C$_{0.3}$N$_{0.7}$Ti-SiC toughed silicon nitride hybrids with non-oxide additives Ti$_3$SiC$_2$

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Abstract: In-situ grown C$_{0.3}$N$_{0.7}$Ti and SiC, which derived from non-oxide additives Ti$_3$SiC$_2$, are proposed to densify silicon nitride (Si$_3$N$_4$) ceramics with enhanced mechanical performance. Remarkable increase of density from 79.20% to 95.48% could be achieved for Si$_3$N$_4$ ceramics with 5vol% Ti$_3$SiC$_2$. The capillarity of decomposed Si from Ti$_3$SiC$_2$, and in-situ reaction between nonstoichiometric TiC$_x$ and Si$_3$N$_4$ were believed to be responsible for densification of Si$_3$N$_4$ ceramics. An obvious enhancement of flexural strength and fracture toughness for Ti$_3$SiC$_2$ doped Si$_3$N$_4$ ceramics was observed. The maximum flexural strength of 795 MPa for Si$_3$N$_4$ composites with 5vol% Ti$_3$SiC$_2$ and maximum fracture toughness of 6.97 MPa m$^{1/2}$ for Si$_3$N$_4$ composites with 20vol% Ti$_3$SiC$_2$ are achieved when mixed powders are hot-press sintered at 1700°C. Pull out of elongated Si$_3$N$_4$ grains, crack bridging, crack branching and crack deflection were demonstrated to dominate enhance fracture toughness of Si$_3$N$_4$ composites.

Keywords: Ti$_3$SiC$_2$; Si$_3$N$_4$; mechanical properties; fracture toughness

1. Introduction

Although a number of alternatives of structural ceramics have been proposed, silicon nitride (Si$_3$N$_4$)-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$_3$N$_4$ 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$_3$N$_4$-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$_3$N$_4$-based ceramics are actively being explored, including gas pressure sintering (GPS) [10], hot-pressing sintering (HPS) [19-25], hot isostatic pressing sintering (HIP) [26], spark plasma sintering (SPS) [25, 27, 28], 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$_3$N$_4$ 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$_2$O$_3$ [4, 30, 31]. A combination of various rare-earth oxides

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and other metallic oxides, such as Y$_2$O$_3$, La$_2$O$_3$, Nd$_2$O$_3$, Sm$_2$O$_3$, Yb$_2$O$_3$, Lu$_2$O$_3$, Al$_2$O$_3$ and MgO, also are effective sintering aids to densify Si$_3$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 Si$_3$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 Si$_3$N$_4$ ceramics from new view point. The last two decades have been witness to the dramatic development on MAX phase cerments 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 (Ti$_3$AlC$_2$) and titanium silicon carbide (Ti$_3$SiC$_2$) [36-38]. The crystal structure of these MAX cerments can be described by alternately stacking of TiC$_6$ and Al/Si atomic planes. The unique combination of excellent properties of Ti$_3$AlC$_2$ or Ti$_3$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 TiB$_2$ [39-41], Al$_2$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 (Ti$_3$AlC$_2$) was chosen as an effective sintering aid to effectively densify B$_4$C ceramics with enhanced sintering ability and mechanical performance simultaneously. High hardness and toughness values of 28.5GPa and 7.02 MPa·m$^{1/2}$ respectively were achieved for B$_4$C composites sintered with 20vol% Ti$_3$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 Ti$_3$SiC$_2$ or Ti$_3$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 Si$_3$N$_4$ matrix and aids, rather than intergranular glassy phase. Motivated by such an idea, these non-oxides cerments are highly expected to play a multifunctional role in densification and enhancement of mechanical properties of Si$_3$N$_4$ ceramics. It is also noteworthy that Al decomposed from Ti$_3$AlC$_2$ and residual O originated from raw Si$_3$N$_4$ powders would be dissolved into Si$_3$N$_4$ grains during high-temperature sintering procedure, which is harmful to the purity and thermal performance of Si$_3$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 91.9W·m$^{-1}$·K$^{-1}$ to 58.0W·m$^{-1}$·K$^{-1}$) for Si$_3$N$_4$ ceramics. Therefore in this work, Ti$_3$SiC$_2$ were introduced to densify Si$_3$N$_4$ ceramics in order to demonstrate that it provided any advantages over the rare-earth oxide system. Besides, the effect of
Ti3SiC2 volume fraction on the microstructure, hardness, flexural strength and fracture toughness was also studied. It is believed that Ti3SiC2 or other members of MAX family would lead to new scientific and technological data providing new insight into functionalization of Si3N4 ceramics.

