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Preparation of submicron boron carbide at a high heating rate

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Abstract. Organosol gel technology is a research hotspot of low-temperature synthesis of ultrafine boron carbide powders at this stage. Based on this technology, trimethyl borate is directly used as a pyrolysis material, which eliminates the process of forming a gel and simplifies the operating procedures. During the experiment, the reaction temperature and heating/cooling rates played a significant role in developing uniform submicron boron carbide powders. In this paper, uniform submicron-sized boron carbide was prepared at a high temperature of 1600℃ and a rapid heating rate of 400℃/min. The ratio of the particle size distribution to 1 μm or less was 91%.

1. Introduction
Boron carbide (B₄C) as a neutron absorbing material has a broad neutron capture energy spectrum, can accommodate helium generated by irradiation, does not form strong secondary radiation, and its nuclear wastes are easy to handle[1]. These advantages over other materials attribute to its wide usage in the nuclear industry. For example, the fast-neutron breeder reactor uses sintered boron carbide pellets as control rods [2]. However, boron carbide is a ceramic material with strong covalent bonds, so its sintering property is reduced. To obtain a higher sintered density, the average particle size of boron carbide powders is less than 1 μm [3].

At present, the preparation of boron carbide mainly includes the carbothermal reduction [4]-[7], self-propagating magnesium reduction [8]-[9], direct synthesis [10]-[12], organosol gel [13]-[15], chemical vapor deposition [16]-[18] and many other components. Among them, the carbothermal reduction has achieved industrialization. However, the obtained boron carbide powders have a large particle size (20-40 μm), ball milling or other pulverization methods are required to prepare boron carbide powders as are necessary for sintering. The manufacturing process is complicated, and the purity of the products is not high. Organosol gel method is the focus of research on the low-temperature synthesis of boron carbide. The essence of the technique is to introduce boron atoms into the organic carbon structure, forming B-O-C bonds to achieve molecular-level mixing of raw materials, thereby lowering the reaction temperature, preparing ultrafine powders. However, boric acid is difficult to form a gel with organics, the yield of this method is low [15],[19], so the technique is still in the laboratory research. In contrast, trimethyl borate itself contains B-O-C bonds, eliminating the need to form a gel process, significantly reducing the operational steps, as shown in figure 1. Therefore, this paper attempts to directly use trimethyl borate as a pyrolysis material to study the optimal conditions for preparing uniform submicron-sized boron carbide.
2. Experimental

The rate of temperature during the reaction has a significant influence on the formation of a uniform fine boron carbide. Due to the limited heating/cooling capability for the tube furnace used (the maximum heating rate can only reach 20°C/min), this experiment designed a corundum micro-reactor to achieve a high heating rate (about 400°C/min). Figure 2 shows a schematic of the reactor. The device consists of a corundum tube with inner diameter of 6 mm, connects the open end of the corundum tube to a T-shaped form to provide a feed (Ar and trimethyl borate) inlet (through another fine corundum tube with an inner diameter of 1 mm) and the gas products’ outlet. Since trimethyl borate is easily decomposed at low temperatures, the experiment used a two-step method: firstly, the micro-reactor was inserted into the furnace tube, and the high-purity Ar was purged. When the tube furnace was preheated to 850°C, the carrier gas Ar and the raw material trimethyl borate were introduced for reaction, and the products were deposited on the bottom of the corundum tube. Secondly, the micro-reactor was removed, and the tube furnace was heated to 1600 °C. Then the micro-reactor was directly pushed into the hot zone to obtain a high-speed heating rate. After the reaction completed, the micro-reactor was quickly withdrawn. The corundum tube was washed with ethanol, and the products were dissolved in ethanol, then dried to obtain the final products.

The pressure changes during the reaction were monitored using an Y-YBS precision digital pressure gauge (by Huai’an Tianyi Instrument Co., Ltd.). The final products were analyzed by X-ray diffraction (Bruker, D8 advance) and Fourier transform infrared spectroscopy (Thermo, Nicolet iS10) for the phase identification. Besides, boric acid content was titrated by automatic potentiometric titrator (Mettler Toledo, T5). After gold spraying, the morphology of the products was analyzed by a cold field emission scanning electron microscope (Hitachi, Japan, S4800). And the particle sizes were characterized using a laser particle size analyzer (HORIBA LA-950).

Figure 1. Comparison of organosol-gel technology and trimethyl borate pyrolysis experiment.
3. Results

3.1. Impacts of the first step pyrolysis temperature

It has been documented that trimethyl borate is stable at 470℃ [20]-[21]. Based on the limitation of the minimum operating temperature of the high-temperature tube furnace, this study selected 650, 750, 850, and 950℃ as the temperatures of the first step of pyrolysis. In the experiment, the flow rate of Ar was controlled at 3-3.5 mL/min, and the feed rate of trimethyl borate was set to 4 mL/h. Exhaust gases were discharged into the air after being absorbed by water. When the temperature reached 650 ℃, the number of bubbles in the absorption bottle was small, and the pressure inside the tube had not changed substantially, as shown in figure 3. However, there was a phenomenon of sucking up indicating that the reaction temperature was low and trimethyl borate could not be completely reacted. When the temperature reached 750 ℃, both the number of bubbles and the pressure increased. But there was a bright white mist at the outlet end instead of depositing at the bottom of the corundum tube. After testing, the substance sticking to the wall of the outlet pipe was boric acid. It was inferred that the reaction temperature was lower, resulting in a slower reaction rate, and the reaction could not be completed entirely within this heating interval. When the temperature reached 850 ℃, the number of bubbles further increased, so do the pressure inside the tube, but no white mist appeared at the outlet end. The temperature also increased to 950 ℃, the pressure inside the tube suddenly went up and down, after 1 h feeding, the pressure rose linearly (not shown in the figure), and the internal corundum gas conduit was blocked. This indicated that the reaction temperature was too high and the products were deposited in the corrugated gas conduit (inner diameter of 1 mm), causing clogging and inability to continue feeding.
Figure 3. Pressure variation in the tube at different temperatures.

