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Microstructure and mechanical properties of Ti₂AlC-reinforced TiAl composites

Ti₂AlC/TiAl composites were successfully in-situ synthesized by reaction hot pressing using Ti, Al, TiC and CNTs as starting materials. The results indicate that the as-sintered composites mainly consist of Ti₂AlC and TiAl phases. The mechanical properties of the 23 wt.% Ti₂AlC/TiAl composite exhibit the highest values, with a flexural strength and fracture toughness of 652.5 ± 76.8 MPa and 6.6 ± 0.5 MPa m^{1/2}, respectively. The complex structure coupled with dispersed Ti₂AlC micro-particulates is responsible for the enhancement in the strength. Toughening of the composite is mainly attributed to crack deflection, crack bridging, crack branching and pull-out of the Ti₂AlC particles, as well as transgranular cracking.

Keywords: Composites; Carbide; Microstructure; Mechanical properties

1. Introduction

Gamma titanium aluminides are considered to have tremendous potential in high temperature applications such as aerospace and automotive parts for turbine blades, turbochargers, or nozzles, and exhaust valves, since they possess a remarkable combination of light-weight, high strength-to-density ratio, high strength at elevated temperature and good corrosion and oxidation resistance [1–4]. However, their applications are hindered by relatively low room temperature ductility, poor fracture toughness and bad hot workability. In the last decades, considerable efforts, such as alloying [5], heat-treatment [6], thermomechanical treatment (TMT) [7], have been devoted to improving these properties. Furthermore, it is well known that the incorporation of ceramic can enhance the mechanical properties of intermetallics and alloys [1].

Ti₂AlC belongs to a large family referred to as $M_{n+1}AX_n$ phases (abbreviated as MAX phases, where M is early transition metal, A is group IIIA or IVA element, and X is C or N, $n = 1–3$), and has been identified as the most attractive reinforcement to TiAl intermetallic, mainly due to its thermal expansion coefficient comparable to TiAl-based alloys and excellent chemical compatibility with TiAl matrix. Furthermore, Ti₂AlC is expected to be able to improve the strength of TiAl alloy with no sacrifice in ductility due to its excellent properties including low density (4.11 g cm⁻³), high Young's modulus (277.6 GPa), high fracture toughness, high damage tolerance, easy machinability, and good oxidation resistance [8–10]. Mei et al. [11] produced

Ti₂AlC/TiAl composites by spark plasma sintering (SPS) of a mixture of Ti, Al and TiC powders. They found that the dispersive Ti₂AlC could improve both fracture toughness and strength of the TiAl matrix. We also produced TiAl/Ti₂AlC composites utilizing in-situ reactive hot pressing of Ti, Al and TiC mixture powders [12]. We found that the fracture toughness and bending strength of the composite with 15 wt.% Ti₂AlC content reached peak values of 7.78 MPa m^{1/2} and 486 MPa. Moreover, Yang et al. [13] prepared Ti₂AlC/TiAl composites by SPS of mechanically mixed, pre-alloyed Ti-50 at.% Al and CNTs. Wang et al. [14] fabricated Ti₂AlC–Al₂O₃/TiAl composites by vacuum sintering Ti-50 at.% Al pre-alloy coated with carbon nanotubes (CNTs). They found that using CNTs as the carbon source lowered the formation temperatures of Ti₂AlC in the Ti–Al–CNTs system. Actually, CNTs would disappear after sintering at high temperature and transform into Ti₂AlC. Ultimately, the composites showed an interpenetrating network structure, and more importantly, the mechanical properties of the composites with some new structures could be enhanced greatly.

In the present work, in-situ TiAl composites reinforced by Ti₂AlC were prepared by mean of a hot pressing sintering method using Ti, Al, TiC and CNTs as starting materials. In order to obtain two different morphologies of Ti₂AlC, we selected CNTs to replace part of the TiC powders as carbon source, which tended to generate fine dispersed Ti₂AlC particles. The phase composition, microstructure and mechanical properties of the composites were investigated.

