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New Borothermal Reduction Route to Synthesize Submicrometric ZrB_2 Powders with Low Oxygen Content

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The ZrB_2 powders with submicrometric particle size and low oxygen content were synthesized by a new borothermal reduction route using ZrO_2 and excess boron as raw materials. The conventional process only contained the borothermal reduction of ZrO_2 with boron at 1550°C. By exploring the mechanism of ZrB_2 particle coarsening during conventional process, a new borothermal reduction route was proposed. This route included the borothermal reduction of ZrO_2 with boron at 1000°C, washing by hot water, and the removal of residual boron oxides at 1550°C, namely, two-step reduction plus intermediate water-washing (RWR). Using conventional process, the particle size and oxygen content of ZrB_2 powder were about 2–3 μm and 0.68 wt%, respectively. Based on the new route, the particle size and oxygen content of ZrB_2 powder were about 0.4–0.7 μm and 0.40 wt%, respectively.

I. Introduction

Due to its high melting temperature, high strength, high thermal and electrical conductivity, ZrB_2 is especially promising for high-temperature structural applications, such as cutting tools, thermal protection structures for hypersonic vehicles, and molten metal crucibles.[1,2] Currently, the ZrB_2 powder can be mainly obtained by the following synthesis routes: direct reaction of elemental precursor powders [reaction (1)],[1] self-propagating high-temperature synthesis [reaction (2)],[3] polymer-precursor route,[4] carbothermal reduction method [reaction (3)],[5] borothermal reduction method [reaction (4)],[6,7] and boro/carbothermal reduction method [reaction (5)].[8,9] To limit the introduction of carbon or metal impurities, the borothermal reduction method is the most interesting way.

$$Zr(s) + 2B(s) \rightarrow ZrB_2(s) \quad (1)$$

$$ZrO_2(s) + 2H_3BO_3(s) + 5Mg(s) \rightarrow ZrB_2(s) + 5MgO(s) + 3H_2O(l) \quad (2)$$

$$ZrO_2(s) + B_2O_3(s) + 5C(s) \rightarrow ZrB_2(s) + 5CO(g) \quad (3)$$

$$ZrO_2(s) + 4B(s) \rightarrow ZrB_2(s) + B_2O_2(g) \quad (4)$$

$$2ZrO_2(s) + B_4C(s) + 3C(s) \rightarrow 2ZrB_2(s) + 4CO(g) \quad (5)$$

The particle size is the first important factor assessing the characteristics of ZrB_2 ceramics. Ultra-fine powders can increase the driving force for sintering and can improve the densification behavior. To reduce the particle size of commercial ZrB_2 powder, ball milling and attrition milling are often carried out before sintering. These processes could effectively reduce the particle size. At the same time, however, they also introduce impurities,[10–12] especially in terms of oxygen content,[10] which has an adverse effect for densification. The particle size of synthesized ZrB_2 powders is influenced by the particle size of raw materials, holding time, and synthesis temperature. Zhao *et al.* prepared ZrB_2 powder by boro/carbothermal reduction of ZrO_2 with B_4C and carbon in an inert atmosphere, and indicated that the particle size of ZrB_2 increased with increasing synthesis temperature.[8] Ran *et al.* synthesized the ZrB_2 powders by borothermal reduction of ZrO_2 with boron, and found that the average particle size increased from 0.15 to 0.66 μm with the increasing synthesis temperature from 1000°C to 1650°C.[7]

Oxygen content is another important factor to evaluate the quality of ZrB_2 powders. It is well known that the oxygen impurities, in the form of B_2O_3 and ZrO_2, are present mainly on the particle surfaces of ZrB_2 powders. To remove the oxygen impurities and to promote the densification of ZrB_2, many additives were used, such as carbon,[11] boron,[13] B_4C,[10] transition metal carbides,[14–16] and silicides.[17] Hence, the direct synthesis of ZrB_2 powders with small particle size and low oxygen content is very important.

