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Microstructural evolution and oxidation behavior of TiB_2–SiC–B_4C composite fabricated by reactive spark plasma sintering

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ABSTRACT

Microstructural evolution and oxidation behavior of TiB_2–SiC–B_4C composite fabricated from Ti–Si-C–B_4C system with different weight ratios via reactive SPS were investigated in detail. Based on the characterizations of SEM, XRD, TEM and HRTEM, it was found that the solid diffusion induces reactions between Ti and B_4C to form TiB_2(TiB), C and Ti(B,C,Si). Afterwards, the results of oxidation tests at 800 °C, 900 °C and 1000 °C demonstrated that the sample with highest TiB_2 contents performed the best oxidation resistance due to the lowest porosity. Furthermore, the smoothly glassy oxidation layer above substrate composed of TiO_2 and B_2O_3 became thicker with temperature increasing, meanwhile, the vaporized B_2O_3 recrystallized into plate-like, rose-like even large-monolithic grains.

1. Introduction

Boron carbide (B_4C) ceramic and its composites exhibit attractively physical and chemical properties, such as low density (2.52 g/cm^3), ultrahigh hardness (55–67 GPa) and neutron absorption capability. In terms of these, B_4C composite attracts widespread attention as a promisingly structural material used for light armor, cutting tools and neutron radiation absorbents in nuclear reactor [1–4]. Whereas, it is difficult to obtain fully dense B_4C materials due to the strong covalent bonding and low self-diffusing coefficient of boron and carbon atoms [5,6]. Besides, the low oxidation temperature (<800 °C) and inherited brittleness (KIC<2.2 MPa m$^{1/2}$) restrict their wide applications in severe accident conditions, such as the absorber material for boiling water reactors [7,8]. Therefore, this article concerns with improving the mechanical properties and oxidation resistance of B_4C ceramics to avoid irrevocable catastrophic consequences.

Nowadays, a variety of second phases are used as sintering aids to promote sintering process and improve flexural strength of B_4C ceramics [9–11]. Typically, TiB_2 and SiC, characterized by high melting point, high hardness, excellent chemical stability and relatively low density, are confirmed as ideal candidates as reinforced additives which can be achieved by in-situ reaction from Ti and Si as well as acting as sintering promoter [12–14]. However, the shortcomings, such as moderate fracture toughness of SiC and poor oxidation resistance of TiB_2, prevent them from being used separately. Fortunately, the combination of TiB_2 and SiC can invariably inherit their advantages and avoid their disadvantages. It has been certified that the fracture toughness of SiC can be enhanced by the addition of TiB_2, as well as the oxidation resistance of TiB_2 can be also improved when SiC is added [15,16]. Accordingly, we employed both TiB_2 and SiC adding to B_4C matrix for improving its flexural strength and oxidation resistance.

Nevertheless, because of the strong covalent bonding and low self-diffusing coefficient of TiB_2–SiC–B_4C system, traditionally solid-state sintering is difficult to achieve fully-dense composite. Reactive sintering has been adopted as an effective way to produce composite from metal-ceramic and ceramic-ceramic system, i.e., Ti-Si-BN-B_4C, B_4C–TiC–Si and TiH–B–SiC [17–20]. Moreover, the in-situ reaction accelerates solid diffusion and generates fresh ceramic particles with finer grain size and higher activity, which enhances the density and bonding strength of matrix [21–24]. Especially for metal-ceramic system, melting metal enriches around grain boundaries to form a liquid pool providing a convenient passageway for diffusion, which transforms the type of bonding interface from physical to metallurgical to improve its bonding strength. Accordingly, metal Ti is designed to be sintering

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aid through reactive SPS sintering for B_4C composite.

Moreover, B_4C composite always works at high temperature in an oxidizing atmosphere, such as cutting tool, armor protection and nuclear reaction generator. Oxidation process causes gradually the erosion of the structure and eventually the degradation of the properties [1,25,26]. Much effort therefore attempts to provide effective approaches for evaluating the service temperature of B_4C composite by improving its oxidation resistance, such as adding the second phase(SiC) [25]. Consequently, in order to further understand the microstructural evolution and oxidation behavior, TiB_2–SiC–B_4C composite is fabricated by reactive SPS at 1600 °C from Ti–SiC–B_4C system with different weight ratios. The phase transformation, microstructural evolution and oxidation behavior of TiB_2–SiC–B_4C composite in air at different temperature is measured. Finally, the microstructural evolution and oxidation behavior of TiB_2–SiC–B_4C composite are illustrated by a series of schematic diagrams.

