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RESEARCH ARTICLE

Synthesis of ultrafine ZrB_2 powders by sol-gel process

Li-Juan YANG, Shi-Zhen ZHU (✉), Qiang XU, Zhen-Yu YAN, Ling LIU

School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

Abstract Ultrafine zirconium diboride (ZrB_2) powders have been synthesized by sol-gel process using zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), boric acid (H_3BO_3) and phenolic resin as sources of zirconia, boron oxide and carbon, respectively. The effects of the reaction temperature, B/Zr ratio, holding time, and EtOH/H_2O ratio on properties of the synthesized ZrB_2 powders were investigated. It was revealed that ultrafine (average crystallite size between 100 and 400 nm) ZrB_2 powders can be synthesized with the optimum processing parameters as follows: (i) the ratio of B/Zr is 4; (ii) the solvent is pure ethanol; (iii) the condition of carbothermal reduction heat treatment is at 1550°C for 20 min.

Keywords ultrafine ZrB_2 powders, sol-gel method, synthesis

1 Introduction

Zirconium diboride (ZrB_2) ceramics have unique properties such as high melting point, high hardness, chemical stability, high thermal conductivity and electrical conductivity, and good thermal shock resistance, which make them suitable for the extreme chemical and thermal environments associated with hypersonic fight, atmospheric reentry, and rocket propulsion. However, densified ZrB_2 with strong covalent bonding and low self-diffusion are required [1–3] for high temperatures and external pressures.

The sintering activity of raw material powders has a direct influence on properties of ZrB_2 ceramic. It is known that the smaller the powder size is, the stronger the sintering force would be. If ultrafine raw material powders can be successfully synthesized, the ZrB_2 ceramic with higher mechanical properties can be obtained under lower sintering temperatures. Consequently, it has been increasingly attractive to synthesize ultrafine ZrB_2 powders in order to enhance the properties of ZrB_2 ceramic.

Currently, ZrB_2 powders are mainly produced by carbothermal reduction and self-propagating high-temperature synthesis (SHS). In conventional carbothermal reduction processing, higher temperature and longer synthesis period are required because coarse powder mixtures are used as reactants. In addition, it will result in reaction products with large particle sizes. In SHS processing, the reaction products may also have nonuniform microstructural characteristics because of nonuniformity temperature as the combustion wave propagates through the samples [4–6].

The sol-gel process is an effective solution-based synthesis method. The most important advantage of solution-based synthesis is that more uniform mixing of components (atomic-scale or molecular-scale mixing) can be achieved, and ultrafine powders could be synthesized [7].

In this work, ultrafine ZrB_2 powders were synthesized by the sol-gel process. The influence of reaction temperature and holding time at the stage of precursor calcinations, the B/Zr ratio, and the EtOH/H_2O ratio at the stage of precursor preparation on properties of synthesized ZrB_2 powders was studied.

2 Experimental

Both of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$, Fuchen Chemical Reagent Co., Ltd., Tianjin, China) and boric acid (H_3BO_3, Beijing Fine Chemical Reagent Co., Ltd., Beijing, China), used respectively as sources of zirconia (ZrO_2) and boron oxide, were of analytical grade. Phenolic resin (2123, Shanghai Qinan Bond Chemical, Shanghai, China) was used as the carbon source, whose char yield was about 55wt.%.

A flow chart for the synthesis of ZrB_2 is shown in Fig. 1. The amounts of $ZrOCl_2 \cdot 8H_2O$, H_3BO_3, and phenolic resin