2. Experimental procedure
2.1 Preparation of samples
Commercially available α-Si3N4 powder (purity>93%, d50=0.7μm, Jinshenghao New Materials Co. Ltd., China) was used as a starting material. As a novel sintering aid, Ti3SiC2 powders (d50=5μm, purity>98%) were kindly provided by Forsman Scientific Co., Ltd., Beijing, China. In order to investigate the effect of Ti3SiC2 content on the mechanical properties, experiments were conducted with various amounts of Ti3SiC2 powders (1 to 20 vol.%%o) embedded in α-Si3N4 powders. To ensure the homogeneity of the mixed powders, α-Si3N4-x vol.% Ti3SiC2 powders (x=1~20) were wet ball-milled for 10h by using ethanol as ball-milling media. The substance was dried at 80℃, and sieved with a filter with a mesh size of 63μm, 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℃/min 1600℃ and 1700℃ 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, α-Si3N4 powders with 2wt.% Alumina (Al2O3, AR, Sinopharm Chemical Reagent Co., Ltd., China) and 5wt.% yttria (Y2O3, 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:

\[ H_v = 0.102 \frac{F}{S} = 0.102 \frac{2F \sin 136^\circ}{d^2} = 0.1891 \frac{F}{d^2} \]  

(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:

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

(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 Ti₃SiC₂ filled Si₃N₄ ceramics as a function of Ti₃SiC₂ volume fraction. For Si3N4 ceramics which HP sintered at 1600°C without aids, the density is only 2.58 g cm⁻³. Partial densification may be attributed to the residual SiO₂ liquid phase during firing at high temperature which always present on Si3N4 powder particles. A remarkable increase to 3.11 g cm⁻³ could be observed for Si₃N₄ ceramics filled with only 5vol% Ti₃SiC₂ when sintered at the same temperature. The enhanced density is even more noticeable than the Si₃N₄ ceramics with 7wt% Y₂O₃-Al₂O₃ aids. These observed results demonstrate Ti₃SiC₂ to be a effective sintering aid to densify Si₃N₄ ceramics. However, further increase in Ti₃SiC₂ content dose not bring any appreciable consolidation.

As expected, higher sintering temperature 1700°C could further promote densification of Si₃N₄ ceramics filled with Ti₃SiC₂. Besides, experimental points are inclined to distribute on a straight line with coefficient of determination (R²) above 0.99, which is accordant with mix law. Due to the complex reaction between Si₃N₄ and Ti₃SiC₂ which will discuss later, it is difficult to determine the theoretical density of the Ti₃SiC₂-Si₃N₄ composites accurately. However, an approximation method could be applied by assuming a nearly full densification for 20vol% Ti₃SiC₂-Si₃N₄ ceramics sintered at 1700°C according to this linear behavior.

Fig. 2 shows the XRD patterns of Si₃N₄ ceramics filled with different volume fraction of Ti₃SiC₂ sintered at 1600°C and 1700°C, as well as 7wt% (Al₂O₃-Y₂O₃) densified Si₃N₄ ceramics. As seen in Fig. 2(a), both α and β phase of Si₃N₄ could be detected when sintering temperature is 1600°C, which suggests only a partial transformation of α phase to the more stable β phase. In contrast, when further improving sintering temperature to 1700°C, all diffraction peaks of α-Si₃N₄ phase disappear (see in Fig. 2(b)). This completely transformation of α to β'-Si₃N₄ phase is believed to be essential to the enhancement of densification and mechanical performance.
Fig. 2 XRD patterns of Ti$_3$SiC$_2$ doped Si$_3$N$_4$ ceramics sintered at (a) 1600°C and (b) 1700°C. Another important feature should be noted here is that the characteristic diffraction peaks of the raw Ti$_3$SiC$_2$ powder nearly disappear completely after sintering. This could be ascribed to the fact that Ti$_3$SiC$_2$ powder is thermal stable up to ~800°C, and the following reaction can be responsible for the decomposition of Ti$_3$SiC$_2$ [51]:

$$3Ti_3SiC_2 \xrightarrow{\sim 800°C \text{ to } \sim 1400°C} 4TiC + Ti_3SiC_y + (6 - 4x - y)C$$ (3)

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

$$Ti_3SiC_2 \xrightarrow{\sim 1300°C} 3TiC + Si$$ (4)

