Microstructures and mechanical properties of Ti$_3$SiC$_2$/Al$_2$O$_3$ and Ti$_3$SiC$_2$-TiC/Al$_2$O$_3$ composite ceramics by modifying Al$_2$O$_3$ content via in-situ synthesized

Jun Ji, Xuye Wang, Jinman Yu, Qinggang Li, Zhi Wang*, Guopu Shi**,

School of Material Science and Engineering, University of Jinan, Jinan 250022, China

* First corresponding author: wangzhi@ujn.edu.cn;
** Second corresponding author: ss_shigp@ujn.edu.cn;
Abstract

Ti$_3$SiC$_2$/Al$_2$O$_3$ and Ti$_3$SiC$_2$-TiC/Al$_2$O$_3$ composite ceramics with various Al$_2$O$_3$ fractions were prepared by Ti, Si, Al, TiC and Al$_2$O$_3$ powers via in-situ reaction. Al$_2$O$_3$ contents in raw materials could influence the reaction process of Ti$_3$SiC$_2$ generated. It would lead to react completely when the Al$_2$O$_3$ volume percentage between 50% to 70%, otherwise TiC as an impurity would be found. Finally the Ti$_3$SiC$_2$/Al$_2$O$_3$ composites with 54.4 wt% Ti$_3$SiC$_2$, and Ti$_3$SiC$_2$-TiC/Al$_2$O$_3$ composites with 54.7 wt% Ti$_3$SiC$_2$ and 9.2 wt% TiC were fabricated successfully. There were two types of TiC existed in composites, called intragranular and intergranular particles. The Ti$_3$SiC$_2$-TiC/Al$_2$O$_3$ composite ceramics with 9.2 wt% TiC showed the higher mechanical properties than Ti$_3$SiC$_2$/Al$_2$O$_3$ composite. From the analyzing of microcrack propagation paths, the dispersed TiC particles as reinforcement agents would cause significant crack deflection, improving the flexural strength and fracture toughness up to 492 MPa and 7.8 MPa.m$^{1/2}$ respectively.

Keywords: Ti$_3$SiC$_2$/Al$_2$O$_3$ composite ceramics; Ti$_3$SiC$_2$-TiC/Al$_2$O$_3$ composite ceramics; in-situ synthesis; mechanical properties.

1. Introduction

Ternary MAX phase ceramics, where M is an early transition metal, A is an A group element and X is carbon or nitrogen, have captured considerable attentions for their combination of metallic and ceramic
properties, making them possible candidates used as structural materials at high temperatures and/or in corrosive environments[1-3]. Ti$_3$SiC$_2$ is the most extensively studied MAX phase, has been synthesized by various pressure sintering methods at high temperatures, which can be mainly conducted by the following three reactions[4-6]:

$$3\text{Ti} + \text{Si} + 2\text{C} \rightarrow \text{Ti}_3\text{SiC}_2 \cdots \cdots (1)$$
$$3\text{Ti} + \text{SiC} + \text{C} \rightarrow \text{Ti}_3\text{SiC}_2 \cdots \cdots (2)$$
$$\text{Ti} + \text{Si} + 2\text{TiC} \rightarrow \text{Ti}_3\text{SiC}_2 \cdots \cdots (3)$$

However, it is not facile to fabricate the single-phase Ti$_3$SiC$_2$ due to its narrow phase region as well as impurity of TiC would be generated inevitably[7,8]. In order to address this problem, Al is often used in in-situ synthesis of Ti$_3$SiC$_2$ as sintering additive[9-12]. Molten Al could remove oxygen, fill gaps and provide a bridging effect among the reacting powder particles, all of which could promote the diffusion reaction[13]. As a result, TiC as impurity will decrease obviously when suitable contents of Al are introduced into in-suit synthesis[13-15].

Although Ti$_3$SiC$_2$ has to be seen as a potential structure/functional material as its combined metallic- and ceramic-like properties, the relatively low strength and hardness limit its further application. Al$_2$O$_3$ ceramics with superb performances such as low price, high hardness, good corrosion resistance and stability at elevated temperatures[16], has been incorporated into Ti$_3$SiC$_2$ to improve the mechanical properties. Composite ceramics can be synthesized by various of sintering methods,
such as self-propagating high-temperature sintering (SHS)[17], spark plasma sintering (SPS)[18] and hot pressing (HP)[19,20]. Qi et al.[21] fabricated Ti$_3$SiC$_2$/Al$_2$O$_3$ composites with various volume contents of Ti$_3$SiC$_2$ under different sintering processes using Ti$_3$SiC$_2$ and Al$_2$O$_3$ as raw materials. Cai et al.[22] reported the Ti$_3$SiC$_2$/TiC-Al$_2$O$_3$ composites synthesized by reactive hot pressing, suggesting that the composites with 20 wt% additions showed the highest flexural strength of 649 MPa and 10 wt% additions displayed the best fracture toughness of 7.15 Mpa$^{1/2}$. Pourali et al.[23] prepared high-purity Ti$_3$SiC$_2$ and Ti$_3$SiC$_2$/Al$_2$O$_3$-Ni composites with different Al$_2$O$_3$-Ni contents. The composites exhibited lower flexural strength and higher compressive strength than single-phase Ti$_3$SiC$_2$.