In this work, the key problem in the conventional borothermal synthesis of ZrB_2 powders was first analyzed, and then a novel process was proposed to produce ZrB_2 powders with small particle size and low oxygen content. The new process includes three steps: (1) borothermal reduction at around 1000°C; (2) water-washing; and then (3) a second reduction stage at 1550°C to remove residual oxygen.

II. Experimental Procedure

The raw materials used in this study were ZrO_2 (D_{50} = 0.6 μm, CSG Holding Co., Ltd, Shenzhen, China) and amorphous boron (average particle size <1 μm, Dandong Chemical Engineering Institute Co., Ltd, Dandong, China) with purities of 99.8% and 96%, respectively. The starting mixtures of ZrO_2 and excess boron were mixed for 24 h in a polythene bottle using ethanol and Si_3N_4 balls, and dried by rotary evaporation. The dried powder mixtures were dry-pressed into disks (about 10-mm diameter and 10-mm thickness). Then, the disks were placed in a

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Table I. Synthesis Process and Oxygen Content of the ZB1, ZB2, ZB3, ZB4, ZB5, and ZB6 Samples

Sample	Process	Oxygen content (wt%)
ZB1	900°C/2 h	–
ZB2	1000°C/2 h	–
ZB3	1550°C/1 h	0.68
ZB4	1000°C/2 h and water-washing	2.68
ZB5	1000°C/2 h and 1550°C/1 h	0.69
ZB6	1000°C/2 h, water-washing and 1550°C/1 h	0.40

graphite crucible, and heated at a rate of 10°C/min to the final temperature in a graphite element furnace (ZT-60-22Y, Shanghai Chen Hua Electric Furnace Co. Ltd., China). The detailed reduction processes of different sample are shown in Table I. The thermally treated disks were immersed into hot water to remove the boron oxides. Then, the powders were washed with de-ionized water and ethanol before drying.

Phase composition was determined by X-ray diffraction (XRD, D/max 2550 V, Tokyo, Japan). The morphology of the synthesized powder was characterized by scanning electron microscopy (SEM, Hitachi S-570, Tokyo, Japan) and a high-resolution transmission electron microscope (HR-TEM, JEM-2010, JEOL Ltd, Tokyo, Japan). Oxygen content was determined by a nitrogen/oxygen determinator (TC600, Leco Corporation, St. Joseph, MI).

III. Results and Discussion

(1) Key Problem in the Borothermal Synthesis of ZrB_2 Powders

Figure 1 shows the XRD patterns of the ZB1, ZB2, ZB3, and ZB6 powders. In addition to ZrB_2 phase, ZrO_2 phase was detected in the ZB1 sample, whereas ZrO_2 phase disappeared in the ZB2 and ZB3 samples. This showed that the borothermal reduction of ZrO_2 with boron could be completed at 1000°C or above. The B_2O_3 phase was observed in the ZB2 sample, but no B_2O_3 phase was detected in the ZB3 sample. Previous thermodynamic calculations showed that ZrO_2 reacted with boron to form liquid B_2O_3 phase below 1200°C based on the following reaction:[7]

$$3ZrO_2(s) + 10B(s) \rightarrow 3ZrB_2(s) + 2B_2O_3(l) \quad (6)$$

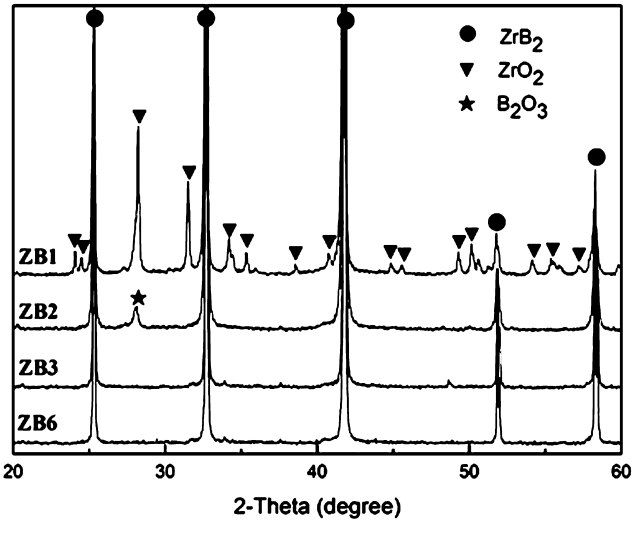

Fig. 1. XRD patterns of the ZB1, ZB2, ZB3, and ZB6 samples.