The Si is believed to be act as lubricating phase between Si$_3$N$_4$ grains to promote densification of Si$_3$N$_4$ ceramics through capillarity. Meanwhile, the residual Si would further react with nitrogen to form Si$_3$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 Ti$_3$SiC$_2$ would further react with Si$_3$N$_4$ through diffusion of C and N according to the following reactions:

$$Ti_3SiC_y \xrightarrow{\text{in situ}} Ti_3C_y + 3Si$$ (5)

$$TiC_x + Si_3N_4 \xrightarrow{} (3.33x - 10)C_{0.3}N_{0.7}Ti + 3SiC + (5.5 - 1.167x)N_2$$ (6)

$$Ti_3C_y + (4.5 - y)C + Si_3N_4 \xrightarrow{} 5C_{0.3}N_{0.7}Ti + 3SiC + 0.25N_2$$ (7)

$$3C + Si_3N_4 \xrightarrow{} 3SiC + 2N_2$$ (8)

$$C + Si \xrightarrow{} SiC$$ (9)

or

$$TiC_x + Ti_3SiC_y + (9.45 - x - y)C + 1.55Si_iN_4 \xrightarrow{} 6C_{0.3}N_{0.7}Ti + 7.65SiC + N_2$$ (10)

It is reasonable to claim that the in situ reaction is responsible for the additional characteristic diffraction peaks of C$_{0.3}$N$_{0.7}$Ti and SiC in XRD patterns. Fig. 3 shows the micro-morphology of polished surface of Si$_3$N$_4$ with different volume fractions of Ti$_3$SiC$_2$ sintered at 1700°C. Due to the lack of sufficient sintering aids, lots of pores could be observed, and grain growth of $\beta$-Si$_3$N$_4$ is not complete for monolithic Si$_3$N$_4$ ceramic (see Fig. 3(a)). However, the microstructures of Ti$_3$SiC$_2$-Si$_3$N$_4$ ceramics (see Fig. 3(b) to Fig. 3(g)) exhibit much more close-grain
structure, and consist of randomly oriented elongated Si$_3$N$_4$ grains which is accordant with XRD results in Fig. 2. The average diameters of grains present slight increasing trend from 0.6771 μm to 0.9802 μm by quantitative image analysis as the amount of Ti$_3$SiC$_2$ increased. Besides, the bright contrasted phase which uniformly embedded in Si$_3$N$_4$ matrix could be observed, and are inclined to aggregate especially when Ti$_3$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 Si$_3$N$_4$ and SiC, which is associated with reaction described by Eq.(10). Additional O element may be originated from surface of raw $\alpha$-Si$_3$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 C$_{0.3}$N$_{0.7}$Ti and SiC, which are believed to affect the mechanical performance of reaction bonded Si$_3$N$_4$ ceramics.

| Spot | EDS chemical analysis (at.%) at different positions in Fig. 3(g) |
|------|-----------------------------------------------------------------|
| A    | Si 52.21 N 35.43 O 1.29 Ti 9.03                                |
|      | Possible phases: Si$_3$N$_4$, SiC                               |
| B    | Si 5.10 N 27.18 O - Ti 50.13 C 17.59                            |
|      | Possible phases: C$_{0.3}$N$_{0.7}$Ti, SiC                      |

The mechanical properties, including Vickers hardness, flexural strength and fracture toughness, of dense Si$_3$N$_4$ ceramics with different Ti$_3$SiC$_2$ content sintered at 1700°C are illustrated in Fig. 4. Clearly, the Vickers hardness of Si$_3$N$_4$ ceramics has been upgraded after modification of Ti$_3$SiC$_2$, and presents slight increase compared with that of Si$_3$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%Ti$_3$SiC$_2$doped Si$_3$N$_4$ composites, which is almost twice that of 7wt% (Y$_2$O$_3$-Al$_2$O$_3$)-Si$_3$N$_4$ ceramics prepared at the same condition. This enhancement of flexural strength could be attributed to the C$_{0.3}$N$_{0.7}$Ti and SiC which originated from reaction bonding between Ti$_3$SiC$_2$ and Si$_3$N$_4$. However, further increment of Ti$_3$SiC$_2$ content reduces the flexural strength of Si$_3$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 Si₃N₄ composites is also effectively boosted after Ti₃SiC₂ decoration, and reaches maximum value of 6.97 MPa m²/³ for 20vol%Ti₃SiC₂-Si₃N₄ ceramics which is 37% higher than that of 7wt% (Y₂O₃-%Al₂O₃)-Si₃N₄ ceramics.

