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Fabrication of hexagonal boron nitride based ceramics by combustion synthesis^①

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[Abstract] Pure h-BN (hexagonal boron nitride) and h-BN based ceramic parts were fabricated by combustion synthesis technique, i. e. self propagating high temperature synthesis (SHS). Components were manufactured by the combustion reaction of 80 MPa nitrogen and the compact made by cool isostatic pressing. In h-BN based ceramic parts, h-BN powder was used as diluent and SiO₂ powder as reinforcing phase. The density of pure h-BN and h-BN-based ceramic parts were 58% and 78% of theoretical density, respectively. With XRD and SEM, phases and microstructures of ceramic parts were analyzed. Mechanical properties were also tested.

[Key words] ceramic; combustion synthesis; self propagating high temperature synthesis

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1 INTRODUCTION

Because atomic packing pattern in hexagonal boron nitride (h-BN) crystals is hexagonal close-packed structure similar to graphite, the properties of h-BN include low thermal expansion coefficient, high thermal conductivity and high resistance to thermal shock and corrosion. Therefore, h-BN can be applied to produce jacket of thermal couple, crucible, pipe, mold, electronic insulation components and parts used in high temperature situations. The traditional processes to produce h-BN parts include normal sintering and hot-pressing sintering^[1, 2].

The typical combustion synthesis, or self-propagating high-temperature synthesis (SHS), is the oldest and most famous "thermit reaction" which has been used in specialized welding and casting^[3~5]. In 1967, Merzhanov and his cooperators, the former USSR scientists, raised the concept of SHS and developed combustion synthesis. Compared with conventional ceramic process, the most obvious advantages of SHS primarily include^[6~9]:

1) the generation of a high reaction temperature which can volatilize low boiling point impurities and, therefore, result in higher purity products;

2) the simple exothermic nature of the SHS reaction avoids the need for expensive processing facilities and equipment;

3) the short exothermic reaction times result in low operating and processing costs;

4) the high thermal gradients and rapid cooling rates can give rise to new non-equilibrium or metastable phases;

5) inorganic materials can be synthesized and

consolidated into a final product in one step by utilizing the chemical energy of the reactions. These advantages make SHS an efficient and economic technique for the production of advanced ceramics.

Combustion synthesis of h-BN ceramics is based on the reaction of boron powder and nitrogen. The advantages are short operating time and low processing costs. This paper study the combustion process of B powder in nitrogen and the effect of h-BN diluent.

2 EXPERIMENTAL

2.1 Preparation of h-BN green compacts

Amorphous B powder (87.3% purity, Yingkou Fine Chemical Plant), h-BN powder (93.4% purity, 15 μ m, Yingkou Fine Chemical Plant) and SiO₂ powder (15 μ m, made by ourselves) were used in the experiment.

Amorphous B powder (30%) and h-BN powder (70%) were dry mixed by a ball mill for 16h. Mixed powders were sealed into a rubber bag and compressed by cool isostatic pressing in 10 MPa N₂. Cylindric green compacts had 48% porosity. With same process, green compacts composed of 50% B+ 40% h-BN + 10% SiO₂ and of 50% B+ 25% h-BN + 25% SiO₂ were made.

2.2 Preparation of h-BN based ceramic parts

The compact was put into a graphite canister with h-BN filling. The canister was placed into the reactor filled with 80 MPa nitrogen and cooled by water, as shown schematically in Fig. 1. Igniting agent was a mixture of Ti powder (50 μ m, 50%, mole fraction) and C powder (amorphous, 50%, mole

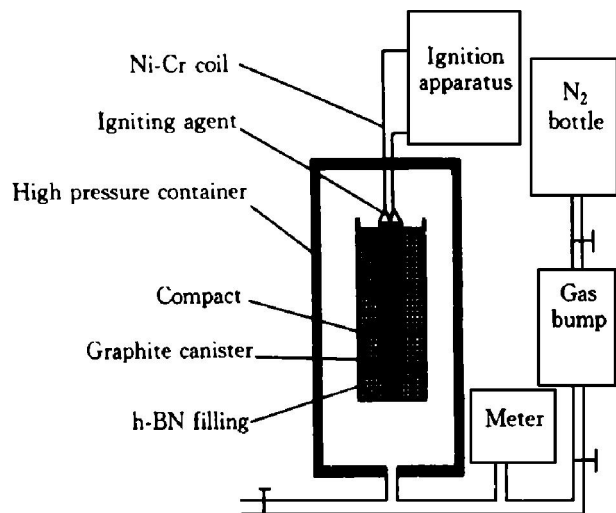


Fig. 1 Schematic representation of reactor with high pressure

fraction). The ceramics was prepared by SHS. Finally, the products were cut into cylindric parts.

