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Microstructure, mechanical properties and thermal shock behavior of h-BN–AlN ceramic composites prepared by combustion synthesis

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ABSTRACT

h-BN–SiC–AlN–TiN ceramic composites with volume content of AlN–TiN ranging from 20% to 70% were prepared by combustion synthesis from powder compacts of B_4C, Si, Al and TiN under 100 MPa nitrogen pressure. The volume fraction of AlN–TiN was found to have a significant influence on the microstructure, mechanical properties and thermal shock resistance of the composites. With the increasing volume content of AlN–TiN, the mechanical properties of the composites were improved remarkably, while thermal shock resistance decreased. Thermal shock tests showed that the critical thermal shock temperature (ΔT) was higher than 1200 °C for the composites with AlN–TiN contents of 30 vol%; while it was decreased to 850 and 670 °C for the composites with AlN–TiN contents of 50 and 70 vol%, respectively.

1. Introduction

Hexagonal boron nitride (h-BN) has received increasing attention because of its excellent combination of high melting point, high thermal shock resistance and thermal conductivity, good chemical inertness and lubricating properties. h-BN is easily machinable using conventional metal cutting techniques, and therefore complex shaped components can be fashioned [1], so h-BN ceramic has been widely used in many fields, such as crucibles, molds and thermal couple protection tubes. However, the low hardness of h-BN has prevented it from being used in a wide range of applications. To overcome this shortcoming, h-BN-based composites were prepared, such as h-BN–SiC [2,3], h-BN–SiO_2 [4], h-BN–AlN [5,6] and h-BN–Al_2O_3 [7,8]. Combined with high strength second phases, the h-BN-based composites exhibit optimal mechanical properties and thermal shock behavior with little effect on the machinable properties.

Combustion synthesis, also called self-propagating high-temperature synthesis (SHS), is a promising technique for fabricating advanced ceramics [9,10]. By utilizing the heat released by exothermic reaction, combustion synthesis can self-sustaining and has the advantages of high reaction temperature, short reaction time and no external power supply. In our previous work, h-BN–SiC ceramic composites were fabricated by combustion synthesis from B_4C and Si powders under high nitrogen pressure [11]. In this paper, AlN–TiN phase was introduced into h-BN–SiC ceramic composites to improve the density and mechanical properties of h-BN composites.

Aluminum nitride (AlN) and titanium nitride (TiN) are also ceramic materials with high melting point, good hardness and chemical stability, so AlN and TiN ceramic have received extensive attention and many researchers prepared by combustion synthesis [12,13]. The reported results show that the powder mixture with the Al:TiB_2 molar ratio of 5:1 has excellent combustion characteristics and mechanical properties [14]. However, TiB_2 can decompose to TiN and BN under high temperature and high nitrogen pressure, so TiN takes the place of TiB_2 in this study to avoid the nonuniformity resulted from the decomposition of TiB_2 during the combustion reaction. TiN acts as diluent to control the combustion synthesis reaction; meanwhile, TiN has good compatibility with AlN at elevated temperature, which can effectively enhance the density and mechanical properties of the composites. Moreover, AlN and SiC can form AlN–SiC solid solution [15,16], and this is very favorable for the improvement of mechanical properties. In this way, the addition of AlN–TiN to h-BN can be expected to improve the strength and fracture toughness of the composite.

In this paper, we attempt to prepare h-BN–SiC-AlN–TiN composites by combustion synthesis of the powder compacts of B_4C, Si, Al and TiN under 100 MPa nitrogen pressure. The combustion synthesis reaction was as follows:

$$\begin{aligned} &B_4C + Si + x(5Al + TiN) + (5x+4)/2\,N_2 \\ &\quad = 4BN + SiC + x(5AlN + TiN) \end{aligned} \tag{1}$$

The AlN–TiN volume fraction in the products can be controlled by the coefficient x in reaction (1). The effect of AlN–TiN volume

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content on the microstructure, mechanical properties and thermal shock resistance was analyzed.