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E-mail: zhusz@bit.edu.cn

were determined according to the following reaction:

$$ZrO_2 + B_2O_3 + 5C \rightarrow ZrB_2 + 5CO \quad (1)$$

First, a hybrid solution was prepared by dissolving a certain amount of $ZrOCl_2 \cdot 8H_2O$ and H_3BO_3 in solvent. Excess H_3BO_3 was generally required because of the volatilization of B_2O_3 at elevated temperature (boiling point of B_2O_3, i.e., under 1 atm (~1.013×10^5 Pa) vapor pressure, is 1860°C) and of the compensation for the formation of gaseous boron oxide (e.g., BO) intermediate products that were removed from the reaction zone by the argon gas stream. The pH value of the hybrid solution was adjusted to 5 by dilute ammonia under stirring to obtain zirconia sol. Phenolic resin dissolved in ethanol was then added dropwise under intensively stirring. The hybrid sol was aged in air for 3 h. Then, the gel was dried at 90°C for 4 h. After grounding and sieving, the precursor powders were obtained. The precursor powders were finally heat-treated at the reaction temperature in flowing argon for carbothermal reduction.

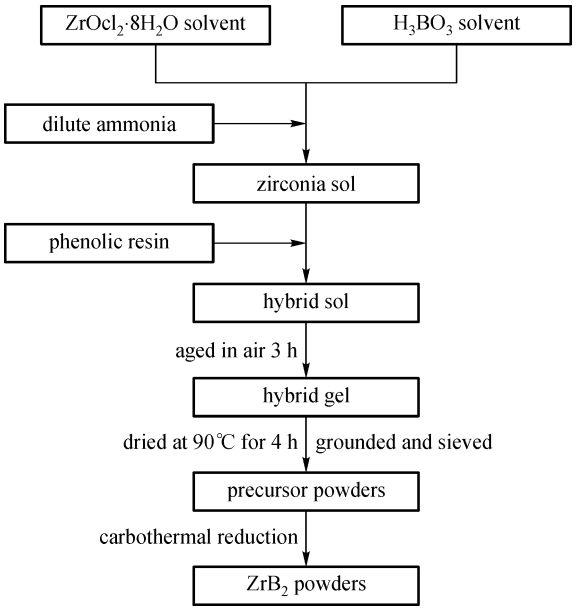

Fig. 1 Flow chart for the synthesis of ZrB_2

X-ray diffraction (XRD, RIGAKU D/Max-rB) with Cu Kα radiation was used to analyze the phase composition of the sintered powders. The microstructure was characterized by field emission scanning electron microscope (SEM, HITACHI S-4800).

3 Results and discussion

At the stage of precursor calcinations, the reaction temperature and holding time were studied.

XRD patterns of the ZrB_2 powders synthesized at different reaction temperatures from 1450°C to 1600°C for 1 h are shown in Fig. 2. It can be seen that at 1450°C, ZrB_2 phase is the predominant phase, and several weak peaks show the presence of ZrO_2 phase, which implied that the carbothermal reduction reaction has not been completed at 1450°C. With the temperature rising to 1500°C, ZrO_2 phase disappears completely, and ZrB_2 phase is the only crystalline phase as observed. XRD patterns show no significant change after 1500°C, which suggests that the carbothermal reduction has been completed at 1500°C.

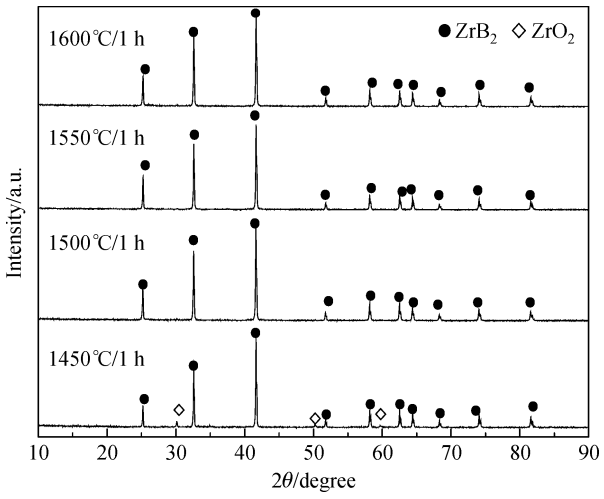

Fig. 2 XRD spectra of ZrB_2 powders synthesized at different reaction temperatures (B:Zr = 3, C:Zr = 5, EtOH:H_2O = 3)