2. Experimental procedure

Commercial powders of Ti (99.8 %, 35 μm), Al (99.6 %, 55 μm), TiC (99.9 %, 20 μm) and CNTs (99.5 %, 1 nm in diameter, 0.5–30 μm in length) were used as the starting materials. In our previous work [12], we developed a series of Ti₂AlC/TiAl composites, and among them, the TiAl/15 wt.% Ti₂AlC composite presented the best mechanical properties. We determine that appropriate Ti₂AlC content is controlled in a range of 15–25 wt.%. Wang et al. [14] prepared Ti₂AlC–Al₂O₃/TiAl composite introducing 1 wt.% CNTs into the powder mixture. In our present work, we selected 1.48 wt.% CNTs of the powder mixture to prepare Ti₂AlC/TiAl composite. Elemental powder blends corresponding to 50Ti/50Al (marked as C0), 62.6Ti/35.31Al/0.61TiC/1.48CNTs (marked as C1), 60.99Ti/34.51Al/3.02TiC/1.48CNTs (marked as C2) and 58.96Ti/33.51Al/6.05TiC/1.48CNTs (marked as C3) (wt.%) were mixed suf-

ficiently by ball milling for 2 h and then cold pressed into cylindrical compacts with a pressure of 5 MPa using a graphite die pre-sprayed with a layer of BN. Their theoretical contents of Ti₂AlC were about 0, 18, 23 and 30 wt.%, respectively. The powder compacts, 30 mm in diameter and approximately 10 mm in height, were hot-pressed at 1350 °C for 2 h at a rate of 10 K min⁻¹ under a pressure of 30 MPa in vacuum.

The phase identification of the as-obtained composites was performed by X-ray diffractometry (XRD). The microstructure of the specimens was investigated using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). The density of the as-obtained composites was determined by the Archimedes method. The Vickers hardness was measured in a microhardness tester at a load of 9.8 N with a dwell time 15 s. The size of specimen for flexural strength and fracture toughness testing was 3 mm × 4 mm × 30 mm. Three-point bend testing was performed using a span of 20 mm with a crosshead speed of 0.5 mm min⁻¹ to measure flexural strength. The fracture toughness was measured using the single-edge pre-cracked beam (SEPB) method with a crosshead speed of 0.05 mm min⁻¹ and a span of 20 mm. A notch with a depth of 0.4 *W* (where *W* is the width of the specimen) and width of 0.15 mm was made.

The flexural strength and fracture toughness of the products were determined from the following formulas:

$$\sigma = 3PL/(2bh^2) \quad (1)$$

$$K_{IC} = Y \times 3PLa^{1/2}/(2BW^2) \quad (2)$$

where *P* is the breaking load of the specimen, and *L*, *b*, *h*, *Y* and *a* are the span, width, height, geometrical factor, and notch depth of the specimen, respectively.

3. Results and discussion

Figure 1 shows the XRD patterns of the products. The product (corresponding to C0 specimen) is composed of TiAl and Ti₃Al phases. From C1 specimen to C3 specimen, as

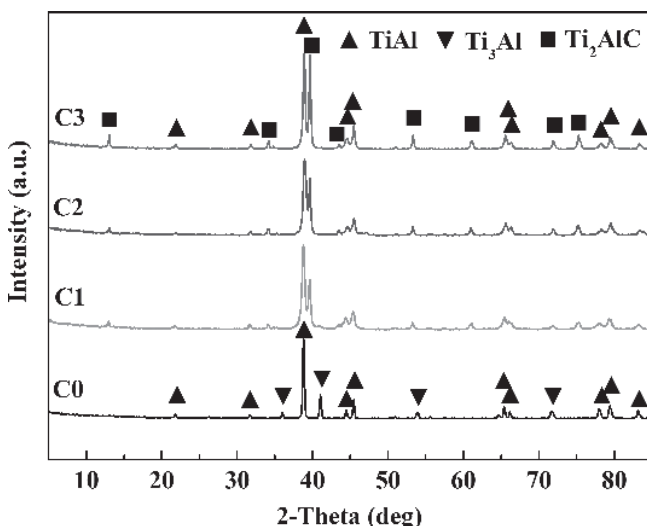


Fig. 1. XRD patterns of the products.

shown in Fig. 1, the as-produced composites mainly consist of γ -TiAl and Ti₂AlC phases. No traces of TiC and single phases are detected. After introducing CNTs, they react with Ti, consuming part of the Ti, so the diffraction peak of Ti₃Al disappears. As seen clearly in Fig. 1, the intensity of Ti₂AlC peaks increases gradually from C1 to C3 specimens. It can be concluded that CNTs took part in the reactions to form the Ti₂AlC reinforcements during sintering. Wang et al. [14] demonstrated that CNTs could promote the reactions to form Ti₂AlC. In the Ti-Al-TiC-CNTs system, both Ti and Al can react readily with CNTs to form carbides under high temperature conditions. Xu et al. [15] thought that among the reaction synthesis compounds TiC, Al₄C₃ and TiAl₃, TiC was the most thermodynamically stable. Hence, the reactions tend to form stable compounds TiC and TiAl. With increasing the sintering temperature, TiAl continues to react with TiC to form Ti₂AlC. Finally, there is no TiC phase detected, which is confirmed by the XRD results as shown in Fig. 1.

