Synthesis and mechanical properties of TiB2/Ti2AlN composites fabricated by hot pressing sintering

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TiB2/Ti2AlN composites with different proportions were successfully fabricated through solid state reaction of Ti/Al/AIN/BN powders and subsequent hot pressing sintering. The reaction mechanism, microstructures and mechanical properties of the composites were investigated. The Vickers hardness of the samples ascended with increases in the TiB2 content and reached the highest value of 11.32 ± 0.12 GPa at a TiB2/Ti2AlN mole ratio of 1:2 (M2T1). TiB2/Ti2AlN composites with a mole ratio of 1:3 (M3T1) and 1:4 (M4T1) exhibited the maximum flexural strength of 497 ± 15 MPa and the highest fracture toughness of 9.52 ± 0.14 MPa·m1/2, respectively, which are 1.3 times and 1.8 times that of pure Ti2AlN (MT0) ceramic.

Key words: TiB2/Ti2AlN composites, In-situ reaction, Hot pressing sintering, Mechanica I properties

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1. Introduction

Ti2AlN is a category of ternary-layered ceramics with the general formula Mm+1AXn (or MAX in short), in which n = 1, 2, 3, M is a transition metal, A is a IIIA or IVA element, and X is C or N. It exhibits a unique combination of both ceramic and metal properties, such as low density, a high elastic modulus, good machinability, and excellent thermal shock resistance and damage tolerance.1,2 These features make Ti2AlN a promising candidate for high temperature applications. However, its low hardness and weak corrosion resistance restrict the potential applications of Ti2AlN as a structural material. Many reinforcing agents (such as Al2O3, TiB2, TiC, and SiC) with high hardness, a high modulus, excellent chemical stability, and compatible thermal expansion coefficients have been incorporated into the MAX phases to improve the mechanical properties.3–12 It is worth noting that most reports are on carbidic MAX materials, such as Ti3SiC2 and Ti3AlC2. Two-phase recombination is often achieved by mechanical mixing, moreover, resulting in a heterogeneous, segregated makeup that seriously affects the performance of composites.

To the authors’ knowledge, research on Ti2AlN composites is still insufficient. Ti2AlN ceramics have good mechanical properties, high electrical conductivity and easy machinability in contrast to Ti2AlC ceramics.2,3 Yan et al. have prepared TiN/Ti2AlN composites via in-situ synthesis, whereas the improvement of the mechanical properties of related samples is not significant, especially with respect to fracture toughness.13 TiB2 enjoys a reputation for high hardness, a high modulus (550 GPa), excellent chemical stability, and an approximate thermal expansion coefficient14 that is a suitable toughening factor. Zhao et al. have fabricated TiB2/Ti2AlN composites from Ti/Al and BN reactants. They reported that the grain size and aspect ratio of Ti2AlN grains were significantly reduced by incorporation of the TiB2 phase and discussed the crystallographic orientation relationship between MAX phases and TiB2.15 However, the proportions of TiB2 and MAX are related to the BN content, and cannot be adjusted, which has limited in-depth study of such attractive composites.

Taking the above into account, this work proposes a Ti–Al–AIN–BN system that obtains the TiB2/Ti2AlN composites with different TiB2 contents. Dense composites with uniform microstructures16 can be fabricated by in-situ synthesis and hot pressing sintering. The reaction mechanism, mechanical properties (including hardness, bending strength and fracture toughness), and morphology were investigated in detail. Investigations of the toughing mechanism of TiB2 particles in TiB2/Ti2AlN composites were also carried out.