2. Experimental procedure

2.1. Preparation

Commercially available powders used in this study was B_4C (99% purity, 5 μm), Si (98% purity, 3 μm), Al (98% purity, 4 μm) and TiN (99% purity, 4 μm). On the basis of reaction (1), the molar ratio of powder mixture of B_4C–Si (molar ratio of B_4C to Si was 1:1) to powder mixture of Al–TiN (molar ratio of Al to TiN was 5:1) was 1:x. By adjusting the x value, AlN–TiN content in h-BN–SiC–AlN–TiN composites can be controlled. The powder mixtures were ball-milled for 24 h in a polyethylene bottle using agate balls as grinding media. Then the milled powders were cold isostatically pressed under 10 MPa pressure, and the cylindrical green compacts with a relative density of about 50% were prepared.

The combustion synthesis was carried out in a high-pressure combustion reactor. The cylindrical green compacts were put into the combustion chamber just under a tungsten ignition coil. When electric current flows through the ignition coil, the compact was ignited and combustion wave propagated. The nitrogen gas with a purity of 99% was used in this work. Nitrogen gas acted as the reaction fuel as well as pressure supply of hot-isostatic during this combustion synthesis process.

2.2. Characterization

The relative density of the products was determined by the Archimedes method using water as immersing medium. Phase composition was identified by X-ray diffraction (XRD, Rigaku, Dmax-rb). The microstructure and fractured surfaces of the products were observed by scanning electron microscopy (SEM, FEI Sirion, USA) with simultaneous chemical analysis by energy dispersive spectroscopy (EDS, EDAX Inc.). Microhardness was measured by Vickers indentation with a 9.8 N load applied 10 s on polished sections. Flexure strength was conducted in three-point bending on 3 mm × 4 mm × 36 mm bars, using a 30 mm span and a crosshead speed of 0.5 mm min^{-1} on a universal testing machine (Instron-1186, USA). Fracture toughness was evaluated by a single-edge notched beam (SENB) test with a 16 mm span and a crosshead speed of 0.05 mm min^{-1} on a universal testing machine (Instron-1186, USA). A notch 2 mm in depth and 0.4 mm in width was machined into test bars of 2 mm × 4 mm × 22 mm using a 0.3 mm diamond blade. A minimum number of five specimens were used for each experimental test.

2.3. Thermal shock tests

Polished and chamfered bars with dimension of 3 mm × 4 mm × 36 mm for thermal shock tests were put into Muffle furnace heated up to the desired temperatures and maintained for 10 min to eliminate temperature gradient effect. The test bars were then dropped into water bath quickly (20 °C). The temperature difference, ΔT, was chosen as 400, 600, 800, 1000 and 1200 °C. The residual flexural strength was measured at room temperature using a three-point bending test. At least four specimens were tested for each condition.

3. Results and discussion

3.1. Phase compositions and microstructures

The reaction (1) is a highly exothermic process ($\Delta H = -1012.5$ kJ/mol ($x = 0$); $\Delta H = -1251.8$ kJ/mol ($x = 1$)), and the adiabatic combustion temperature is 3475 K ($x = 0$) and 3608 K ($x = 1$), which considerably exceeds the empirical criteria of 1800 K for combustion synthesis reactions [17]. So this reaction is expected to be self-sustaining readily.

Fig. 1 shows the X-ray diffraction patterns of the as-synthesized combustion products with different AlN–TiN content. h-BN, SiC, AlN and TiN were identified in the as-synthesized products, and no other phases and remaining raw materials were found. This indicated reaction (1) was carried out completely. The relative diffraction intensity of h-BN phase decreased as the AlN–TiN contents increased. It was also can be found that the diffraction angle of AlN and SiC can hardly be distinguished because of the formation of AlN–SiC solid solution in the products for the same hexagonal structure and similar lattice parameter ($a = 3.1094$ and $c = 4.9792$ for AlN, $a = 3.081$ and $c = 5.031$ for SiC).