When the temperature is above 1200°C, ZrO_2 reacted with boron to form gaseous B_2O_2 phase according to reaction (4). This should be the reason why B_2O_3 phase existed in the ZB2 sample, and disappeared in the ZB3 sample.

The oxygen contents of ZB3 and ZB4 powders are shown in Table I. It can be seen that the oxygen content of ZB3 and ZB4 was 0.68 and 2.68 wt%, respectively. In spite of the water-washing process, the oxygen content of ZB4 was far higher than that of ZB3 sample. This indicated that high-temperature treatment was more effective to decrease the oxygen content compared with the water-washing process. The SEM images of ZB3 and ZB4 powders are shown in Fig. 2, and the TEM image of ZB4 is shown in Fig. 3. Compared with ZB3, the particle size of the ZB4 product was obviously finer. Based on the SEM observation, the particle size of ZB3 and ZB4 samples was about 2–3 μm and about 0.3–0.5 μm, respectively.

The above result indicated that ultra-fine ZrB_2 powders (0.3–0.5 μm) could be obtained at low temperature (~1000°C). Although most of the oxygen can be removed by the water-washing process, its content (2.68 wt%) was still too high for the preparation of ZrB_2-based ceramics. Increasing synthesis temperature could decrease the oxygen content. For example, ZrB_2 powder with low oxygen content of 0.68 wt% was obtained at high temperature of ~1550°C. However, this powder had a coarser particle size of 2–3 μm. Accordingly, the key issue in the borothermal synthesis is how to solve the above conflicting problems and produce a ZrB_2 powder with small particle size as well as low oxygen content.

(2) Synthesis of Submicrometric ZrB_2 Powders with Low Oxygen Content

As mentioned above, the particle size of synthesized ZrB_2 powders is influenced by both particle size of raw materials and reduction processes. Coarse raw materials, long holding time, or high synthesis temperature would lead to the coarsening of ZrB_2 powders. Based on the XRD results, borothermal reduction could proceed to completion at 1000°C. The high synthesis temperature (~1550°C) has also induced the coarsening of the raw materials before the ZrO_2 reacts with the boron to form the ZrB_2 phase, which was very similar to the synthesis process of HfC ultra-fine powder.[18] To prevent the coarsening of the starting ZrO_2 particles, in this study. the borothermal reduction was first held at low temperature to synthesize ZrB_2 phase at where the coarsening of ZrO_2 and boron was very restricted, and then was held at high temperature to remove the oxygen impurity. By this two-step process, ZB5 sample was prepared. As shown in Table I and Fig. 2, the oxygen content and particle size of ZB5 were 0.69 wt% and 2–3 μm, respectively. The oxygen content of ZB5 sample was lower than that of ZB4 sample, whereas the particle size of ZB5 sample was bigger than that of ZB4 sample, and close to that of ZB3 sample.

Previous studies on densification of boron-containing ceramics, such as B_4C, TiB_2, and ZrB_2, have indicated that the existence of B_2O_3 is a very important factor in promoting coarsening through evaporation–condensation kinetics.[19–21] To reduce the adverse effect of the B_2O_3 phase for the ZrB_2 particle coarsening, a water-washing process was added before the second-step reduction was carried out. By two-step reduction plus an intermediate water-washing process (RWR, reduction-wash-reduction), the ZB6 powder was obtained. The XRD pattern of the ZB6 sample showed that the RWR route could obtain pure phase ZrB_2 powders (Fig. 1). As shown in Table I, Figs. 2 and 3, the oxygen content and particle size of ZB6 were about 0.43 wt% and about 0.4–0.7 μm, respectively. The particle size of ZB6 sample was considerably smaller than that of ZB3 sample, whereas the oxygen content was comparable. This result demonstrated that the two-step reduction plus intermediate