2. Experimental

2.1 Preparation

Commercially available Ti (99.99%, 300 mesh), Al (99.5%, 1–2 μm), AIN (99.5%, 2 μm), BN (98.5%, 1 μm),
Sn (99.5%, 100 mesh) purchased from Aladdin Chemical Co., China, were used as the starting materials. Ti, Al, AlN and BN were mixed with ethanol according to Eq. (1) \((x + 2y)Ti + 2xA1 + (y - 2x)AlN + 2xBN = xTiB_2 + yTi_2AlN\) (1)

The mole ratio of Sn was 0.2, which was used as an additive to synthesize pure TiB2/Ti2AlN composite. Proper addition of Sn could solve the evaporation loss of Al and the thermal explosion simultaneously.17) In order to homogenize the mixture, planetary ball milling with an agate ball was carried out at a speed of 300 rpm in ethanol for 8 h at a ball-to-powder ratio of 8:1. The resulting slurry was dried at 70°C under vacuum, ground using a high-purity Al2O3 mortar and pestle, and then screened through a 100-mesh size sieve. The mixture was calcined at 1450°C for 1 h in a flowing Ar atmosphere (99.99% pure).

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2.2 Characterization

The phase composition of the composites was determined by X-ray diffraction (XRD) analysis with a Miniflex 600 diffractometer (Tokyo, Japan) using Cu Ka radiation. The morphology and microstructures of the composites were characterized by scanning electron microscope (TESCAN VEGA 3 LMH). Bulk density and theoretical density were evaluated by the Archimedes method and the rule of mixtures, respectively. The density of monolithic Ti2AlN and TiB2 were 4.31 and 4.50 g/cm³, respectively.3) Vickers hardness was measured on the polished surfaces of the specimens using a HV-1000 Vickers hardness instrument with a load of 4.9 N and duration of 15 s. Flexural strength was evaluated by the three-point bending method according to GB/T 6569-2006 using a universal testing machine. The dimensions of the specimens for measurement of flexural strength were 3 mm × 4 mm × 36 mm. The bars were loaded with spans of 30 mm, and the crosshead speed for bending strength was 0.5 mm/min. Fracture toughness was evaluated using single-edge notched bending beams (2 mm × 4 mm × 22 mm) (width × height × length) with a notch depth and radius of 2 and 0.15 mm, respectively, using a span of 16 mm and a crosshead speed of 0.05 mm min⁻¹. At least five specimens were prepared for each test.

3. Results and discussion

3.1 Phase composition and microstructure

As shown distinctly in Fig. 1, pure-phase TiB2/Ti2AlN mixtures with different mole ratios have been synthesized with no obvious impurities detected. During the heating process, Ti powder reacts with other raw materials to obtain the final resultants. Briefly stated, the overall reactions taking place in the system can be described as follows:

\[3Ti + 2BN = TiB_2 + 2TiN\] (2)
\[TiN + Ti + Al = Ti_2AlN\] (3)
\[2Ti + AlN = Ti_2AlN\] (4)

Reactions 2–4 have been confirmed both in terms of theoretical thermodynamics and experimentally in previous works.1),2,3,15,18,19)

Figure 2 shows XRD patterns of the composites hot pressed at 1300°C, which are similar to those of the mixtures. As demonstrated by these XRD patterns, all the peaks can be indexed using the reflections of Ti2AlN and TiB2, indicating high purity of as-prepared ceramics.
All the scanning electron microscope (SEM) images of fracture surfaces indicate the presence of two distinct phases with different grain sizes in TiB2/Ti2AlN composites (Fig. 3). As shown in Fig. 4, the SEM and energy dispersive X-ray spectrometry (EDS) analyses (inset) reveal that the coarse grains with a typical ternary layered character are Ti2AlN, while the fine grains are TiB2 (about 400 nm). The grain size of Ti2AlN in these composites, especially in samples M3T1 and M2T1, is relatively smaller than that of pure Ti2AlN (MT0). The grain size of Ti2AlN tends to decrease with increases in the TiB2 content, which suggests that in situ formation of TiB2 can effectively inhibit the growth of Ti2AlN grains. In the case of M2T1, especially, some agglomeration of TiB2 can be observed due to an excess of TiB2 [Fig. 4(b)].