2.3 Analysis on products

With XRD, phases of h-BN ceramic were analyzed. With SEM, fracture surfaces of h-BN ceramic were analyzed.

The products were cut into some samples 4 mm wide, 3 mm high and 40 mm long. The three-point bending strength of samples was tested with an Instron-1186 electron testing machine.

The apparent density was tested by Archimedes principle. Vickers hardness testing machine was used to test the Vickers hardness of samples.

3 RESULTS AND DISCUSSION

3.1 Analysis on phases and structure of h-BN parts

In combustion process, diluent is needed in order to lower the combustion temperature, decrease the quantity of liquid phase and make the reaction process complete. The diluent used in this experiment was h-BN powder. The influence of amount of h-BN on adiabatic temperature is shown in Fig. 2. According to Fig. 2, compacts can be ignited when h-BN powder is less than 80% and there is liquid phase in the reaction when h-BN powder is less than 70%. Because there is heat exchange with the environment, the combustion temperature is lower than the theoretical adiabatic temperature. The reaction of boron and nitrogen is expressed by



N_2 with low pressure is calculated by the perfect gas equation. The ratio of N_2 and B in unit volume is gained by

$$\beta = \left[\frac{\varphi}{1 - \varphi} \right] \frac{n_{N_2}}{n_B} = \left[\frac{\varphi}{1 - \varphi} \right] \frac{p}{RT} \frac{M_B}{\rho_B} \quad (2)$$

where β is the molar ratio of N_2 and B, n_{N_2} and n_B

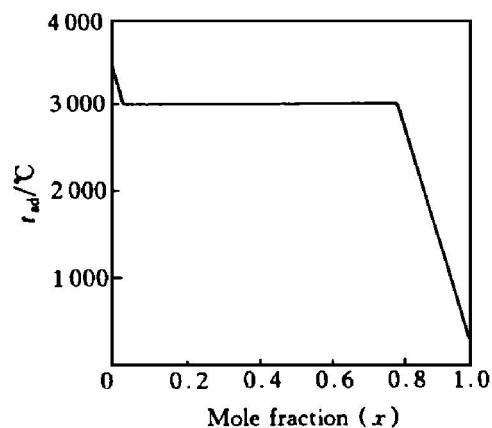


Fig. 2 Influence of h-BN diluent content on adiabatic temperature

are the quantities of N_2 and B in unit volume, p is the pressure of N_2 , R is the gas constant, T is the absolute temperature, φ is the initial porosity of the sample, M_B is the atomic mass of B and ρ_B is the density of B. As $\beta \geq 0.5$, the reaction is complete. As $\beta < 0.5$, N_2 is not enough and the reaction is not complete. By equation (2), β increases with increasing p and φ .

If there is diluent in the compacts and the pressure of N_2 is very high (80 MPa), equation (2) is modified as

$$\beta' = \left[\frac{\varphi}{1 - \varphi} \right] \frac{n_{N_2}}{(1 - c)n_B} \quad (3)$$

where c (mole fraction, %) is the content of diluent, n_{N_2} is given by van der Waals equation:

$$\left[p + \frac{a}{V^2} n^2 \right] (V - nb) = nRT \quad (4)$$

where a and b are van der Waals constants, for N_2 , $a = 0.139 \text{ L}^2 \cdot \text{MPa} / \text{mol}^2$, $b = 0.03913 \text{ L} / \text{mol}$. At room temperature, 80 MPa pressure, 45% porosity and without diluent, β' is about 0.5. Therefore, N_2 in the small pores is enough to make the reaction process complete.

After the compact has been ignited, there are inconstant combustion and cracks on the top. Then there is constant combustion. There are also inconstant combustion and cracks at the end of the compact because of increasing heat loss. In this experiment, the fillings of h-BN powder slow down the cooling velocity to avoid inconstant combustion and cracks, and the high pressure nitrogen provides reacting gas and makes products compact similar to hot isostatic pressing.

