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Formation of laminar Ti-Al-N solid solution and interfacial atomistic structure of TiB_2-AlN-B_4C composite

ABSTRACT

Keywords:
TiB_2-AlN-B_4C
Reactive SPS
Ti-Al-N solid solution
Interface structure

Reactive spark plasma sintering was performed to synthesize TiB_2-AlN-B_4C composite at 1650 °C for 5 min. The results of mechanical tests indicated that the addition of Ti less than 10 wt% is beneficial to its mechanical performances. X-ray diffraction and scanning electron microscope (equipped with energy disperse spectroscopy) reveal the reactions between Ti, B_4C and AlN to form TiB_2 ceramic and laminar Ti-Al-N solid solution that consumes more fracture energy owing to its multilamellar structure and larger aspect ratio. Transmission electron microscope provided an insight into interfacially atomistic structure, surprisingly, two types of diffraction spots were identified as $(0\bar{3}31)Ti_2AlN$ and (010)AlN, furthermore, their incoherent interphase boundary composed by atomic facets was illustrated.

1. Introduction

Boron carbide is considered as a promisingly structural material used for light armor and neutron radiation absorbent in nuclear reactor, due to its low density, ultra-high hardness and neutron absorption capability [1–3]. Unfortunately, the low self-diffusion rate and strong covalent bonding cause boron carbide powders barely to be sintered directly without sintering aids [4]. A variety of additives such as pure metals, oxides, borides and carbides have been reported to promote sintering of boron carbide [5–7]. They are designed to occur interfacial reactions with boron carbide, producing new phases around the grain boundaries to improve their bonding strength and accelerate solid phase diffusion. Typically, Ti was confirmed as an ideal sintering-promoter, besides, reacting with boron carbide to produce TiB_2 ceramic as reinforcement [8]. Meanwhile, based on our previous work, multilamellar Ti-Al-N solid solution, obtained by in-situ reaction between Ti and AlN, significantly improve the mechanical properties of Ti/AlN composites [9].

Despite they have been separately verified to be effective, the studies of consolidated TiB_2-AlN-B_4C ternary-system composites are scarce. Therefore, Ti and AlN were introduced together as the sintering additives for boron carbide. This work aims to investigate microstructural evolution, phase transformation and interfacial atomistic structure of TiB_2-AlN-B_4C ternary-system. In this work, reactive SPS was employed to fabricate TiB_2-AlN-B_4C composite from Ti/AlN/B_4C system at 1650 °C for 5 min. The Ti-Al-N solid solution with multilamellar structure was identified by XRD and observed by SEM equipped with EDS. The crystal orientation and interfacial atomic structure were characterized by TEM.

2. Experimental section

Commercial powders of AlN (an average particle size of 1 μm) and B_4C (an average particle size of 3 μm) with different Ti wt.%(an average particle size of 5 μm) were used as starting materials and their compositions were listed in Table 1. The composites were prepared via ball-milling and spark plasma sintering technology (DR.SINTER type SPS-3.20, Sojitz Machinery Corporation, Japan) with pulse duration of 3.3 ms and a current on-off ratio of 12:2 (Fig. 1a), and heated at 1650 °C with a heating rate of 100 °C/min, then holding under an applied pressure of 30 MPa for 5 min.

Archimedes method determined the relative densities of specimens. Flexural strength and fracture toughness of composites were achieved by three-point bending method and single-edge notched beam test by an electromechanical universal testing machine (Instron-5980, Instron Corporation, USA). For indentation test of hardness, a load of 1Kg was applied by pressing the indenter perpendicular to the polished surface (Shimadzu Vickers hardness tester HSV-20, Japan). X-ray diffraction (XRD, D8-Advance, Bruker Corporation, Karlsruhe, Germany) with Cu Ka (1.54 Å) radiation, field-emission scanning electronic microscopy (SEM, Hitachi S-4800, Hitachi, Japan) equipped with an energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd., Japan) evaluated the phase composition and microstructure of composites.

3. Results and discussion

Mechanical properties of TiB_2-AlN-B_4C composite with different compositions are detailed in Table 1. Generally, the increase of relative density was consistent with the increase of Ti weight ratio, moreover, the relative density, Vickers hardness, flexural strength and fracture toughness reached the maximum value for 10TAB

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Table 1
Raw material composition and mechanical properties of composites.

Group	Raw material composition (wt%)	Relative Density (%)	Hardness (GPa)	Flexural Strength (MPa)	Fracture toughness ($MPa \cdot m^{1/2}$)
0TAB	Ti:AlN:B_4C = 0:50:50	96.6 ± 1.32	26.2 ± 2.81	449.37 ± 29.52	5.32 ± 0.41
5TAB	Ti:AlN:B_4C = 5:47.5:47.5	98.1 ± 1.17	27.8 ± 2.38	633.23 ± 25.62	6.75 ± 0.56
10TAB	Ti:AlN:B_4C = 10:45:45	98.4 ± 0.98	28.3 ± 2.02	670.47 ± 17.28	6.83 ± 0.32
15TAB	Ti:AlN:B_4C = 15:42.5:42.5	98.2 ± 1.19	28.1 ± 2.46	564.22 ± 33.14	6.51 ± 0.46
20TAB	Ti:AlN:B_4C = 20:40:40	98.2 ± 1.45	27.9 ± 2.38	532.11 ± 28.71	6.17 ± 0.37