In our previous work[19], Ti$_3$SiC$_2$/TiC-Al$_2$O$_3$ composites were synthesized from Al$_2$O$_3$, Ti and SiC powders, while amounts of TiC as third-phase existed in composite ceramics. Now we prepared biphase Ti$_3$SiC$_2$/Al$_2$O$_3$ and multiphase Ti$_3$SiC$_2$-TiC/Al$_2$O$_3$ composites using Ti, Si, Al, TiC and Al$_2$O$_3$ powders via hot pressing. It can influence the generated reaction of Ti$_3$SiC$_2$ by modifying the contents of Al$_2$O$_3$, and the TiC disappear with the volume percentage of Al$_2$O$_3$ from 50 to 70%. Although our work is fundamental, it is rare to see the high-purity Ti$_3$SiC$_2$/Al$_2$O$_3$ composites with 50 vol% Ti$_3$SiC$_2$ through in-situ synthesis. The composition, micro-structure and mechanical properties of all
samples were further investigated.

2. Materials and experimental methods

The raw materials employed herein were fine powders of the following types: dry Al₂O₃ (99.6% pure, ~0.5 µm), Ti (99.6% pure, ~5 µm), TiC (99.5% pure, ~2 µm), Si (99% pure, ~1 µm), and Al (99% pure, ~30 nm). The proportions of each group with different volume fractions of Al₂O₃ and mixed powders are shown in Tab. 1.

The mixed powders in the molar ratio of 1.0Ti/2.0TiC/1.2Si/0.3Al and Al₂O₃ powders were dispersed evenly in ethanol at 200 rpm for 4 h in a planetary mill (XQM-2, China), following which the resulting slurry was dried in a drying oven at 70 °C and sifted using a 50 mesh sifter. Subsequently, the raw materials were sintered in a vacuum hot-pressing furnace (VVPgr-80–2300, China) at 1450 °C for 1.5 h under a vacuum pressure of <8.0×10⁻³ MPa, and the pressure was maintained at 30 MPa below uniaxial pressure when the sintering temperature was 1450 °C. Finally, the sintered samples were allowed to cool naturally to room temperature prior to their removal from the furnace.

The obtained samples were polished using SiC powder and then cut into long columns measuring 3 mm × 4 mm × 3 mm using an inner circle cutting machine with a chamfering and span of 0.3 and 30 mm, respectively. All samples were then cleaned under ultrasonication in ethanol over 20 min. The density of samples were determined by using
the Archimedes water immersion method. The flexural strength and fracture toughness of the samples were measured using the three-point bending method on an electromechanical universal testing machine (CMT5504, MTSSYSTEMS, China) with a cross-head speed of 0.5 mm/min and a span of 30 mm. The microhardness of the samples was determined using a Vickers hardness tester (HV-100IS, China) at a load of 100 N for 20 S. The phase compositions of the obtained samples were determined by XRD (D8 ADVANCE, Bruker). Microstructural investigations were performed by SEM (FEIQUANTA FEG 250, USA) and TEM (Tecnai G2F20).

Table 1. Compositions of raw materials.

| Sample | Al₂O₃ (vol%) | Mixed Power (vol%) |
|--------|-------------|-------------------|
| 1      | 80          | 20                |
| 2      | 70          | 30                |
| 3      | 60          | 40                |
| 4      | 50          | 50                |
| 5      | 40          | 60                |

3. Results and discussion

3.1 Composition and microstructure

XRD patterns of the synthesized composites ceramics are shown in Fig 1. Sample 1 was composed of Ti₃SiC₂, Al₂O₃ and TiC phase, and the
relatively lower peak of TiC indicated the less impurity content as well. As the volume fractions of Al₂O₃ decreased from 70% to 50%, the intensity of the TiC peak vanished. Samples 2-4 consisted only of the Al₂O₃ and Ti₃SiC₂ phases, indicating that the mixed powder reacted completely during the sintering process. However, as displayed in sample 5, when the volume percentage of Al₂O₃ down to 40%, amounts of TiC were detected again.