2. Experimental section

2.1. Material preparation

Commercial powders of Ti (99.9% pure, an average particle size of 5 μm), SiC (99.9% pure, an average particle size of 1 μm) and B_4C (99.9% pure, an average particle size of 3 μm) were used as raw materials and their weight percentage were listed in Table 1. The raw powders (with the mass of 35 g) were ball-milled in ethanol medium with PEG2000 (Polyethylene Glycol) as dispersing agent for 24 h, then the mixture was dried in vacuum (about 6×10^{-1}Pa) at 80 °C for 8 h. The dried powder was loaded into a graphite die with a 40 mm inner diameter. Finally, the composites were fabricated via spark plasma sintering apparatus (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, and heated at 1600 °C with a heating rate of 100 °C/min, and then holding under an applied pressure of 30 MPa for 5 min. Finally, the samples were cut into bars with a size of 3 mm × 5 mm × 30 mm, and polished to detect the properties, microstructure and oxidation behavior.

2.2. Oxidation measurement

The specimens were ultrasonically cleaned and dried, and then weighed with a precision of 0.0001 g before and after the oxidation test. The oxidation tests were performed in a static air furnace at a designed temperature (800 °C, 900 °C and 1000 °C respectively) for 1 h and cooling in air to obtain the mass gain percentage and flexural strength retention.

2.3. Material characterization

Archimedes method was used to determine the relative density of specimens. The flexural strength of polished composite was achieved by three-point bending method with a crosshead speed of 0.5 mm min^{-1} and span of 30 mm at room temperature according to electromechanical universal testing machine (Instron-5980, Instron Corporation, USA). Both relative density and flexural strength of specimens listed in Table 1. The phase composition and microstructure were evaluated using X-ray diffraction (XRD, D8-Advance, Bruker Corporation, Karlsruhe, Germany) with Cu Ka (1.54 Å) radiation, scanning electronic microscopy (SEM, Hitachi S-4800, Hitachi, Japan) equipped with an energy dispersive spectroscopy (EDS). The thin sample of composite prepared by mechanical and ion beam milling was observed by a Transmission Electron Microscopy (TEM, JEM-2100 F, JEOL Ltd., Japan) operated at 200 kV to detect its nanostructure.

3. Results and discussion

The XRD patterns of specimens with various compositions are shown in Fig. 1a, and the main peaks are identified such as B_4C, SiC, TiB_2, TiB and C. With the increase of Ti content in raw materials, the intensity of B_4C peaks decreases and even hardly to be identified in 20TSB, while, the intensity of TiB_2 peaks significantly increases, and the shape of SiC peaks remains stable. These indicate that there is a significant reaction between Ti and B_4C, whereas SiC is barely involved. Under the experimental conditions, the following reactions have been identified in the Ti–B_4C system [27,28].

$$Ti + B_4C \rightarrow TiB_2 + TiC \quad (1)$$

$$B_4C + 4TiC \rightarrow 4TiB + 5C \quad (2)$$

$$B_4C + 2TiC \rightarrow 2TiB_2 + 3C \quad (3)$$

Based on the above reactions, it can be concluded that Ti initially reacts with B_4C to form TiB_2 and TiC (reaction 1), then, the redundant B_4C captures TiC to generate TiB, TiB_2 and C (reaction 2 and 3). As the Ti content increasing, the reactions consume more B_4C to produce more TiB, TiB_2 and C, which is well matched to the tendency of XRD patterns in Fig. 1. Moreover, the gradually inconspicuous peaks of B_4C are attributed to the consumption of reactions and the cover by the high-intensity peaks of TiB_2 and SiC.

After three-point bending test, the fracture surfaces of specimens are observed by SEM to obtain micrographs which are displayed in Fig. 1(b–e). Although grain shapes and sizes are diversiform, the composite possesses homogeneous without distinct segregation at grain boundary and interfacial reaction area. Fig. 1b presents abundant large grains (d > 3 μm) and pores (yellow-dot circle) in 5TSB, and the fracture method of grains mostly are trans-granular fracture owing to the compact and indistinct grain boundary. With increasing Ti content, small grains (d < 3 μm) take the place of large grains and pores turn to be decreased even vanished, which well keeps consistent with the improvement of relative density in Table 1. Furthermore, the clear grain boundary indicates the fracture crack breaks 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.

A detailed microstructural characterization of the 20TSB specimen was detected using TEM. Fig. 2a and b are bright field images

Table 1
Raw material composition and mechanical properties of composites.

Sample Group	Raw material composition (wt.%)	Relative Density(%)	Flexural Strength(MPa)
Blank sample	$B_4C = 100$	88.6 ± 2.42	221.49 ± 26.84
5TSB	Ti:SiC: B_4C = 5:47.5:47.5	95.8 ± 1.07	432.72 ± 17.53
10TSB	Ti: SiC: B_4C = 10:45:45	96.7 ± 0.92	487.04 ± 16.91
15TSB	Ti:SiC:B_4C = 15:42.5:42.5	98.2 ± 1.11	552.25 ± 19.26
20TSB	Ti: SiC: B_4C = 20:40:40	98.4 ± 1.06	527.61 ± 18.36