}_4$ -based ceramics at high temperatures.

Table 2 Selected results on mechanical properties of  $\text{Si}_3\text{N}_4$  ceramics by pressure-assisted sintering

Composition	Sintering conditions	Vickers hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPa.m <sup>1/2</sup> )	Ref.
$\alpha$ - $\text{Si}_3\text{N}_4$ +4wt% $\text{Al}_2\text{O}_3$ +6wt% $\text{Y}_2\text{O}_3$	Hot isostatic pressing at 1700 °C, 20MPa, 3h	16.4	730	6.5	[26]
$\alpha$ - $\text{Si}_3\text{N}_4$ +5wt% $\text{Al}_2\text{O}_3$ +5wt% $\text{Y}_2\text{O}_3$	Hot press at 1800 °C, 30MPa, 1.5h	16.1	-	5.2	[19]
$\alpha$ - $\text{Si}_3\text{N}_4$ +4wt% $\text{Al}_2\text{O}_3$ +6wt% $\text{Y}_2\text{O}_3$	Hot press at 1700 °C, 50MPa, 1.5h	17.01	-	-	[20]
$\alpha$ - $\text{Si}_3\text{N}_4$ +30vol% $\beta$ - $\text{Si}_3\text{N}_4$ whiskers+5wt% $\text{Al}_2\text{O}_3$ +5wt% $\text{Y}_2\text{O}_3$ +5wt% $\text{CeO}_2$	Hot press at 1700 °C, 30MPa, 30min	19.0	794	8.6	[21]
$\alpha$ - $\text{Si}_3\text{N}_4$ +4wt% $\text{Al}_2\text{O}_3$ +4wt% $\text{Y}_2\text{O}_3$ +15vol% $\text{SiC}$ whiskers	Hot press at 1800 °C, 30MPa, 30min	16	680	6.1	[53]
$\alpha$ - $\text{Si}_3\text{N}_4$ +5wt% $\text{Al}_2\text{O}_3$ +4wt% $\text{Y}_2\text{O}_3$ +3wt% $\text{TiC}$	Gas pressure sintering at 1750 °C, 2MPa	16.4	475	7.6	[10]
$\alpha$ - $\text{Si}_3\text{N}_4$ +5vol% $\text{Ti}_3\text{SiC}_2$	Hot-pressed at 1700 °C for 90min	19.78	795	4.88	This work
$\alpha$ - $\text{Si}_3\text{N}_4$ +20vol% $\text{Ti}_3\text{SiC}_2$	Hot-pressed at 1700 °C for 90min	20.11	549	6.58	This work

#### 4. Conclusions

In summary, we proposed non-oxide  $\text{Ti}_3\text{SiC}_2$  (one of typical MAX cermets) as a novel sintering aid to densify  $\text{Si}_3\text{N}_4$  ceramics with enhanced mechanical properties. A remarkable relative density increment of 20.5% (from 2.58 to 3.11 g·cm<sup>-3</sup>) could be observed for 1600 °C hot-presssintered  $\text{Si}_3\text{N}_4$  ceramics doped with only 5vol%  $\text{Ti}_3\text{SiC}_2$  compared with  $\text{Si}_3\text{N}_4$  ceramics without aids. Further increase in sintering temperature to 1700 °C brought appreciable consolidation of nearly full dense  $\text{Ti}_3\text{SiC}_2$ - $\text{Si}_3\text{N}_4$  ceramics. XRD and EDS investigations demonstrated the formation of  $\text{C}_{0.3}\text{N}_{0.7}\text{Ti}$  and  $\text{SiC}$  which resulted from *in-situ* reaction between  $\text{Ti}_3\text{SiC}_2$  and  $\text{Si}_3\text{N}_4$  through diffusion of C and N. The Vickers hardness of  $\text{Ti}_3\text{SiC}_2$  doped  $\text{Si}_3\text{N}_4$  ceramics increased slight compared with that of  $\text{Si}_3\text{N}_4$  ceramics containing conventional oxides aids. Nevertheless, an obvious enhancement of flexural strength and fracture toughness could be observed. A maximum flexural strength of 795 MPa could be obtained for 5vol%  $\text{Ti}_3\text{SiC}_2$  doped  $\text{Si}_3\text{N}_4$  composites. Moreover, the fracture toughness of  $\text{Ti}_3\text{SiC}_2$  densified  $\text{Si}_3\text{N}_4$  composites exhibited a remarkable increase with increasing in volume fraction, and reached maximum value of 6.97 MPa·m<sup>1/2</sup> for 20vol%  $\text{Ti}_3\text{SiC}_2$ - $\text{Si}_3\text{N}_4$  ceramics. Pull out of elongated  $\text{Si}_3\text{N}_4$  grains, crack bridging and deflection were demonstrated to promote fracture toughness of  $\text{Ti}_3\text{SiC}_2$  densified  $\text{Si}_3\text{N}_4$  composites. With these successes, MAX phase densified  $\text{Si}_3\text{N}_4$  ceramics with enhanced strength and toughness will be necessary to meet demands of potential future markets for

advanced ceramics. Further efforts are encouraged to be devoted to thermal properties investigations of MAX enabled Si<sub>3</sub>N<sub>4</sub> composites.

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