The SEM images of ZrB_2 powders synthesized at different reaction temperatures (1450°C–1600°C) for 1 h are shown in Fig. 3. It can be observed from Fig. 3 that the particle size of synthesized ZrB_2 decreases with the increasing of reaction temperature. The main reason for this phenomenon is that higher temperature promotes ZrB_2 grains nucleate much more rapidly than growing. Furthermore, the grain morphology shows clubbing at 1450°C and 1500°C, but it changes to sphericity when the reaction temperature is up to 1550°C and 1600°C. It is caused by that the crystal structure of ZrB_2 that is hexagonal, which may cause crystal grains preferentially growing in a certain direction (*z*-axis). However, the grains growth rate increases due to higher temperature, so the preference growing disappears gradually. Comparing Fig. 3(c) with 3(d), it can be found that the particle size almost has no change from 1550°C to 1600°C. However, there were several adjoining particles that sintered together at 1600°C. It is because the reaction course was associated with sintering at high temperature. Therefore, it has limited effect on reducing the size of crystal grains through the increase of reaction temperature. Based on analysis of the phase and microstructure of

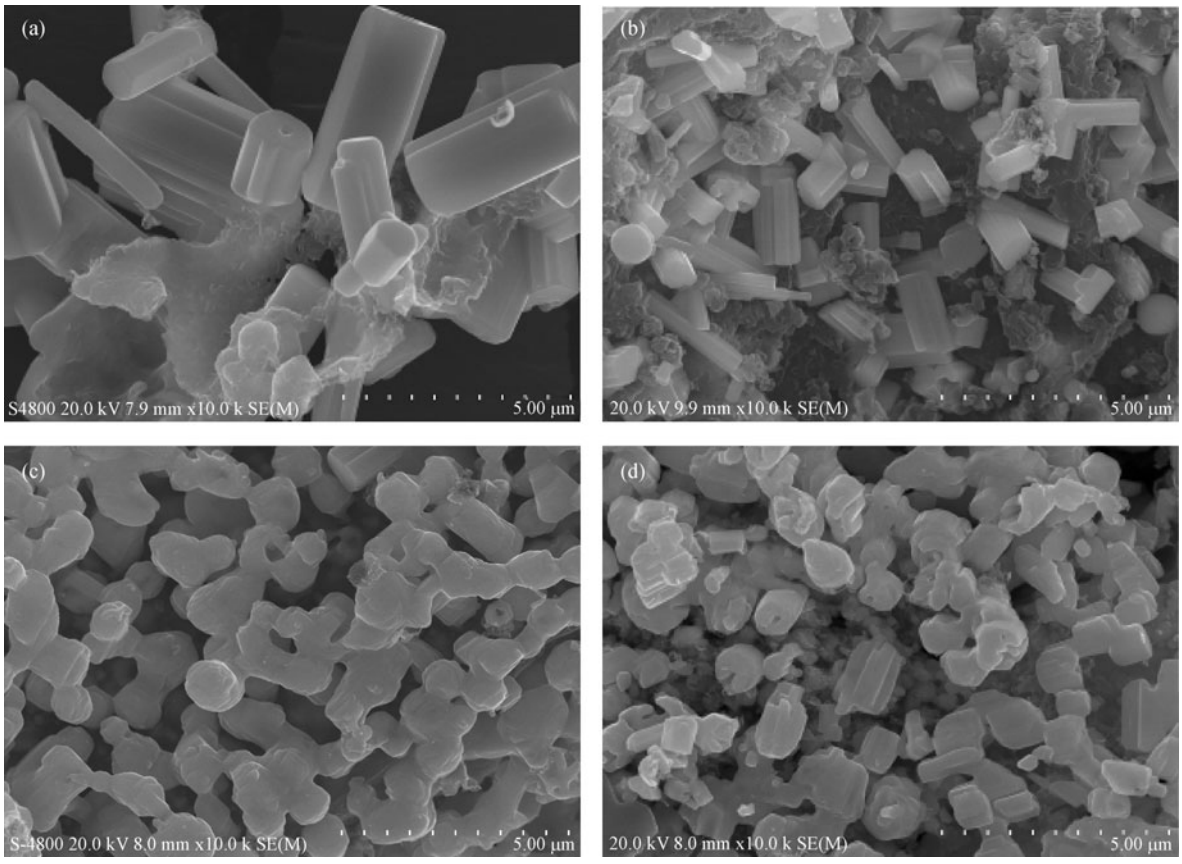

Fig. 3 SEM images of ZrB_2 powders synthesized at different reaction temperatures: **(a)** 1450°C; **(b)** 1500°C; **(c)** 1550°C; **(d)** 1600°C

synthesized powders, the optimum reaction temperature should be 1550°C.