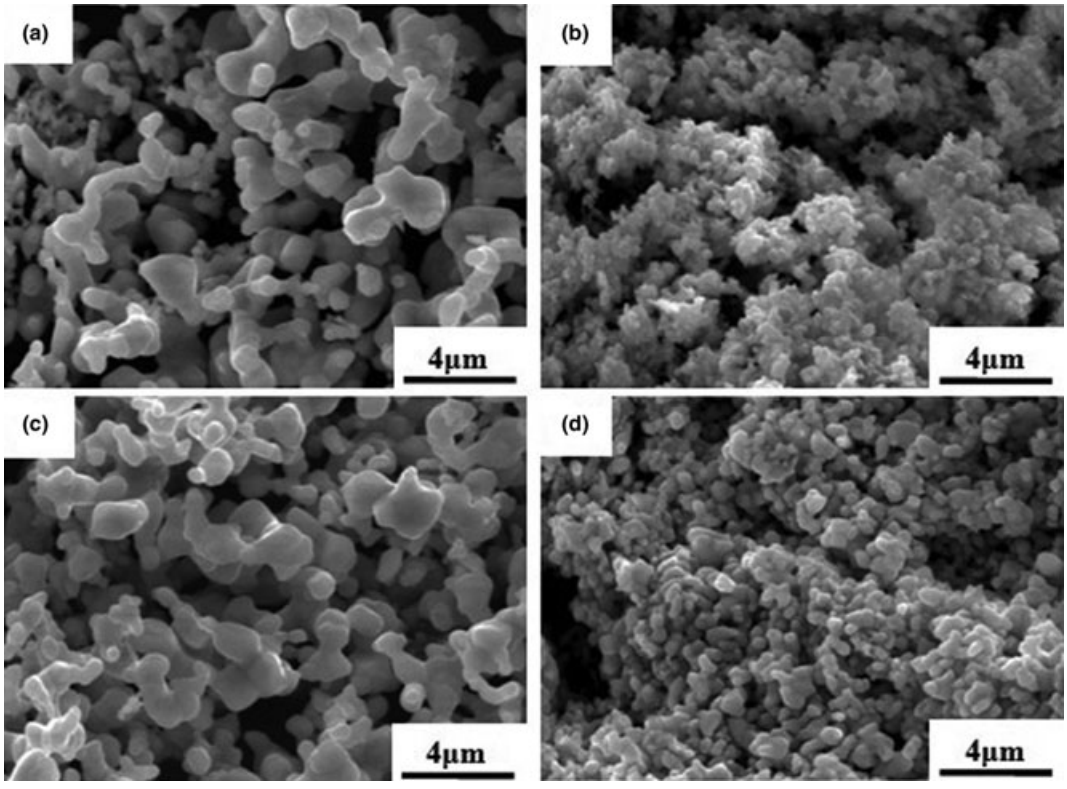

Fig. 2. SEM images of the ZB3 (a), ZB4 (b), ZB5 (c), and ZB6 (d) samples.