70% diluent content was used in the samples. XRD patterns are shown in Fig. 3(a). SEM pictures of fracture surfaces of final products are shown in Fig. 4(a). The samples were cut to $d 6 \text{ cm} \times 20 \text{ cm}$ columns with 58% theoretical density. The results show that the shape of h-BN grains are thin flakes. We can conclude that diluent makes B powder dis-

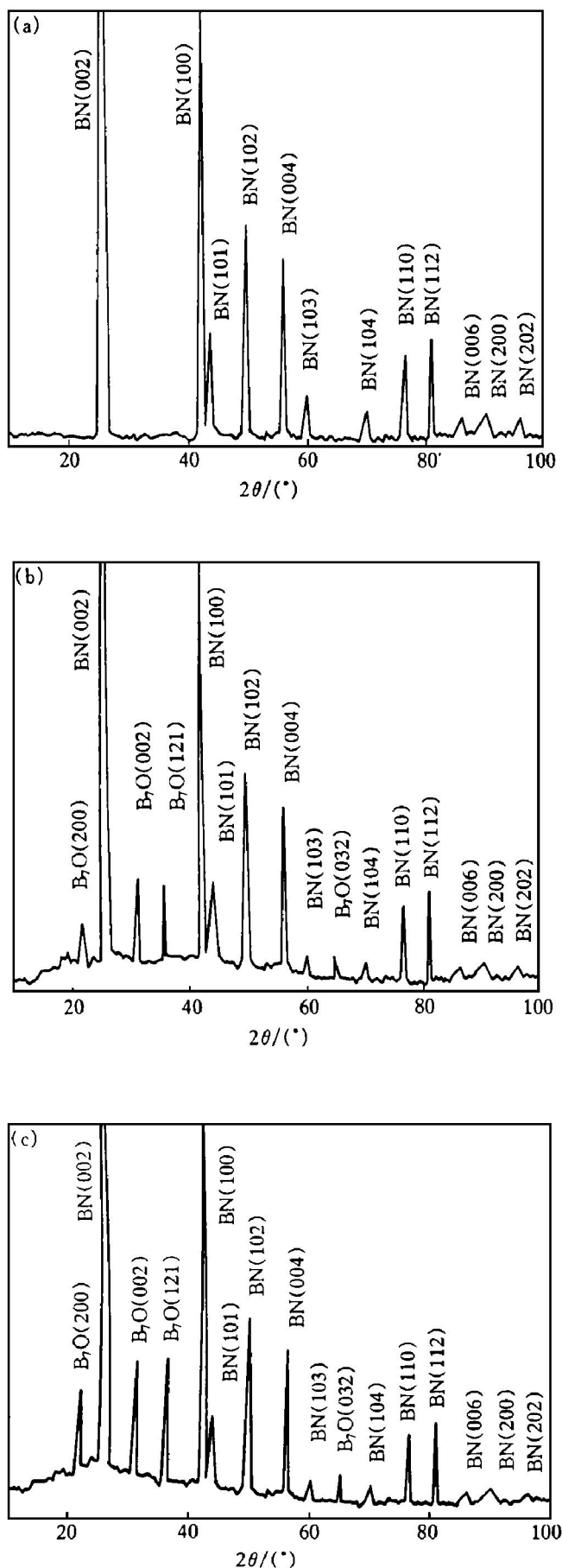


Fig. 3 XRD patterns of products

(a) —30% B+ 70% h-BN; (b) —50% B+ 40% h-BN+ 10% SiO₂; (c) —50% B+ 25% h-BN+ 25% SiO₂

perse highly to react with nitrogen completely.

The density, three-point bending strength and hardness of pure h-BN ceramics are 1.70 g/cm³, 39

MPa and HV 108, respectively.

3.2 Analysis on phases and structures of h-BN based parts

In h-BN based composite, SiO₂ additive was added into compacts to reinforce the parts. XRD patterns are shown in Figs. 3(b) and (c). SEM pictures of fracture surfaces of final products are shown in Figs. 4(b) and (c). The samples were cut to $d 6 \text{ cm} \times 20 \text{ cm}$ columns with 78% theoretical density. We can conclude that adding SiO₂ additive can increase the relative density of the parts because the liquid phase fill the space among h-BN powder during the combustion process.

After the combustion process, the melted SiO₂ phase becomes non-crystal because of large cooling rate. Therefore, there are no SiO₂ diffraction peaks in the XRD patterns. Compared with the XRD patterns of pure h-BN, the XRD patterns of h-BN + SiO₂ have higher background. The higher the SiO₂ content is, the higher the background is. In the samples added with SiO₂ additive, there is B₇O phase whose content increases with increasing SiO₂ content because B powder reacts with the melted SiO₂ phase. In this experiment, there is a layer of translucency which is B₂O₃ on the surface of the samples added with 25% SiO₂ additive. It can be deduced that there are some reactions between B and the SiO₂ phase. Therefore, the reactions between B and the additive phase should be thought over before deciding which additive and how much content are used.