The mass fraction of each phase was calculated by the following equation:

\[ W_i = \frac{I_i / K_i}{\sum_{i=1}^{n} I_i / K_i} \times 100 \% \]  \hspace{1cm} (1)

Where \( W_i \) was the mass fraction of i phase, \( I_i \) was the intensity of selected lines in the diffraction pattern of i phase, \( K_i \) was the reference intensity of i phase based on RIR value. In this method, the mass fraction was calculated according to the intensity of the sharp peaks for each phase. Thus, (104), (104) and (200) diffraction peaks were selected for analysis of Ti₃SiC₂, Al₂O₃ and TiC phase, respectively. The mass fraction of each phase was shown in Tab. 2. Data based on quantitative method from eq. (1) indicated that the Al₂O₃ content could affect the in-situ sintering reaction of Ti₃SiC₂. Optimum Al₂O₃ content (45.6-66.4 wt%) would produce a high-purity Ti₃SiC₂ phase without any TiC impurity when sintering was carried out at 1450 °C, 30 MPa for 90 min. While the Al₂O₃ fractions beyond or below this range resulted in an incomplete in-situ
reaction, leading to the formation of the TiC phases.

Tab. 2. The mass fraction of Ti₃SiC₂, Al₂O₃ and TiC phase.

|     | Al₂O₃ (wt%) | Ti₃SiC₂ (wt%) | TiC (wt%) |
|-----|-------------|---------------|-----------|
| 1   | 76.8        | 19.7          | 3.5       |
| 2   | 66.4        | 33.6          | -         |
| 3   | 57.9        | 42.1          | -         |
| 4   | 45.6        | 54.4          | -         |
| 5   | 36.1        | 54.7          | 9.2       |

TEM micrograph and SEAD patterns of sample 5 were presented in Fig. 2. Fig. 2a and 2b exhibited that the small-size TiC particles were distributed inside the Al₂O₃ and Ti₃SiC₂ crystal respectively, while large-size TiC particles were found around grain boundary (Fig. 3c). The size of intragranular particles are below 50nm while intergranular particles are above 200nm. This phenomenon was also reported by Chai[24] and Wang[25]. Furthermore, selected area electron diffraction (SEAD) analysis of the area indicated by the white oval is illustrated in Fig. 2d, 2e and 2f. For Ti₃SiC₂, the d-spacings of the three diffraction spots are 0.156, 0.343, and 0.141 nm respectively, which are consistent with the (1 1 0), (0 0 5), and (1 1 5) crystal planes of the Ti₃SiC₂ grains. The incident beam is parallel to the [1 -1 0] axis. Similarly, the (0 1 2), (1 0 1), and (1 1 3) planes of the Al₂O₃ crystal with zone axis [1 2 -1] and (1 1 1), (2 0 0) and (3 1 1) planes of TiC particle with zone axis [0 1 -1] are also indexed.
SEM back scattered electron image of synthesized composite ceramics was shown in Fig. 3. The diameters of the Ti₃SiC₂ and Al₂O₃ grains were approximately 2 – 5 µm, and no abnormal growth was observed. TiC gains were clearly observed in the fracture surface of sample 5 (Fig. 2e), while the other four groups only consist of Ti₃SiC₂ and Al₂O₃ crystals. Because sample 1 was only composed of 3.5 wt% TiC, most of which embedded in the Ti₃SiC₂ and Al₂O₃ grains, resulting in TiC particles undetected in Fig 3a. In addition, the interface combination was close and no obvious pores could be found, demonstrating the sintering densification of the Ti₃SiC₂/Al₂O₃ ceramics.

Fig. 4 shows the relative density of samples 1-5. It can be clearly found that the relative density of all the samples are more than 99%, and there is no obvious trend of patterns as the decreased of Al₂O₃, revealing sintering densification of Ti₃SiC₂/Al₂O₃ and Ti₃SiC₂-TiC/Al₂O₃ composite ceramics.

3.2 Mechanical properties

The mechanical properties including Vickers’ hardness, flexural strength, and fracture toughness of samples 1–5 are described in Figure 5. With the reducing of Al₂O₃, the Vickers’ hardness of the samples1-4 decline simultaneously (Fig. 5a). Sample 4 shows the lowest Vickers’ hardness (14.6 GPa) among all the samples investigated possibly due to
the mass of Ti$_3$SiC$_2$, while sample 5 displays higher hardness compared to 4 on account of TiC generated. Fig. 5b shows the flexural strength of samples 1–5. As can be seen from the figure, the flexural strength of the composites first decrease and then increase a bit. Compared to sample 4, the strength of sample 5 improves from 485 to 492 MPa. The curve of toughness displays uptrend from 5.4 to 7.8 MPa.m$^{1/2}$ with the increasing of in-situ generated Ti$_3$SiC$_2$ content. Sample 5 owns the higher fracture toughness than sample 4 mainly because of the TiC particles, considering approximate fractions of Ti$_3$SiC$_2$ in both specimen.