Fig. 2 shows the SEM images of composites with AlN–TiN volume fraction of 20% (a), 60% (b), respectively. At AlN–TiN volume fraction of 20%, large amount of light gray flake h-BN with 1–2 μm

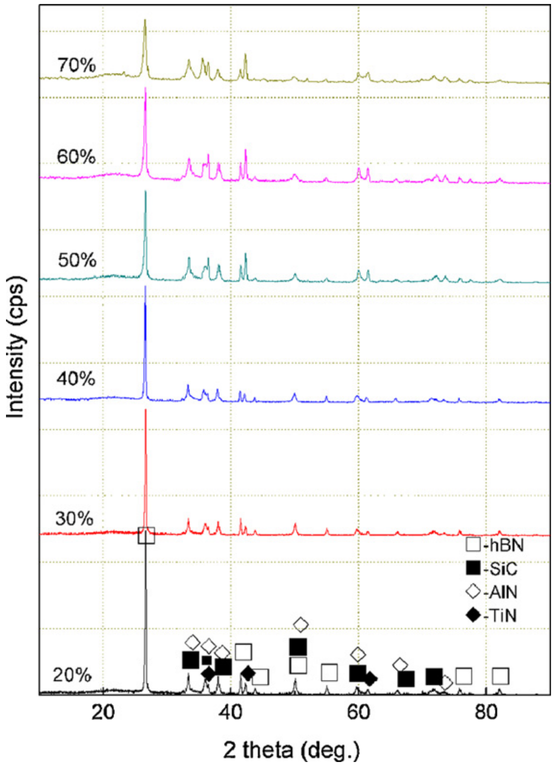

Fig. 1. XRD patterns of combustion products obtained under 100 MPa nitrogen pressure.

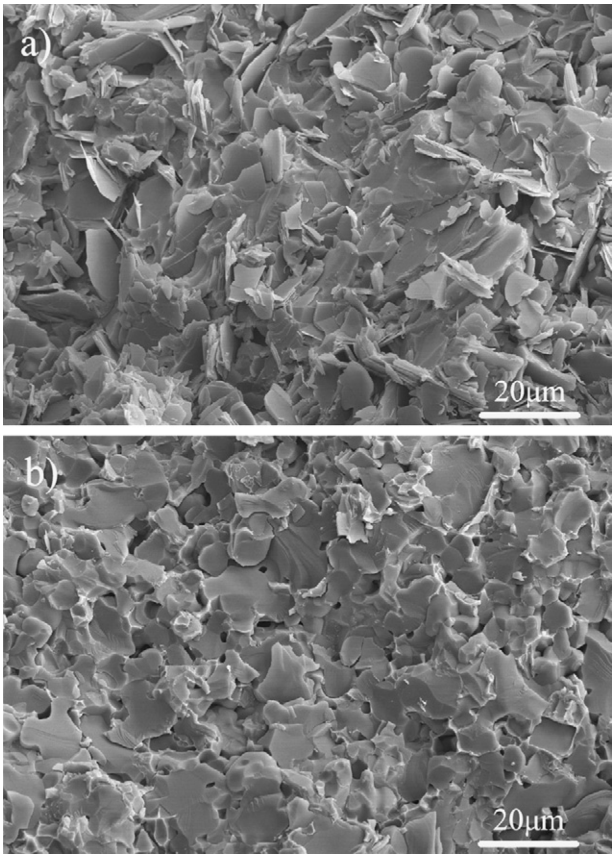

Fig. 2. Fracture morphology of samples with AlN–TiN of (a) 20 vol% and (b) 60 vol%.