Figure 2 shows SEM morphologies of the Ti₂AlC/TiAl composites after etching. Two different morphologies of Ti₂AlC can be obtained. The synthesized Ti₂AlC reinforcing agents, as shown in Fig. 2, are mainly distributed at the grain boundaries with cluster morphologies. Other Ti₂AlC micro-particulates are dispersed in the matrix, which constitutes intragranular structure, and is responsible for the significant strengthening and toughening effect on the Ti₂AlC/TiAl composite. Furthermore, the composites show an interpenetrating network structure. According to the EDS results, the wall of network cells is identified to be Ti₂AlC. As can be seen clearly in Fig. 2, the proportion of Ti₂AlC increases and the TiAl grain size decreases gradually from C1 specimen to C3 specimen. Unfortunately, the agglomeration phenomenon of Ti₂AlC micro-particulates clearly increases (Fig. 2f), which will compromise the properties of the composite.

The mechanical properties of the Ti₂AlC/TiAl composites are summarized in Table 1. The density of C0, C1, C2 and C3 specimens is about 3.79, 3.82, 3.84 and 3.85 g · cm⁻³, respectively. The Vickers hardness of TiAl + Ti₃Al alloy (C0 specimen) and the in-situ Ti₂AlC/TiAl composites is significantly lower than that of Ti₂AlC (5.8 ± 0.5 GPa) [16]. Moreover, when the theoretical content of Ti₂AlC is 23 wt.% (C2 specimen), the flexural strength reaches a maximum value of 652.5 ± 76.8 MPa, which is significantly higher than that of TiAl (477.5 ± 43.6 MPa), 18 wt.% Ti₂AlC/TiAl composite (649.9 ± 23.8) and Ti₂AlC (432 ± 12 MPa) [16], as shown clearly in Table 1. We guess that the network structure, the decreased grain size and the dispersed Ti₂AlC particulates in the product are beneficial to the improvement of strength. Microstructural evolution can be postulated such that the Ti₂AlC inhibited grain growth and the grain-boundary mobility. With increasing Ti₂AlC content (30 wt.%), the flexural strength of the product (C3 specimen) decreases quickly, and the value drops to 444.2 ± 128.9 MPa. Why does the strength of C3 specimen decrease? We guess that the clustered regions of the Ti₂AlC in the C3 specimen will have detrimental effects on the strength. Actually, as shown in Fig. 2, too many Ti₂AlC particulate aggregates rather than continuous network walls exist in the microstructure of the C3 specimen. The microstructure of Ti₂AlC particulate aggregates was usually not as perfect as that of dispersed

