

Fabrications, microstructure and mechanical behaviors of h-BN matrix ceramic

XIAO-JU GAO^{a,b*}, CONG ZHANG^b, ZHI-PENG LI^b, JIAN-WU CAO^b, DONG-MING YAN^{b,c}, WEI-MING LI^{b,c}, DA-JI LI^b, MING-JUN GU^b

^aScience and Technology on Thermostructural Composite Materials Laboratory, Northwestern Polytechnical University, Xi'an 710072, China

^bNo. 52 Institute of China North Industry Group, Yantai 264003, China

^cYantai Jinli New Materials Co., Ltd

Turbostratic boron nitride (t-BN) powders have been synthesized through reactive sintering process using B and N₂, h-BN matrix ceramic has been sintered using the obtained t-BN powders and the commercial h-BN as raw materials and Al₂O₃/Y₂O₃ as sintering aids. The compositions, morphologies, porosity, and mechanical properties of the as fabricated composites were investigated. The results show that after sintering at 1850°C for 2 h, the unique uniform with card-house structure of h-BN was observed. The combination effect of sintering-aids densification and card-house structure densification is the main mechanism which controls the microstructure evolution of h-BN. When the reactive synthetic temperature of t-BN is 1350°C for 2h, the Al₂O₃/Y₂O₃ ratio is 3: 2 and total contents of sintering ads is 15wt%, the porosity and flexural strength of the sintered body reaches the optimum, respectively.

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1. Introduction

Hexagonal boron nitride (h-BN) and related composites have unique chemical and physical properties, such as good dielectric properties, lower relative permittivity and dielectric loss angle, low density, high melting point, high thermal conductivity, excellent manufacturability owing to its layered structure similar to that of graphite, and corrosion and oxidation resistance [1-5]. Nowadays, they are widely used in aerospace, metallurgical, refractory, lubricants, and chemical engineering [6-9]. However, it is difficult to be densified by traditional sintering techniques owing to its strong covalent bonds. The addition of sintering aid and reactive sintering are one of the most effective methods to solve this problem. In recent years, SiO₂/BN [10], Al₂O₃/BN [11], ZrO₂/BN [12], AlN/BN [13,14] and Sialon [15,16] composites have been developed. But the mechanical properties and thermal shock resistance of these composites could not satisfy the requirements of hypersonic aerospace vehicles. Reactive sintering is through chemical reactions to complete the synthesis of composition, are still attracting researchers' attentions.

Al₂O₃/Y₂O₃ ceramics have been regarded as one of the most promising ceramics in the future due to their high strength, outstanding corrosion resistance and excellent high-temperature properties [17]. Meanwhile, with the addition of Al₂O₃/Y₂O₃ combined with sintering process,

self-toughening card-house structures can be formed to enhance the toughness and flexural strength, therefore the thermal shock resistance of BN composites could be improved [18,19].

In the present work, h-BN matrix ceramic was fabricated with the addition of Y₂O₃/Al₂O₃ as sintering aids. The process and mechanism of reactive synthesizing t-BN powder was studied, the microstructures and mechanical properties of the obtained h-BN matrix ceramic have been discussed.

2. Experimental

The samples were made of h-BN matrix ceramic. The method of processing the samples is as shown in Fig. 1. The starting B powder (mean particle size < 3 μm, pureness > 95%, Dandong Chemical Industry Institute, China) and N₂ (high purity) were used for reacting to synthesize the t-BN powder, the commercial hexagonal boron nitride (High Purity, Dandong Chemical Engineering Institute, China) were selected for matrix materials. The B powders were drying ball-milled with agate balls for 12 h in a plastic bottle and then sieved (mesh 200) for the next steps. The obtained t-BN and commercial h-BN powder with Y₂O₃ (Fine Grade, Shanghai Junyu, China) and Al₂O₃ (Fine Grade, Shanghai Junyu, China) used as the sintering additives was

ball-milled in methanol for 24 h using agate balls as media. After being dried, crushed and screened through a 200 mesh sieve, the powder was compacted by die-pressing (SL-45, Shanghai Mechanics, China) at the pressures of 200 MPa. Sintered body was obtained in a graphite resistance furnace at 1850 °C for 2 h.

In order to analyze the reactive sintering mechanism, TG-DTA analysis (SDT Q600 Type, TA Co., America) was conducted from room temperature (RT) to 1500°C (limited by apparatus) at a heating rate of 10°C/min in flowing high purity nitrogen. X-ray diffraction analysis (XRD-6000, Hitachi Co., Japan) using Cu Ka radiation was conducted to determine the phase compositions of the obtained samples after crashed to powders. Microstructures of the fracture surfaces of the reacted compacts were observed by scanning electron microscopy (SEM, S-570, Hitachi, Japan) at 15 kV.