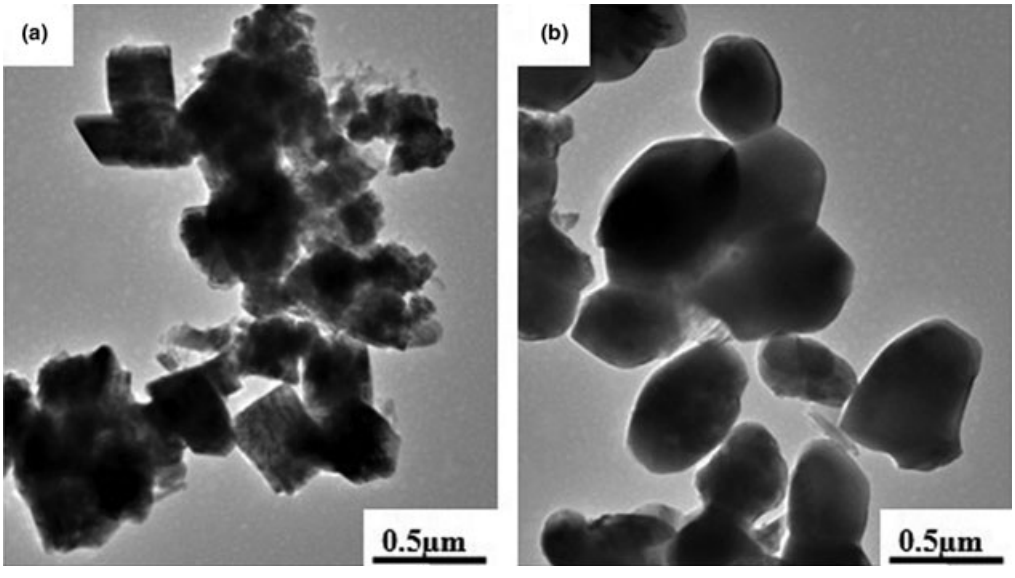

Fig. 3. TEM images of the ZB4 (a) and ZB6 (b) samples.

water-washing process was very effective to prepare the ZrB_2 powder with both small particle size and low oxygen content. At the same time, this result also further confirmed that the coarsening of ZrB_2 particles mainly depend on the presence of boron oxides. In addition, the TEM images reveal that the synthesized ZrB_2 powders have different morphologies. The ZB4 sample has faceted morphology, whereas ZB6 sample displays spherical morphology (Fig. 3).

Next, the removal mechanism of the residual B_2O_3 phase in the second-step reduction after water-washing will be explored. At high temperature, B_2O_3 could react with boron to form gaseous B_2O_2 based on the following reaction:

$$2B_2O_3(l) + 2B(s) \rightarrow 3B_2O_2(g) \quad (7)$$

In our experiment, the furnace pressure remained below 20 Pa during the whole reduction process. Here, assuming a B_2O_2 partial pressure of 20 Pa, thermodynamic calculation shows that reaction (7) is thermodynamically favorable above 1250°C. Hence, the residual B_2O_3 could be eliminated by the formation of gaseous B_2O_2. One mole of ZrO_2 needs only

3.33 moles boron to form ZrB_2 and B_2O_3 according to the reaction (6). However, it was noted that the molar ratio of boron and ZrO_2 should be higher than 3.33 to ensure the existence of residual boron to remove the remained B_2O_3 after water-washing based on the reaction (7). On the other hand, the B_2O_3 could also be removed by high-temperature evaporation:

$$B_2O_3(l) \rightarrow B_2O_3(g) \tag{8}$$

Eventually, the residual B_2O_3 after water-washing was further eliminated by its evaporation and the formation of gaseous B_2O_2 in the second-step reduction at 1550°C, which resulted in the decrease of oxygen content from 2.68 to 0.40 wt%.

IV. Summary

The conventional borothermal synthesis includes two negative aspects. First, the decrease of particle size of ZrB_2 powders apparently conflicts with a low oxygen content. Second, the coarsening of ZrB_2 powders mainly depends on the presence of boron oxides. Based on the above two features, a new borothermal reduction route was developed, namely, two-step reduction plus intermediate water-washing (RWR). The ZrB_2–B_2O_3 powder mixtures were first prepared by borothermal reduction of ZrO_2 with excess boron at 1000°C. Then, most of the B_2O_3 phase was removed from the ZrB_2–B_2O_3 powder mixtures by water-washing process. Finally, the residual B_2O_3 was further eliminated by its evaporation and the formation of gaseous B_2O_2 at 1550°C. Using conventional process, the particle size and oxygen content of ZrB_2 powder were about 2–3 μm and 0.68 wt%, respectively. Based on the proposed new RWR route, the particle size and oxygen content of ZrB_2 powder were about 0.4–0.7 μm and 0.40 wt%, respectively.

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