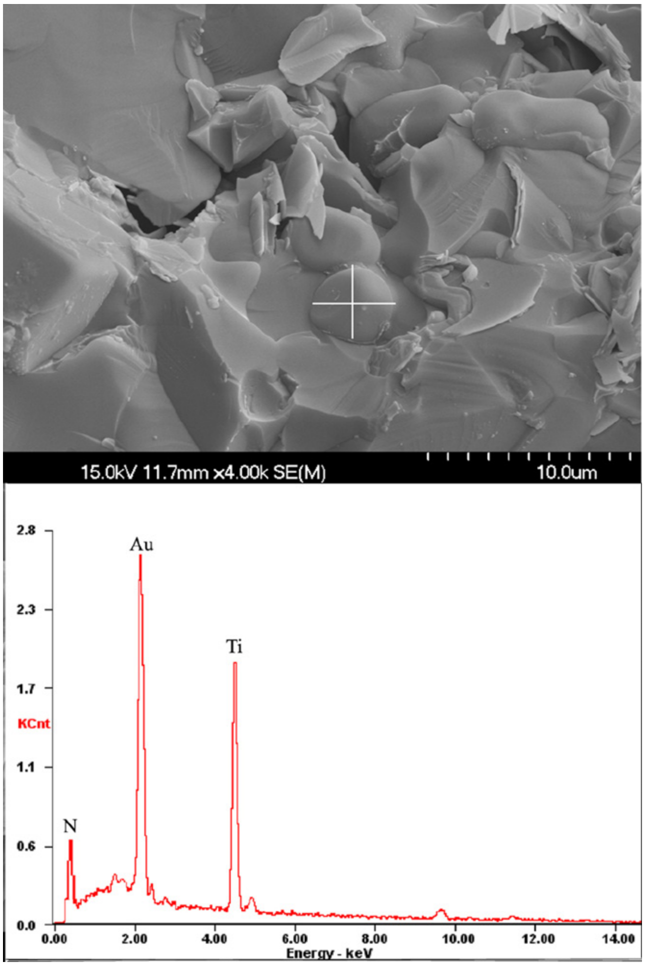

Fig. 3. SEM image of TiN grains in the sample with AlN–TiN of 70 vol%.

in thickness and more than 20 μm in diameter was observed, while AlN grains were segregated by large flake h-BN grains. With the increasing of AlN–TiN volume content, the AlN grains show the character of liquid-phase sintering. Meanwhile the content and the grain size of flake shape h-BN decreased. The h-BN grains were embedded partially in the AlN grains or grain boundaries at AlN–TiN volume fraction of 60% (Fig. 2(b)). This implies that flake h-BN effectively inhibited the grain growth of AlN and avoided abnormal grains so that h-BN–AlN ceramic composites possessed a relatively dense microstructure. SiC phase was dissolved into the AlN phase to form AlN–SiC solid solution, so SiC grains can hardly be seen. TiN grains presenting spherical shape were embedded thoroughly in the AlN grains, as shown in Fig. 3, which shows the good compatibility between AlN and TiN at elevated temperature.

3.2. *Mechanical properties*

Table 1 shows the relative density and microhardness of h-BN–AlN ceramic composites prepared by combustion synthesis with various content of AlN–TiN. Since the poor sinterability of the plate like h-BN particles, the relative density of the composites and Vickers hardness were relatively low, especially the volume fraction of AlN–TiN less than 50%. With the increasing AlN–TiN content in composites, the relative density and Vickers hardness of the composites increased. This can be attributed to the increasing content of high strength AlN–TiN phase. During the combustion synthesis process, molten Al filled up the pores in the green compacts, which resulted in higher relative density, and this helps improve the mechanical properties of the composites.

Table 1
Relative density and Vickers hardness of h-BN–AlN ceramic composites with different volume content of AlN–TiN.

Volume fraction of AlN–TiN (vol%)	Relative density (%)	Vickers hardness (GPa)
20	85.3	0.17 ± 0.02
30	86.2	0.18 ± 0.02
40	87.5	0.30 ± 0.01
50	90.5	0.65 ± 0.04
60	94.4	1.07 ± 0.08
70	95.5	1.18 ± 0.10

Fig. 4 shows the mechanical properties of combustion synthesized h-BN–AlN composites with different volume content of AlN–TiN. As expected, the flexural strength and fracture toughness increase obviously with the increasing volume content of AlN–TiN. A sharply improvement on mechanical properties was found when volume fraction of AlN–TiN was changed from 50% to 60%. This can be explained by the different main phase and crack propagation path in the composites. When volume fraction of AlN–TiN was less than 50%, h-BN was the main phase and controls the mechanical properties, and intergranular fracture was the major fracture mode. The improvement of mechanical properties was attributed to the increasing of the relative density of the composites. However, when AlN–TiN volume fraction was larger than 50%, AlN was the main phase and controls the mechanical properties. The fracture mode of the composites was transgranular fracture. Meanwhile, microcrack toughening introduced by weak BN phase and crack deflection caused by TiN particles resulted in the remarkable improvement on bending strength and fracture toughness of the h-BN–AlN ceramic composites.

3.3. *Thermal shock resistance*

Residual strength after thermal shock, as developed by Hasselman [18], is an important index to evaluate the thermal shock resistance for ceramics. The composites with AlN–TiN volume fraction of 30%, 50% and 70% were chosen in this study to valuate the thermal shock resistance by water quenching under different temperature.