Figure 4 shows the XRD patterns of ZrB_2 powders synthesized at 1550°C for different holding time (10–60 min). It is observed that ZrB_2 and ZrO_2 are the predominant phases when powders were at 1550°C for 10 min. The existence of the ZrO_2 phase implies that 10 min is not long enough to complete the carbothermal reduction reaction at 1550°C. With prolonging the holding time to 20 min, the ZrO_2 phase can no longer be found, and the ZrB_2 phase is the only crystalline phase as observed. The XRD spectra of powders for longer holding time (30 and 60 min) keep the same with that for 20 min. It suggests that the completion of the carbothermal reduction needs at least 20 min at 1550°C. Figure 5 shows SEM images of ZrB_2 powders synthesized at 1550°C with different holding time (20–60 min). It can be seen that the single particle size changed negligibly with different holding time, while several adjoining particles sintered together with more holding time. Thus, 20 min is selected as the holding time after combining the phase analysis with the observation of microstructure of synthesized ZrB_2 powders.

As the phenolic resin is not insoluble in deionized water, which could prevent the loss of boron, the hybrid solvent of ethanol and deionized water is required. Figure 6 shows the SEM images of ZrO_2 grains synthesized at 1550°C without holding time when the ratio of $EtOH:H_2O$ is different. It is seen that the size of ZrO_2 grains changed greatly due to the difference of $EtOH:H_2O$. The less the quantity of deionized water is, the finer the ZrO_2 grains are.

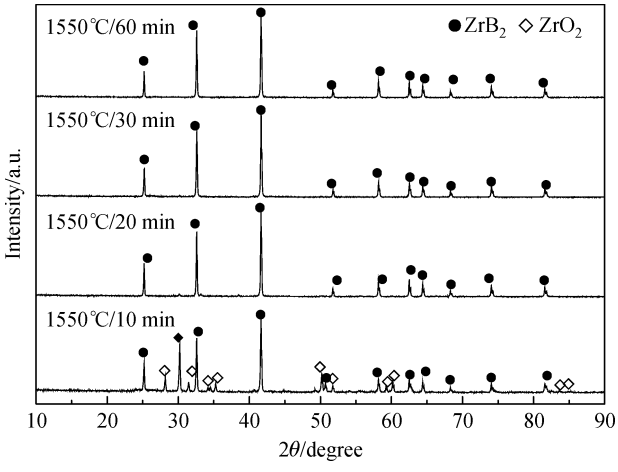

Fig. 4 XRD spectra of ZrB_2 powders synthesized at 1550°C for different holding time (B:Zr = 3, C:Zr = 5, $EtOH:H_2O$ = 3)