Fig. 4 Mechanical properties of Ti₃SiC₂ doped Si₃N₄ 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 Si₃N₄ ceramics with different Ti₃SiC₂ contents, as well as 7wt% (Y₂O₃-Al₂O₃). Clearly, the polished surfaces of Ti₃SiC₂ doped Si₃N₄ ceramics become much smoother than the monolithic Si₃N₄ ceramic which HP sintered at 1700℃, corresponding to the enhancement of densification. Besides, it can be seen that the area of indentation presents no obvious change for Ti₃SiC₂ doped Si₃N₄ ceramics, which is consistent with the stable Vickers hardness. However, the cracks obviously become shorter especially when the Ti₃SiC₂ 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) Si₃N₄-7wt% (Al₂O₃-Y₂O₃), (b) Si₃N₄-3vol% Ti₃SiC₂, (c) Si₃N₄-5vol% Ti₃SiC₂, (d) Si₃N₄-10vol% Ti₃SiC₂, (e) Si₃N₄-15vol% Ti₃SiC₂, (f) Si₃N₄-20vol% Ti₃SiC₂

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

![Fig. 6 Typical fracture surfaces of Si$_3$N$_4$ with (a) 7wt% (Al$_2$O$_3$-Y$_2$O$_3$), (b) 10vol% Ti$_3$SiC$_2$](image1)

Another mechanism of the enhanced fracture toughness of Si$_3$N$_4$-Ti$_3$SiC$_2$ composites could be ascribed to the crack branching, deflection and grain bridging by \textit{in-situ} derived C$_{0.3}$N$_{0.7}$Ti and SiC grains embedded in Si$_3$N$_4$ matrix, which illustrated in Fig. 7. Due to the superior hardness of C$_{0.3}$N$_{0.7}$Ti and the thermal mismatch between Si$_3$N$_4$ and C$_{0.3}$N$_{0.7}$Ti, there exists residual stress around C$_{0.3}$N$_{0.7}$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 C$_{0.3}$N$_{0.7}$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 Si$_3$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 Ti$_3$SiC$_2$ doped Si$_3$N$_4$ ceramics present the same level or even better compared with Si$_3$N$_4$ ceramics sintered with oxide aids. Moreover, due to the superior mechanical and thermal properties of in situ formed C$_{0.3}$N$_{0.7}$Ti and SiC, Si$_3$N$_4$ ceramics obtained in this work are believed to have a significant competitive advantage and to promote the development of Si$_3$N$_4$-based ceramics at high temperatures.

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

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

4. Conclusions

In summary, we proposed non-oxide Ti$_3$SiC$_2$ (one of typical MAX cermet) as a novel sintering aid to densify Si$_3$N$_4$ ceramics with enhanced mechanical properties. A remarkable relative density increment of 20.5% (from 2.58 to 3.11 g cm$^{-3}$) could be observed for 1600$^\circ$C hot-presssinteredSi$_3$N$_4$ ceramics doped with only 5vol% Ti$_3$SiC$_2$ compared with Si$_3$N$_4$ ceramics without aids. Further increase in sintering temperature to 1700$^\circ$C brought appreciable consolidation of nearly full dense Ti$_3$SiC$_2$-Si$_3$N$_4$ ceramics. XRD and EDS investigations demonstrated the formation of C$_{0.3}$N$_{0.7}$Ti and SiC which resulted from in-situ reaction between Ti$_3$SiC$_2$ and Si$_3$N$_4$ through diffusion of C and N. The Vickers hardness of Ti$_3$SiC$_2$ doped Si$_3$N$_4$ ceramics increased slight compared with that of Si$_3$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%Ti$_3$SiC$_2$ doped Si$_3$N$_4$ composites. Moreover, the fracture toughness of Ti$_3$SiC$_2$ densified Si$_3$N$_4$ composites exhibited a remarkable increase with increasing in volume fraction, and reached maximum value of 6.97 MPa$^{1/2}$ for 20vol% Ti$_3$SiC$_2$-Si$_3$N$_4$ ceramics. Pull out of elongated Si$_3$N$_4$ grains, crack bridging and deflection were demonstrated to promote fracture toughness of Ti$_3$SiC$_2$ densified Si$_3$N$_4$ composites. With these successes, MAX phase densified Si$_3$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 Si₃N₄ composites.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (Grant No. 2017YFA0204600), the National Natural Science Foundation of China (Grant No. 51802352), the China Postdoctoral Science Foundation (Grant No. 2017M612996).

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