3.2 Mechanical properties
The mechanical properties of the TiB2/Ti2AlN composites are listed in Table 1. The Vickers hardness and flexural strength of MT0 are 4.27 ± 0.17 GPa and 368 ± 12 MPa, respectively, which is slightly higher than those of pure Ti2AlN (Vickers hardness 4.0 Gpa and flexural strength 350 MPa). This is attributed to the addition of Sn, which dissolves into Ti2AlN and plays a solid solution strengthening effect. With increments in the TiB2 molar contents (Fig. 5), the Vickers hardness value increases from the initial 4.27 ± 0.17 GPa of MT0 to a maximal 11.32 ± 0.12 GPa of M2T1, which is approximately three times that of monolithic Ti2AlN. Since TiB2 has a high hardness of about 25–35 GPa, the incorporation of TiB2 effectively improves the overall Vickers hardness of the composite. In addition, the TiB2 reinforcing agent signifi-
significantly inhibits the grain-boundary migration of Ti$_2$AlN grains, resulting in a fine-grained Ti$_2$AlN matrix. This grain-refining effect causes a positive improvement in the mechanical behaviors of TiB$_2$/Ti$_2$AlN composite.

Figure 6 presents the flexural strength of TiB$_2$/Ti$_2$AlN composites with different TiB$_2$ molar contents. Initially, the flexural strength increases from 377 ± 8 MPa to 497 ± 15 MPa as the mole ratio of TiB$_2$ to Ti$_2$AlN ranges from 1:4 to 1:3, after which it decreases to 381 ± 11 MPa at a mole ratio of 1:2. The maximum value of M3T1 is 1.4 times that of pure Ti$_2$AlN.\(^{20}\) There is almost no difference among the flexural strengths of MT0, M4T1 and M2T2, however, a result probably related to the following reasons: First, as we can see from the SEM images of fracture surfaces (Fig. 3), TiB$_2$ can inhibit the growth of Ti$_2$AlN grains. According to the Hall–Petch relationship, the hardness should increase with decreases in grain size, however the refinement of M4T1 is not quite as obvious as in the M3T1 and M2T1 samples, and the flexural strengths of MT0 and M4T1 are almost the same as a result. Secondly, the flexural strength of pure TiB$_2$ is lower than that of pure Ti$_2$AlN, Which show flexural strengths of 300 and 350 Mpa, respectively.\(^{20,22}\) Based on the rule of mixtures,\(^{23}\) the flexural strength of Ti$_2$AlN/TiB$_2$ composites should decrease with the presence of TiB$_2$ particles. What is more, TiB$_2$ agglomeration also decreases flexural strength, as demonstrated by other researchers.\(^{24}\) Thus the flexural strengths of MT0 and M2T1 are almost the same.

As shown in Fig. 7, the fracture toughness of the TiB$_2$/Ti$_2$AlN composites is significantly higher than that of pure Ti$_2$AlN (MT0), with the maximum value of 9.52 ± 0.14 MPa·m$^{1/2}$ for M4T1. The increase in fracture toughness can be assigned to a mismatch of the thermal expansion coefficients between TiB$_2$ and Ti$_2$AlN that form a plastic zone at the tip of the main crack when the composite is subjected to tensile stress, and microcracks in this region are extended to form new surface cracks and consume energy. Because of the relatively low fracture toughness (\(<5\) MPa·m$^{1/2}$)\(^{21}\) and potential agglomeration of TiB$_2$, the fracture toughness decreases to 6.38 ± 0.14 MPa·m$^{1/2}$ for M2T1.