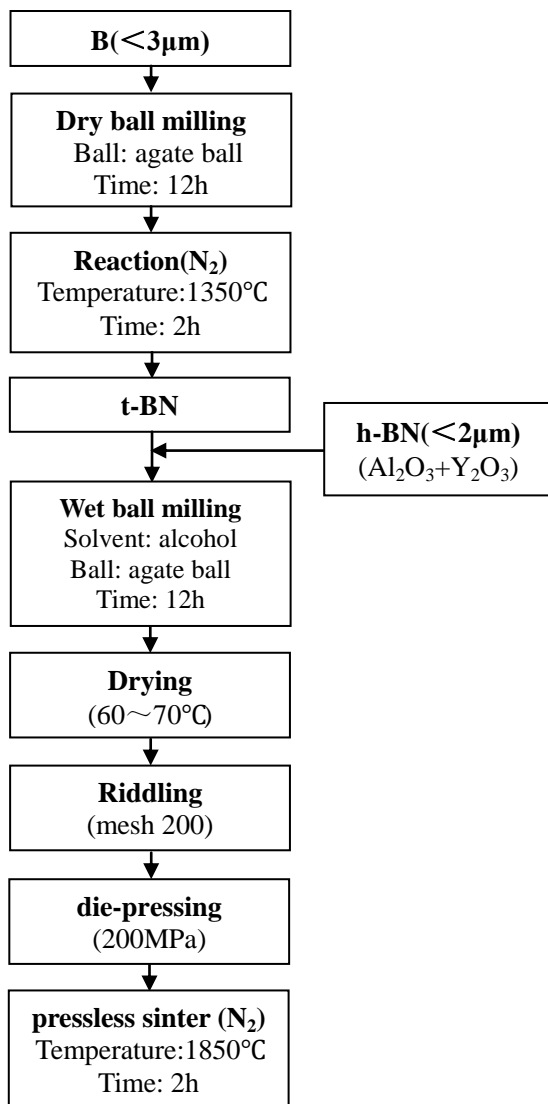


Fig. 1. Preparation of BN matrix ceramic.

The sintered samples were machined into rectangular specimens of 3 mm (thickness) × 4 mm (width) × 20 mm

(length), one surface perpendicular to thickness was polished and the edges of the bar were chamfered to minimize failures. Porosity was determined by Archimedes water-displacement method. Flexural strength was determined by three-point bending test at a support distance of 16 mm and a cross-head speed of 0.5 mm/min (Instron 1195, Instron, UK) with the polished surface as the tension side.

3. Results and discussion

3.1. Reactive sintering mechanism analysis

The reactions in the sintering, the standard Gibbs free energy was adopted as the thermodynamics basic criterion. The main reactions are shown as follows:

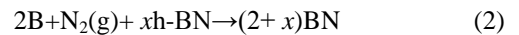


Fig. 2 showed the TG-DTA results. From the DTA curves we can see that there is apparent endothermic and weight increment peak for boron in N₂ atmosphere. This result is related to the reaction of boron and N₂ as showed in equation (1).

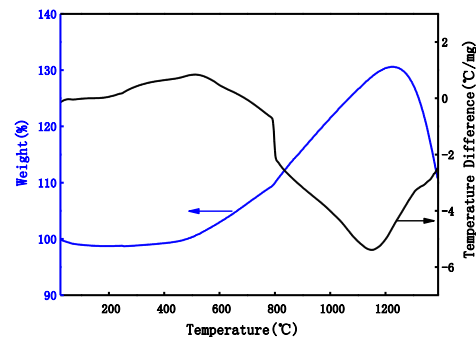


Fig. 2. TG-DTA curves of B in N₂.

Consequently, the final products that could be present in the composite from the reactions mentioned above are uniformed BN. The typical XRD results of the powder compacts soaked at different temperatures for 120 min shown in Fig. 3. The peaks of t-BN appeared from 1150°C, indicating the reaction started at this temperature. The reaction completed at around 1350°C. At this area, the B powder gradually reacts completely, and turbostratic-type t-BN with low crystallinity is formed. Here, t-BN can be regarded as semi-crystalline h-BN with an ordered inlayer and disordered interlayer structure [20]. When the sample was soaked at 1550°C, new crystal planes of h-BN appeared, this process is referred to as the meso-graphitic stage [21]. As the result, the t-BN can be obtained at the temperature of 1350 °C for 2h.