From the macro appearance, the samples added with 10% SiO₂ are more uniform than those added with 25% SiO₂. There is more h-BN diluent in the former, so B powder is dispersed more highly and the structure of the final products is more uniform. There is more SiO₂ additive and less h-BN diluent in the latter, so there are h-BN concentrated fields where some white spots can be seen in the appearance of the samples. Both of them have the same strength. SEM results showed that SiO₂ additive decreases grain size. The reason is that SiO₂ liquid phase hinders the growth of h-BN grains. Contrarily, the grains in pure h-BN samples grow easily. With increasing additive content and the same B content, h-BN content decreases and there are uneven structures in the samples. In the uneven structure, some grains are thin and the others very big, which can be seen from the microstructures.

The color of the pure h-BN samples is white, and that of the h-BN based samples is grey.

The density, three-point bending strength and hardness of h-BN based composite are 1.79 g/cm³, 79 MPa and HV 212, respectively. Compared with the pure h-BN samples, the h-BN based ceramics has high strength because of SiO₂ additive.

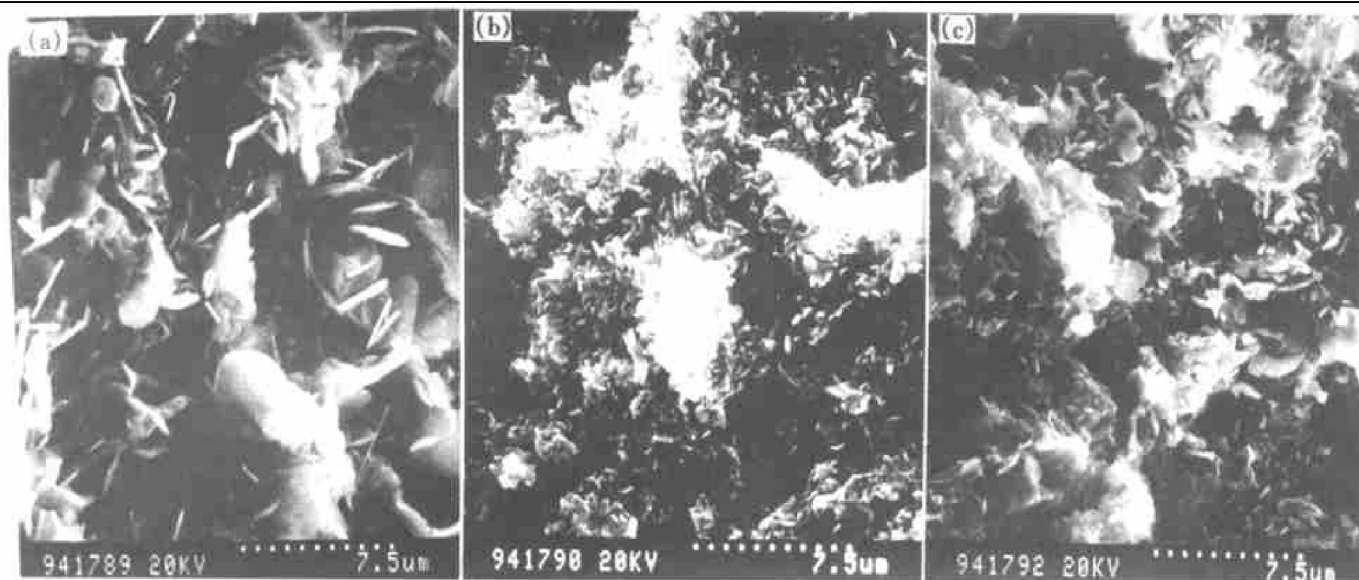


Fig. 4 SEM pictures of fracture surfaces of final products
(a) —30% B+ 70 h-BN; (b) —50% B+ 40% h-BN+ 10% SiO₂; (c) —50% B+ 25% h-BN+ 25% SiO₂

4 CONCLUSIONS

Pure h-BN ceramics and h-BN based ceramics could be prepared by combustion synthesis technique through the reaction of compacts with N₂ (80 MPa). Compacts for pure h-BN ceramics were composed of h-BN diluent (70%, 15 μm) and amorphous B powder. The relative density of compacts was 48% and the relative density of h-BN ceramic parts was 58%. Compacts for h-BN based ceramics were composed of h-BN diluent (15 μm), amorphous B powder and SiO₂ additive. The relative density of compacts was 48% and the relative density of h-BN-based ceramic parts was 78%. The h-BN diluent added into the compacts can lower the combustion temperature, and the SiO₂ additive can decrease the grain size, increase the relative density and reinforce the parts.

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