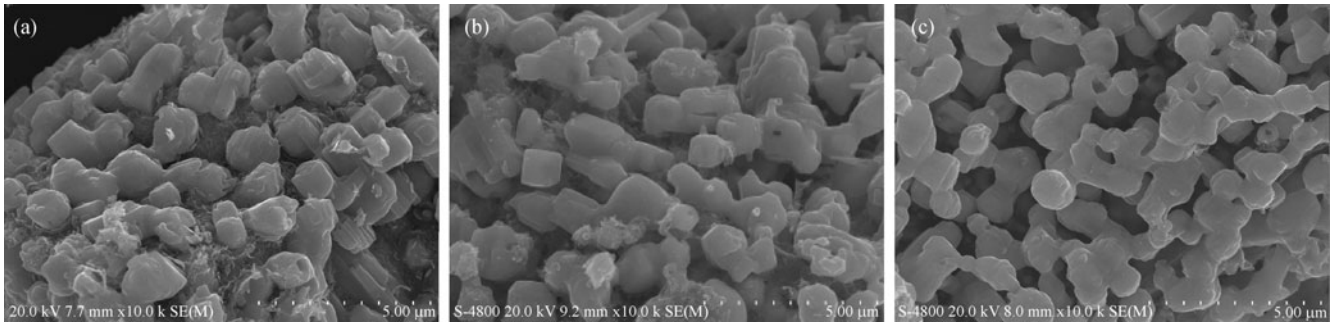

Fig. 5 SEM images of ZrB_2 powders synthesized at 1550°C for different holding time: **(a)** 20 min; **(b)** 30 min; **(c)** 60 min