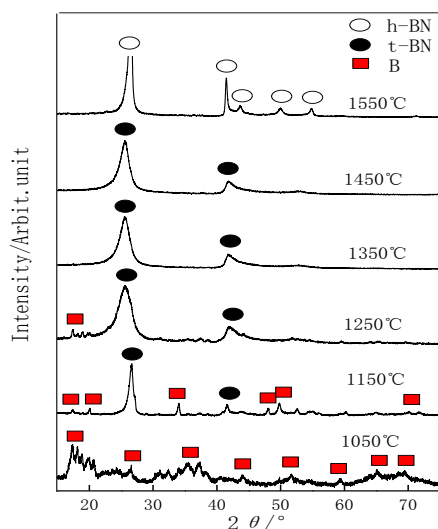


Fig. 3. XRD pattern of reactive sintering BN.

3.2. Microstructure analysis

The SEM images of as obtained samples after reactive sintering are shown in Fig. 4. Almost no card-house structure in Fig. 4(a) and the particles with diameter of about 1 μm was obtained. With the increase of the temperature, card-house structure gradually formed. While the specimen sintered at 1750 $^{\circ}\text{C}$ consisted of card-house structure grains in part. At 1850 $^{\circ}\text{C}$, the microstructure became more uniform and adopted a compact arrangement with card-house structure. As the result, the optimal temperature in this work can be 1850 $^{\circ}\text{C}$.

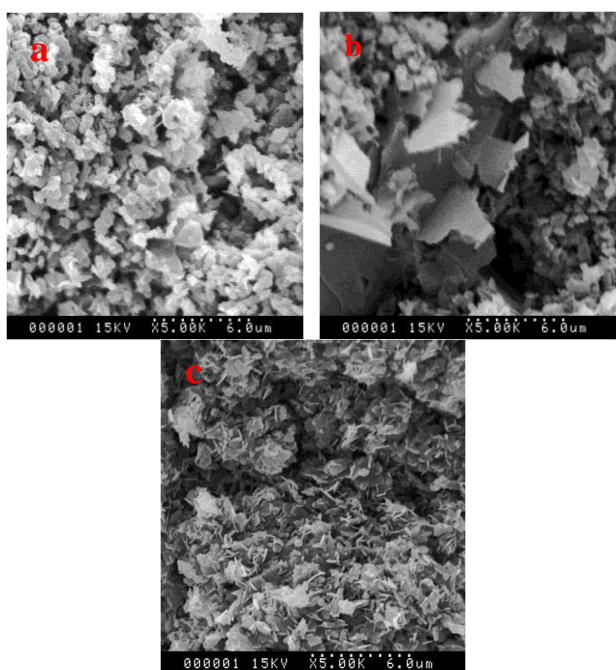


Fig. 4. SEM images of as obtained samples (a) 1650 $^{\circ}\text{C}$; (b) 1750 $^{\circ}\text{C}$ and (c) 1850 $^{\circ}\text{C}$.

Fig. 5 showed the SEM images of h-BN samples with sintering aids of 5 wt%(a), 15 wt%(b) and 20 wt%(c). It can be demonstrated that the sample with 15 wt% sintering aids has better microstructure compared with other samples. The card-house structure in Fig. 5(b) is more uniform than others. That because when the containing of Y_2O_3 and Al_2O_3 is 15wt%, they can efficiently stop the BN layer expansion, and is good for the structure unified. However, with continuous increase of sintering aids, a partial aggregation appeared and forms the blocks (Fig. 5(c)) resulting in the brittleness and low material strength.

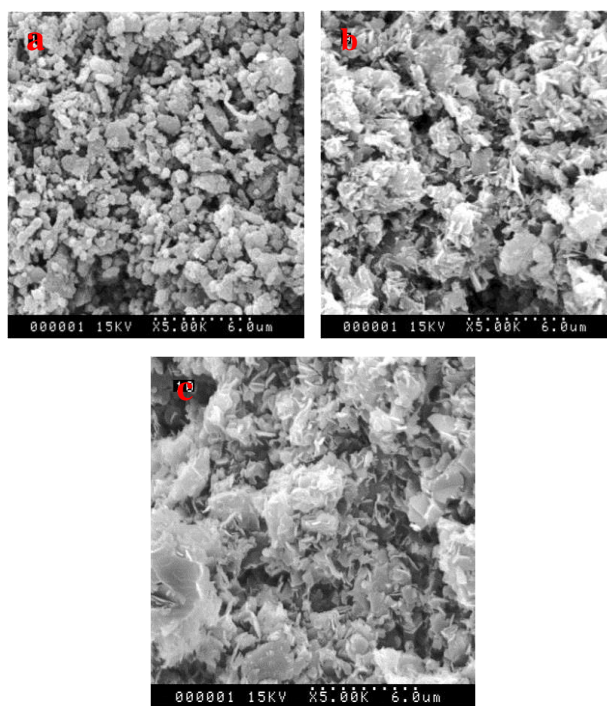


Fig. 5. SEM images of h-BN samples with sintering aids of 5%(a), 15%(b) and 20%(c).