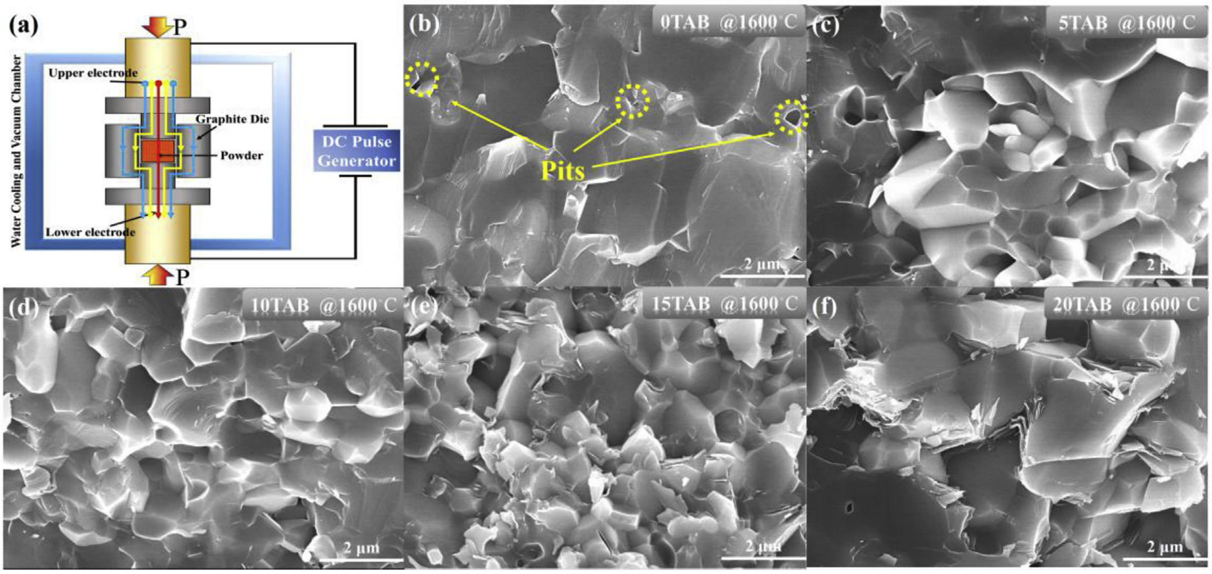

Fig. 1. Schematic diagram of SPS process (a) and SEM micrographs detailing fracture surface ( ) of TiB_2-AlN-B_4C composite.

group of 98.4%, 28.3 GPa, 670.47 MPa and 6.83 MPa $m^{1/2}$. For ceramic composite, there are abundant researches suggested that the relative density is closely related to mechanical properties [10]. Accordingly, the addition of Ti less than 10 wt% is capable of improving the mechanical properties of TiB_2-AlN-B_4C composite by promoting its densification, while further addition is harmful.

As shown in Fig. 1(b–f), microstructures and morphologies of TiB_2-AlN-B_4C composite after three-point bending test were observed by SEM. The general structure of the AlN-B_4C consolidated directly from the powders with no Ti additives, and their large-scale grains homogeneously combined without distinct grain boundary to product abundant pores in Fig. 1b. With Ti addition, the grain shapes and sizes of composites become diversiform with clear interfaces. Furthermore, as Ti content increasing, small-scale grains (Fig. 1c–f) take the place of large-scale grains (Fig. 1b) and pores decrease even to be vanished, besides, the large grains gradually develop into fine and clear-edged particles. These results suggest that the fracture crack propagates through the boundary rather than the whole grain (inter-granular fracture), and it is beneficial to the fracture strength of composite owing to the more consumption of fracture energy, which is acting like whisker-reinforced mechanism [11].

The composition and crystal structure of the TiB_2-AlN-B_4C composite were determined by XRD analyses (Fig. 2a). The XRD

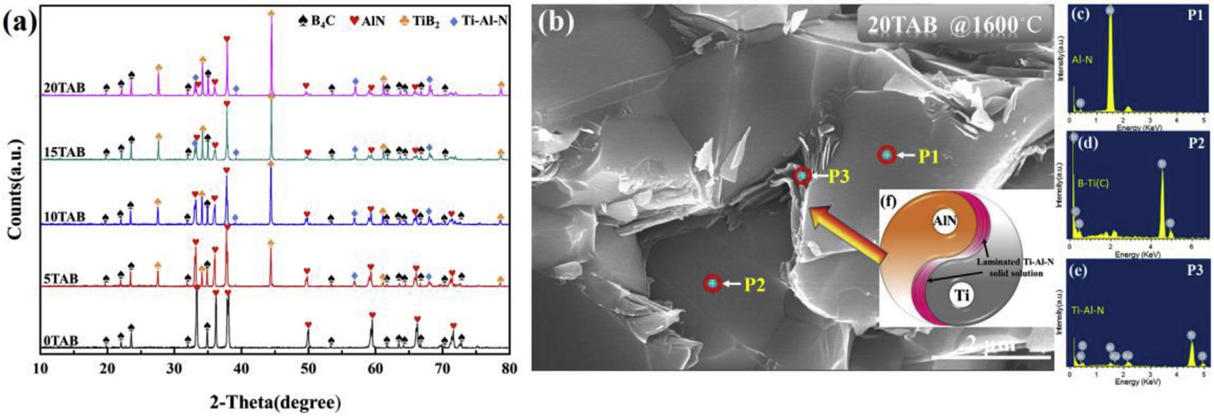

Fig. 2. XRD patterns (a), SEM micrograph (b) with EDS (c–e) point element analysis and schematic diagram of Ti-Al-N solid solution (f) from TiB_2-AlN-B_4C composite.