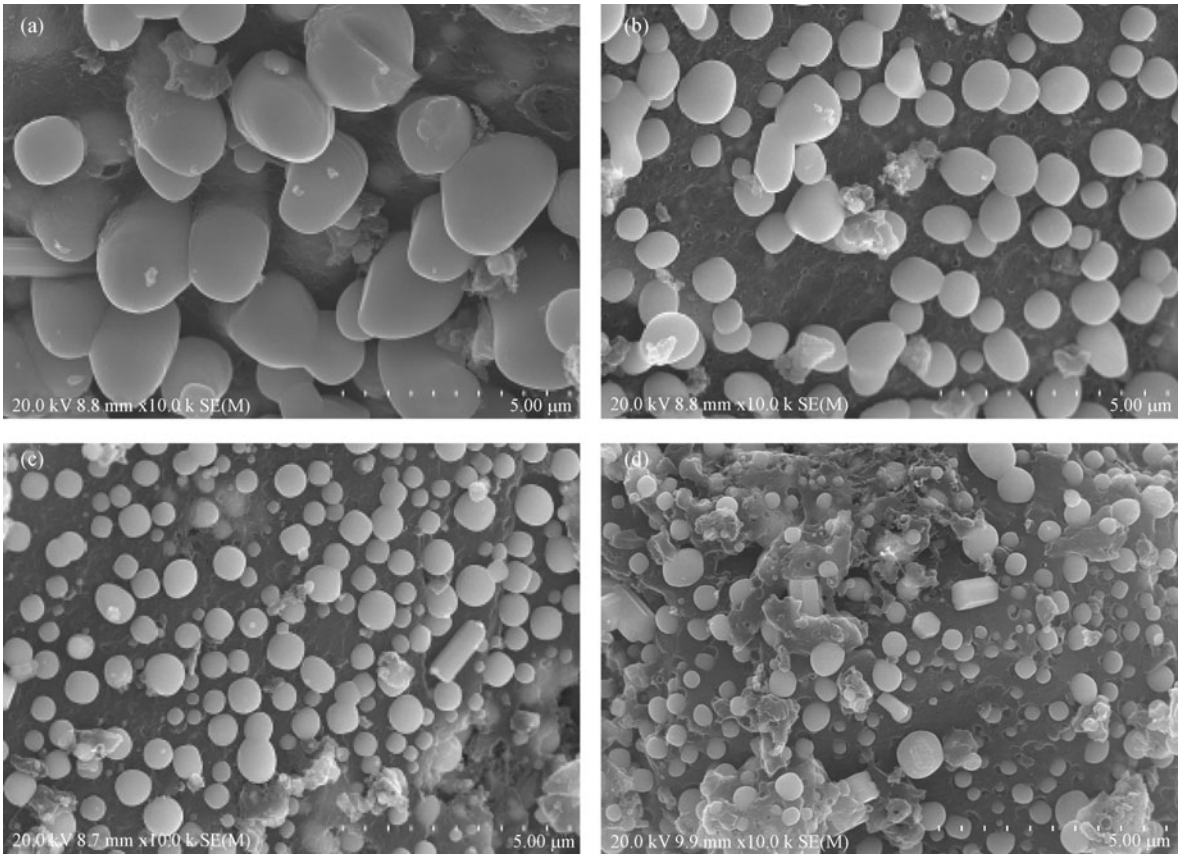

Fig. 6 SEM images of ZrO_2 grains synthesized with **(a)** EtOH:H_2O = 3, **(b)** EtOH:H_2O = 5, **(c)** EtOH:H_2O = 7, and **(d)** pure EtOH

In the course of preparing the zirconia sol, the obtained zirconium hydroxide colloidal particles, whose formula can be expressed as $[Zr(\mu\text{-}OH)_8(OH)_8(H_2O)_8]\cdot xH_2O$, is a highly water-bearing sediments. The nonbridging hydroxyl in the structure of zirconium hydroxide colloidal particles causes dehydration reaction as follows:

$$\text{Zr–OH} + \text{Zr–OH} \rightarrow \text{Zr–O–Zr} + H_2O \qquad (2)$$

Thus the original hydrogen bond connection changes into a Zr–O–Zr bond connection, resulting in hard agglomerates. However, if zirconia sol is prepared in anhydrous ethanol, zirconium hydroxide particles, once generated, will be separated effectively by anhydrous ethanol, which prevents particles from collision and inhibits the formation of large particles. Thus, the existence of H_2O is harmful to form the ultrafine particle structure of ZrO_2 colloidal. However, ZrO_2 grains size directly impact on the size of the ZrB_2 powders synthesized. To get ultrafine ZrB_2 powders as expected, pure ethanol is chosen as the solvent at the cost of boron loss.

According to the carbothermal reduction reaction (Eq. (1)), the ratio of B:Zr is 2. However, the boiling

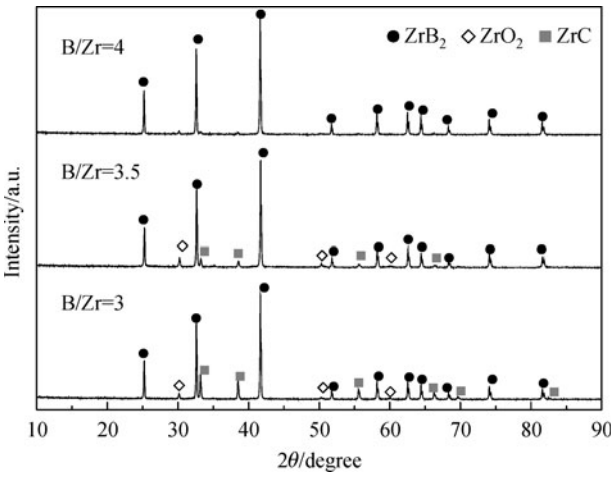

Fig. 7 XRD patterns of ZrB_2 powders synthesized with different B:Zr (C:Zr = 5, pure EtOH)