3.3 Porosity and Flexural strength

Fig. 6 shows the samples' strength and the porosity sintered at 1850 $^{\circ}\text{C}$ for 2h, with different ratio ($w(\text{Al}_2\text{O}_3):w(\text{Y}_2\text{O}_3)$ is 3:1, 3:2, 1:1 and 2:3 respectively) of sintering ads. As can be seen, the total amount of sintering aids is 5wt%, with an increase in the proportion of Y_2O_3 , the strength increases and porosity decreases. And when the ratio is about 3: 2, the strength of the samples is higher. However, with the continuous increase in the proportion of Y_2O_3 , the samples' strength decreases and porosity increases.

This is because with the increase in the proportion of Y_2O_3 , lowest eutectic point temperature of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ system is reduced, increasing the proportion of yttrium aluminate, the yttrium aluminates melting liquid phase and promote the rearrangement and material migration of h-BN particles, thereby obtaining the sintered body with a relatively low porosity. However when the Y_2O_3 content is more over, insufficient liquid yttrium aluminate generated,

leading to an incomplete densification process, then the strength of the material decreases and the porosity increases.

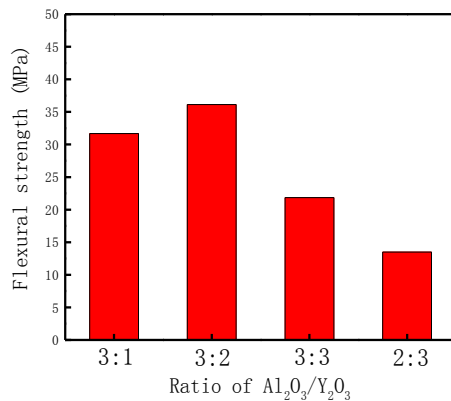
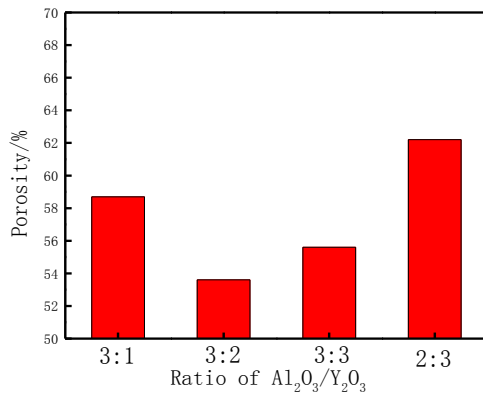


Fig. 6. Effect of proportion of sintering additives on the strength and porosity of the sample (the total content of sintering additives is 5wt%).

Fig. 7 shows the samples' strength and the porosity sintered at 1850 °C for 2h, with different content (5%, 10%, 15% and 20%) of sintering aids when the ratio of Al₂O₃/Y₂O₃ is 3:2. As can be seen, with increasing the content of sintering aids, the strength increases and porosity decreases. And when addition of the sintering aids is 15wt%, the strength of the samples is higher. However, with the continuous increase of sintering aids, the samples' strength decreases and porosity increases. This may be because more over sintering aid can lead to excessive liquid, grains agglomerate and form large blocks to connect to each other, causing a higher porosity and an uneven distribution of pores, therefore the strength is lower, meanwhile less content of sintering aids will not be well to promote the sintering process.

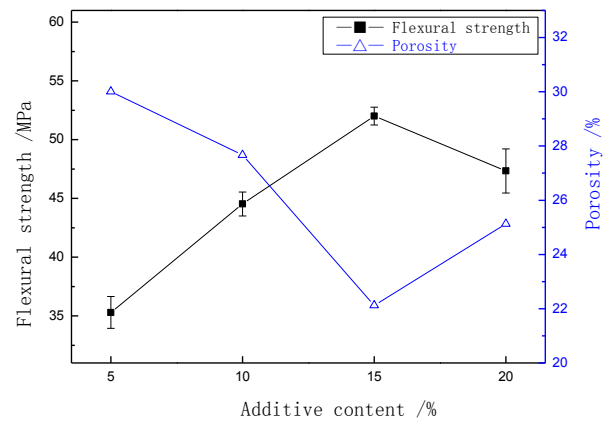


Fig. 7. Effect of sintering aid content on the properties of samples (1850 °C×2h).

4. Conclusions

- (1) As the result, the t-BN can be obtained at the temperature of 1350 °C for 2h.
- (2) At 1850 °C, the microstructure became more uniform with card-house structure.
- (3) The optimized ratio of Al₂O₃/Y₂O₃ was 3:2, and the optimized addition of sintering aids is 15wt%. At this conditions, sufficient liquid could be formed in the process of pressless sintered h-BN, which promotes the orientation arrange and sintering of h-BN particles.

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*Corresponding author: gxjg2933@163.com