3.3 Microcrack analysis

Samples 4 and 5 were selected for microcrack analysis because of the superior toughness. As can be found in Fig. 6, both samples showed irregular fracture paths, clearly indicating that they fractured in both intergranular and transgranular modes. It should be pointed out that transgranular fracture and particle pullout were mainly observed in laminar Ti$_3$SiC$_2$ grains, which absorbed most of the crack propagation energy and caused significant deflection and increase in the crack propagation path. In addition, there is a pit of square particle with the diameter of 200nm in Fig. 6c, which most likely result from the pullout of TiC nano-particle. TiC grains with such small size preferred being pulled out rather than cleaved. Moreover, TiC as intergranular particle would result in crack deflection. When a crack met with the TiC particle, the
crack direction changed due to the hindering effect of TiC. The deflection would increase the demand of fracture energy, which is beneficial to improve the fracture toughness of composite ceramics.

Al$_2$O$_3$ ceramics have high strength and low fracture toughness, and the fracture mode is mainly intergranular fracture. As shown in Fig.7, in the Al$_2$O$_3$ ceramics, the microcracks propagated along the vulnerable grain boundaries, resulting in the formation of macroscopic cracks and making the ceramics fragile. Ti$_3$SiC$_2$ with low strength and high toughness, as the increasing of its fractions, the composite ceramics caused transgranular fracture and particle pullout, resulting in the absorption of a large amount of fracture energy, which contribute to the improvement in toughness. When part of Al$_2$O$_3$ was replaced by TiC, the fine intergranular particle would provide dispersion strengthening and toughening effect. Thus the Ti$_3$SiC$_2$-TiC/Al$_2$O$_3$ composite ceramics displays higher flexural strength and fracture toughness than Ti$_3$SiC$_2$/Al$_2$O$_3$, based on the same Ti$_3$SiC$_2$ fractions as a prerequisite.

4. Conclusion

In this research, Ti$_3$SiC$_2$/Al$_2$O$_3$ and Ti$_3$SiC$_2$-TiC/Al$_2$O$_3$ composite ceramics with different Al$_2$O$_3$ contents were synthesized by in-situ reaction via hot pressing sintering. Based on the analysis above, the conclusions of this paper can be summarized as follows:

(1) The volume fractions of Al$_2$O$_3$ in raw materials could affect the
reaction process of in-situ synthesis of $\text{Ti}_3\text{SiC}_2$. When the $\text{Al}_2\text{O}_3$ volume percentage between 50% to 70%, the reaction will finish completely, otherwise TiC as an impurity would be found.

(2) Based on the quantitative method, the maximum of $\text{Ti}_3\text{SiC}_2$ mass fractions is 54.4% in $\text{Ti}_3\text{SiC}_2/\text{Al}_2\text{O}_3$ composites. To the best of our knowledge, this is the first report on $\text{Ti}_3\text{SiC}_2/\text{Al}_2\text{O}_3$ composites with high contents of $\text{Ti}_3\text{SiC}_2$ by in-situ reaction.

(3) Under the premise of equal $\text{Ti}_3\text{SiC}_2$ contents, $\text{Ti}_3\text{SiC}_2$-TiC-$\text{Al}_2\text{O}_3$ composite ceramics show better mechanical properties than $\text{Ti}_3\text{SiC}_2/\text{Al}_2\text{O}_3$ due to the dispersed TiC as the reinforcement agent.

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Conflicts of Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, and we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.
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**Figure Captions**

Fig. 1. XRD patterns of samples sintered by hot pressing.

Fig. 2. TEM micrograph and SEAD patterns of sample 5. Intragranular TiC particles in (a) Ti$_3$SiC$_2$ and (b) Al$_2$O$_3$ crystal; Intergranular TiC around grain boundary (c); SEAD patterns of Ti$_3$SiC$_2$ (d) and Al$_2$O$_3$ (e) and TiC (f).

Fig. 3. SEM image of all samples. (a): sample 1; (b): sample 2; (c): sample 3; (d): sample 4; (e): sample 5.

Fig. 4. The relative density of samples 1-5.

Fig. 5. The mechanical properties of sample 1-5. (a) Vickers’ hardness; (b) flexural strength and fracture toughness.

Fig. 6. Fracture mode for sample 4: (a) and (b); sample 5: (c) and (d).

Fig. 7. The diagram of microcrack propagation paths in Al$_2$O$_3$ and Ti$_3$SiC$_2$-TiC/Al$_2$O$_3$ ceramics.