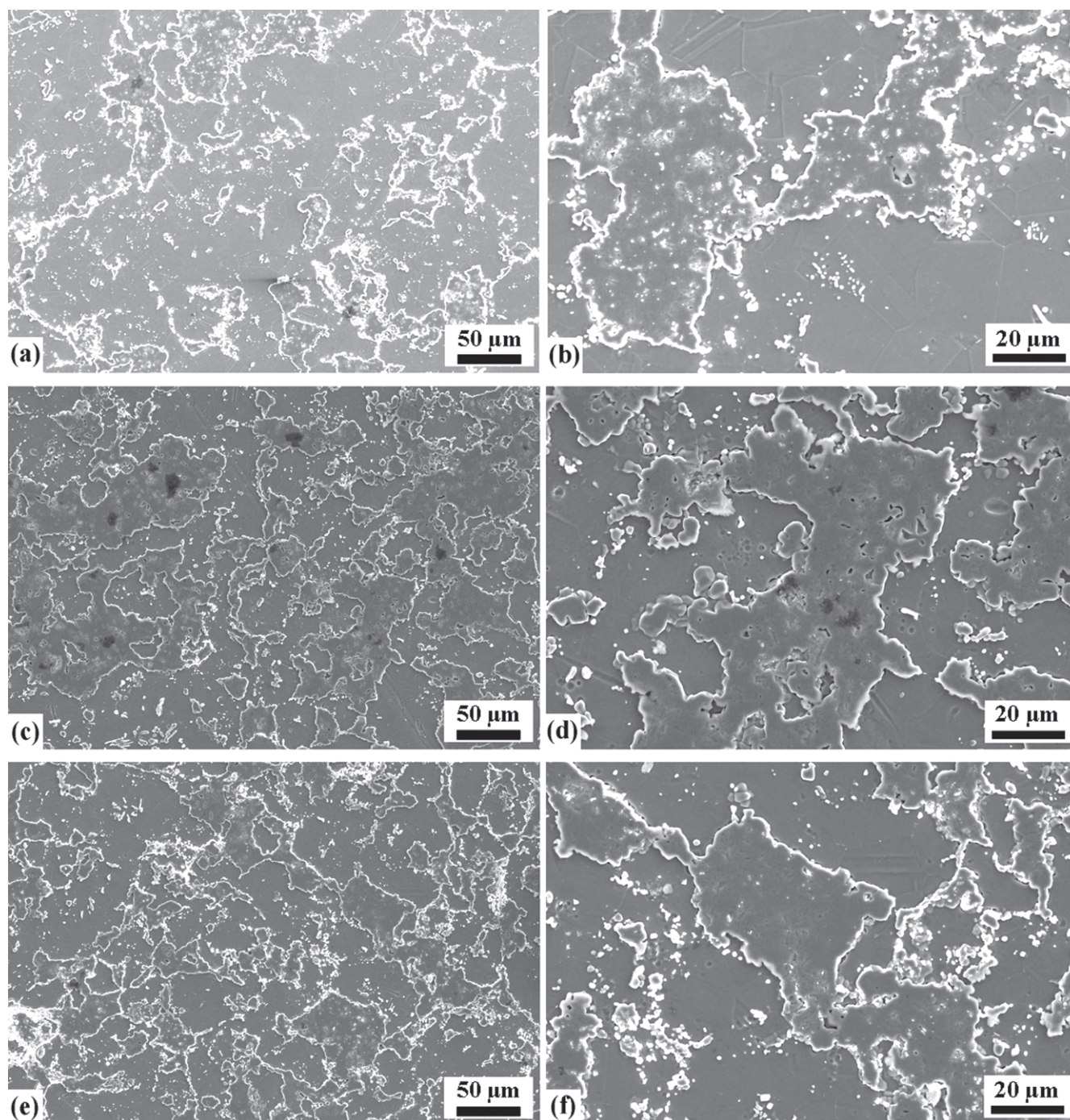


Fig. 2. SEM morphologies of the Ti₂AlC/TiAl composites after etching: (a) and (b) C1 specimen, (c) and (d) C2 specimen, (e) and (f) C3 specimen.

Table 1. Characteristics of TiAl, Ti₂AlC and Ti₂AlC/TiAl composites.

Sample	Density (g cm ⁻³)	Vickers hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPa m ^{1/2})	Sources
C0	3.79	1.59	477.5 ± 43.6	5.8 ± 0.1	In our work [16]
C1	3.82	1.57	649.9 ± 23.8	6.1 ± 0.1	
C2	3.84	1.61	652.5 ± 76.8	6.6 ± 0.5	
C3	3.85	2.02	444.2 ± 128.9	5.2 ± 0.1	
Ti ₂ AlC	3.97	5.8 ± 0.5	432 ± 12	6.5 ± 0.2	

small Ti₂AlC particulates, so the cracks would easily cross through the aggregates. Therefore, if Ti₂AlC content is too high, the flexural strength will decrease. Combined with Fig. 2, it can be concluded that the near network structure, appropriate Ti₂AlC content, the dispersed Ti₂AlC micro-particulates and strong interface combination strength can play an important role in the enhancement of the flexural strength.