The change in pressure was mainly caused by the gas generated by the reaction. The entire reaction process was not sealed, but open, so the pressure changes were minimal and could only be compared through the overall trend. At the beginning of the reaction, the pressure changed considerably. When the reaction proceeded for some time, the amount of the solid product carbon would affect the feed rate more or less, so the pressure dropped.

3.2. Analysis of the first step pyrolysis products
The reaction temperature was set at 850°C, and the first pyrolysis product was mainly concentrated at the bottom of the corundum tube. Depending on the shape of the corundum tube, the first step pyrolysis products were cylindrical, and the products were deposited from the outside to the inside. Compared to the solid phase reaction mechanism of the gel process, the reaction proceeded more thoroughly, the products were more homogeneously mixed and was more suitable for industrial production. Figure 4 shows the XRD analysis of the first-step pyrolysis products with a broad peak; the main reason is that the products are mostly amorphous and the amorphous form of the reaction is also generally larger than the crystal of the same substance. There is a sharp diffraction peak consistent with the position of the boron oxide standard card PDF#06-0297 at 28°; and no distinct carbon diffraction peak appears in figure 4, but the products are black, so it is inferred that the carbon in the products is mainly amorphous carbon, which is not detected. Figure 5 is a comparison of the Fourier transform infrared spectrum of the products at 850 °C with pure boric acid. As seen in figure 5, the absorption peaks attributed to boric acid, mainly, the intense bands of O-H stretching (3224 cm⁻¹), B-O stretching (1472 cm⁻¹), and B-O-H deformation (1195 cm⁻¹) vibrations, further illustrating that also contains a certain amount of boric acid [22].
Figure 4. XRD pattern of the first-step pyrolysis products obtained by reaction at 850°C for 4 h.

Figure 5. The infrared spectrum of the pyrolysis products at 850 °C: (a) infrared spectrum of pyrolysis products at 850°C; (b) infrared spectrum of pure boric acid.

The first-step pyrolysis product was cylindrical, to facilitate scanning, it was divided into two along the axial direction. Figure 6 presents SEM images of the first-step pyrolysis product. Because boric acid is readily soluble in water, wherein (b) is a micrograph of the same product after washing with hot water for 40 seconds. Time period should not be too long, because the carbon produced will be dispersed into small particles in water. In figure 6(b), one can see that boric acid is scattered over the carbon base. This form is more closely mixed than direct mixing of boric acid and carbon powder in industrial production. Moreover, the product is produced layer by layer by gas phase cracking, and it is expected to achieve a more uniform distribution of boric acid and carbon by the reaction ratio in the transverse and longitudinal directions.
Figure 6. SEM images of 850 °C pyrolysis products: (a) untreated; (b) treated with hot water.

3.3. Impacts of the second step reaction temperature and time

The experiment used the same batch of raw materials to react at 1400 °C and 1600 °C respectively. The flow rate of Ar was controlled at 1 ml/min. During the process, the pressure changes at different reaction temperatures were recorded with a precision digital pressure gauge. It can be seen from figure 7 that the higher the reaction temperature, the faster the pressure changes, and it can quickly return to the background pressure. During the reaction, the heat and total reaction time have a leading role in the formation of products morphology (including uniformity). The higher the reaction temperature, the faster the reaction rate. However, at high temperature, the longer the reaction time, the more severe the agglomeration of the products. Therefore, the experiment accurately controlled the reaction time by pressure changes. It is apparent from figure 7 that the reaction was completed when the reaction temperature of 1600°C was maintained for 20 minutes.

Figure 7. Pressure changes at different reaction temperatures and reaction times.

The experiment was carried out at 1600°C for 20 min, and products were analyzed by XRD. Figure 8 shows that the products coincide with the position of the diffraction peak of the boron carbide standard card PDF #35-0798, indicating that the products are boron carbide.
The particle size distribution of boron carbide powders formed in this study is shown in figure 9. As seen in this plot, boron carbide particles exhibited a bimodal size distribution with 91% of the particles (D90) in the size range of 0.15-1.00 μm. About 60.87% of powders had particles with a size range from 455 to 877 nm.

4. Conclusions
In this paper, boron carbide was prepared by using trimethyl borate as a pyrolysis feedstock. Since the raw material itself contained the B-O-C bond, it was no longer necessary to prepare it separately. In the experiment, the pyrolysis products of trimethyl borate at 850 °C were mainly boron source and carbon. The reaction temperature and total reaction time in the subsequent carbothermal reduction process were found to have a dominant effect on the formation of product morphology (including the uniformity). The higher the reaction temperature, the faster the reaction rate. The process is dominated by the nucleation rate, whereas boron carbide particles of uniform size are readily formed. And at the same reaction temperature, the longer the reaction time, the more likely it is to cause the agglomeration of product particles. In this paper, a uniform submicron-sized boron carbide was obtained at 1600°C at high heating/cooling rate of 400 °C/min rapid, and the proportion of the product size below 1 μm reached 91%.
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