Fig. 5 shows the residual flexural strength of h-BN–AlN composites as a function of thermal shock temperature. Results indicate that residual strength does not present evident change when critical thermal shock temperature Δ*T* was less than 600 °C. The Δ*T* as high as 670 and 850 °C were obtained by composites with

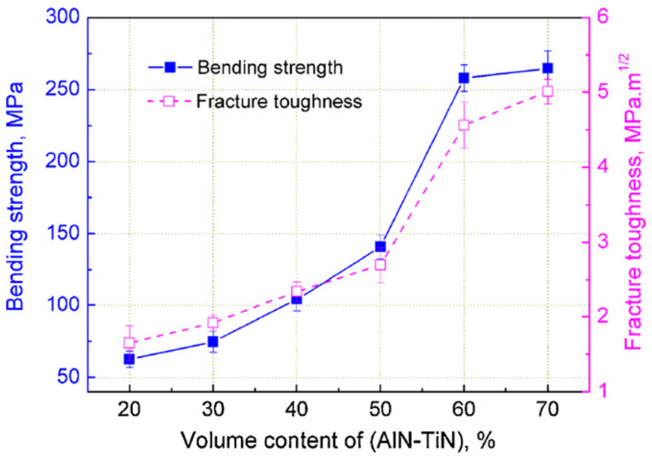

Fig. 4. Mechanical properties of combustion synthesized products.

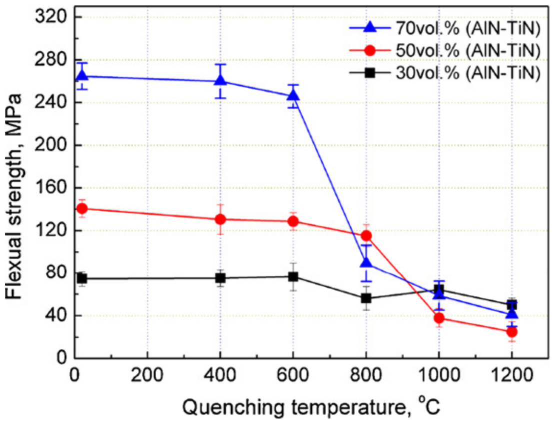

Fig. 5. Residual strength of h-BN–AlN composites as a function of thermal shock temperature.

AlN–TiN volume fraction of 70% and 50%, respectively, before losing more than 30% of their initial flexural strength. It is notable that ΔT of composites with AlN–TiN volume fraction of 30% was higher than 1200 °C, indicating excellent thermal shock resistance. It should also be noted that the composites with 30 and 50 vol% of AlN–TiN quenched above ΔT have a modest decrease of residual strength, while composites with AlN–TiN of 70 vol% seems to follow Hasselman's theory [18], which predicts *s* sharp decrease in strength at a critical thermal shock temperature difference.

Thermal stress fracture resistance can be expressed by R [19]:

$$R = \Delta T = \frac{\sigma_f(1-\nu)}{E\alpha} \qquad (2)$$

where σ_f is flexural strength, ν is Poisson ratio, E is the Young's modulus, α is thermal expansion coefficient. Higher values of R indicates greater resistance to fracture initiation during quenching. It can be found from Eq. (2) that higher E and α, by increasing the volume content of AlN–TiN, can lead to decrease thermal shock resistance. Thus h-BN–AlN composites with appropriate thermal shock resistance and mechanical properties can be fabricated through modulating of AlN–TiN volume content.

4. Conclusions

h-BN–SiC-AlN–TiN ceramic composites were prepared by combustion synthesis from the powder compacts of B_4C, Si, Al and TiN under high nitrogen pressure, and effect of volume content of AlN–TiN on the microstructure, mechanical properties and thermal shock behavior was investigated. With the increased content of AlN–TiN, the grain size of h-BN and AlN decreased, and the fracture mode of the composites transformed from intergranular mode to transgranular mode. The relative density and mechanical properties improved obviously as the AlN–TiN phase increased. Thermal shock test results showed that the composites with AlN–TiN content of 30, 50 and 70 vol% retained more than 70% of the initial strength for water quenching (20 °C) exceeding 1200, 850 and 670 °C, respectively. The h-BN–SiC-AlN–TiN composites with optimized properties can be fabricated by means of adjusting the AlN–TiN volume content.

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