The fracture toughness of the product (C2 specimen) has the highest value of $6.6 \pm 0.5 \text{ MPa m}^{1/2}$, which is higher than that of Ti₂AlC ($6.5 \pm 0.2 \text{ MPa m}^{1/2}$) [16], 18 wt.% Ti₂AlC/TiAl composite ($6.1 \pm 0.1 \text{ MPa m}^{1/2}$) and TiAl ($5.8 \pm 0.1 \text{ MPa m}^{1/2}$). Such results indicate the network structure accompanied with the dispersed Ti₂AlC particulates, the decreased grain size, and appropriate Ti₂AlC content in the product have great potential to improve the fracture toughness of the composite. The deformation and damage of either the matrix or the reinforcement are constrained by each other. With increasing Ti₂AlC content to 30 wt.% (C3 specimen), the fracture toughness decreases due to the agglomeration of Ti₂AlC particulates, which will decrease resistance to crack propagation. And we find that higher Ti₂AlC content will adversely affect the fracture toughness of the composite. In order to analyze the toughening mechanism of the as-produced Ti₂AlC/TiAl composite, the fracture surface and typical crack propagation patterns of the C2 specimen is shown in Fig. 3. It can be seen from Fig. 3 that crack deflection, crack bridging and crack branching are present in the sample, which can enhance the crack growth resistance and lead to higher fracture toughness. The crack deflection will extend the effective crack length and absorb more fracture energy. Faber's research [17] indicated that the toughening effect could be enhanced by increasing crack deflection angle. As shown in Fig. 3b, crack deflection with a big deflection angle of 90° occurs during crack propagation. Bridging of the Ti₂AlC particles (Fig. 3b) before fracture can facilitate reduction of the crack driving force. The bridged Ti₂AlC particles span the crack, and display crack bridging tractions over the bridging length, thus shielding the far-field driving force. Moreover, we can find transgranular cracking and pullout of Ti₂AlC particles in the specimen (Fig. 3a). As seen in Fig. 3a, the plate-like grains and uneven fracture

surface are clearly observed. Delamination and kinks both occur in Ti₂AlC grains, contributing to the high fracture toughness and damage tolerance.

4. Conclusions

Fully dense Ti₂AlC/TiAl composites were successfully in-situ synthesized by reaction hot pressing using Ti, Al, TiC and CNTs as starting materials. The composites consist of Ti₂AlC and TiAl phases. The optimal mechanical properties were displayed by the 23 wt.% Ti₂AlC/TiAl composite, including Vickers hardness, flexural strength and fracture toughness of 1.61 GPa, $652.5 \pm 76.8 \text{ MPa}$ and $6.6 \pm 0.5 \text{ MPa m}^{1/2}$, respectively. The complex structure coupled with dispersed Ti₂AlC micro-particulates is responsible for the enhanced strength. Toughening of the composite is mainly attributed to crack deflection, crack bridging, crack branching and pull-out of the Ti₂AlC particles as well as transgranular cracking.

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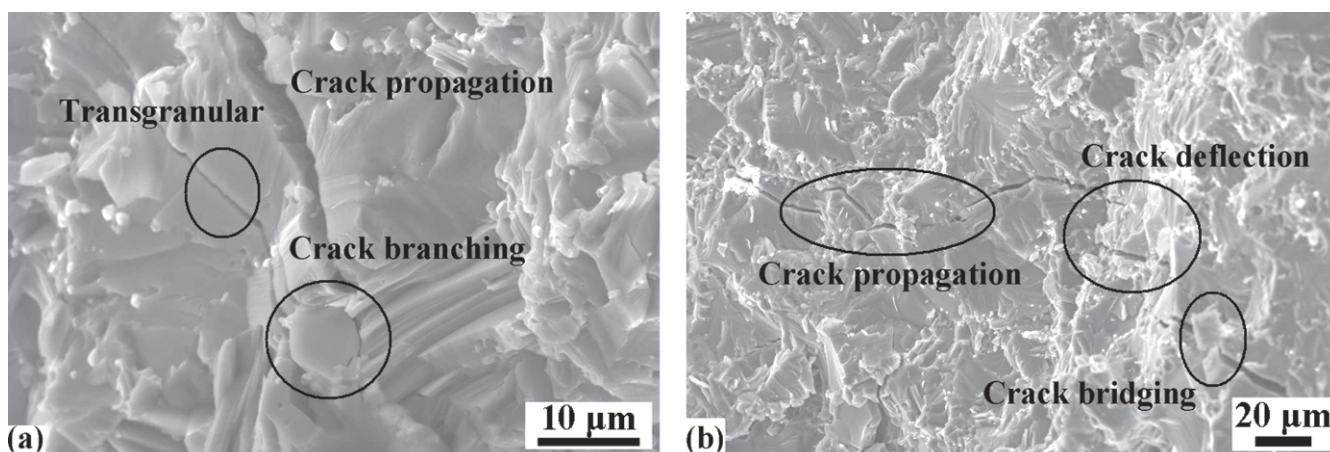


Fig. 3. (a) Fracture surface and (b) typical crack propagation patterns of the product corresponding to C2 specimen.

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