### 3.3 Toughening mechanism

In order to further examine the toughening mechanism, the microstructures of the samples were investigated in detail. Figure 8 shows magnified images of the crack propagation path in an M3T1 composite induced by the Vickers indentation using a load of 9.8 N with a dwell of 30 s. The deflection [Fig. 8(b)], bridging [Fig. 8(c)], and branching [Fig. 8(d)] of cracks are observed. These factors
consumes propagation energy and benefit of improving the fracture toughness. In this system, TiB2 enhanced Ti2AlN matrix can be explained by the following toughening mechanisms:

1. The mismatched coefficients of thermal expansion (CTE) of the TiB2 phase and Ti2AlN matrix produce residual stress at the composite interface. When the composite is cooled down from the fabrication temperature, thermal residual stress arises due to the thermo-elastic mismatch between constituents.25) Compared with the CTE of Ti2AlN (8.8 \times 10^{-6} \text{ m/K}),\text{26) the lower CTE of TiB2 (8.1 \times 10^{-6} \text{ m/K})\text{27) induces residual thermal compressive stress at the TiB2 and Ti2AlN interfaces during the cooling process.28) When cracks meet the TiB2 grain boundaries, they consequently tend to be deflected and to propagate along the grains. The Ti2AlN matrix around the second phase particles generates a radial compressive stress (\sigma_r) and a tangential tensile stress (\sigma_t). More energy is required to propel the main-crack to deflect and prolong the route expansion, thus increasing the fracture toughness of the Ti2AlN materials.

2. Crack bridging. When meeting TiB2 or Ti2AlN grains, the main-crack produces an interlocking phenomena with TiB2 or Ti2AlN particles [Fig. 8(c)]. The thinning of main-cracks indicates that the crack bridge causes a forced closure of the two crack surfaces, moreover, which restrains expansion of the crack to improve the fracture toughness of the TiB2/Ti2AlN composites.

On the other hand, mechanical properties such as toughness and yield strength decrease with increases in the grain size. The fine-grain toughening of TiB2 can contribute to excess crack deflection through a meeting of grain boundaries, which is described by the Hall-Petch equation\text{29) and Irwin:30)\text{
\begin{align}
\delta &= \delta_0 + kd^{-1/2} \quad (5) \\
K_{IC} &= Y\sigma\sqrt{\alpha} \quad (6)
\end{align}
For Eq. (5), \delta is the yield stress of a polycrystal, \delta_0 is the yield stress for a single crystal or a polycrystal with an infinitely large grain size, and k is the Hall-Petch parameter. As for Eq. (6), \text{K}_{IC} is the plane strain fracture toughness, Y is a constant related to the sample’s geometry, \sigma is the critical applied stress that can cause failure and \alpha is the critical crack size.

With the addition of the proper TiB2 content, therefore, the TiB2 particles are homogenously distributed on the
substrate, inhibiting the grain growth of the matrix in the sintering process, refining the grain size and improving the strength of the composites. With the addition of more TiB$_2$ particles, the compatibility between different particles deteriorates making agglomeration of TiB$_2$ inevitable during the preparation of TiB$_2$/Ti$_2$AlN composites, and the mechanical performance decreases as a result. The amounts and sizes of the added particles must be controlled reasonably to avoid making the sizes of the second phase particles when the material is cooled from the sintering temperature to room temperature and the stress induces microcracking; otherwise the increase in the second phase particle will cause microcracks in the material and most of the residual stress relaxation will cause substantial damage to the properties of the composite ceramics$^{31,32}$.

4. Conclusions

TiB$_2$/Ti$_2$AlN composites with different TiB$_2$ contents were successfully fabricated by in-situ hot pressing. The effects of TiB$_2$ as a second phase on the microstructure, Vickers hardness, flexural strength and fracture toughness were studied. TiB$_2$ particles exhibit a significant strengthening and toughening effect on a Ti$_2$AlN matrix. The composites show excellent mechanical properties in comparison with pure Ti$_2$AlN, and optimal mechanical properties—flexural strength of 497 ± 15 MPa, fracture toughness of 8.05 ± 0.12 MPa m$^{1/2}$ and Vickers hardness of 9.08 ± 0.09 GPa, were achieved for M3T1 composites.

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