point of B_2O_3, i.e., under 1 atm vapor pressure, is 1860°C, so excess boron is generally required to compensate for the volatilization of B_2O_3 at elevated temperatures and the formation of gaseous boron oxide (e.g., BO) intermediate products, which will be removed from the reaction zone by the argon gas stream. XRD patterns of ZrB_2 powders synthesized with different B:Zr from 3 to 4 at 1550°C for 20 min are shown in Fig. 7. It can be seen that ZrC and ZrB_2 are the predominant phases, and several weak peaks show the presence of ZrO_2 phase at B:Zr = 3, which implies that the source of boron oxide (B_2O_3) is not enough. With the increase of the ratio of B:Zr, ZrC and ZrO_2 phase reduces until it disappears fully when B:Zr is up to 4. The SEM images of ZrB_2 powders synthesized with different at 1550°C for 20 min are shown in Fig. 8. It shows that the B:Zr changes induce no apparent influence on the particles size. According to the phase analysis and microstructure of the powders, ZrB_2 powders synthesized with B:Zr = 4 has have small crystallite size in the range of 100–400 nm and high purity. Therefore, the optimum B:Zr is selected to be 4.

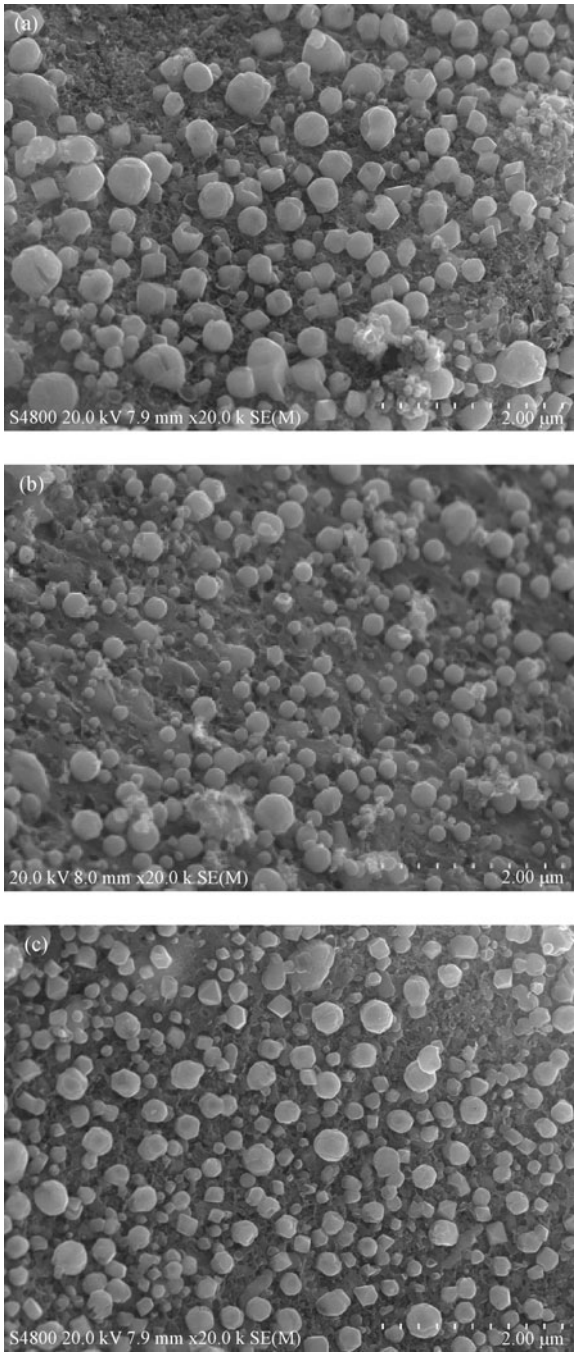

Fig. 8 SEM images of ZrB_2 powders synthesized with **(a)** B:Zr = 3, **(b)** B:Zr = 3.5, and **(c)** B:Zr = 4

4 Conclusions

Ultrafine ZrB_2 powders have been successfully synthesized by sol-gel process via carbothermal reduction. After analyzing the phase compositions and micromorphology of ZrB_2 powders synthesized under different processing parameters, it is found that the ZrB_2 powder size decreases with elevating the carbothermal reduction temperature. Moreover, the existence of H_2O in solvent would prevent from forming the ultrafine structure of ZrO_2 colloidal particles, which has direct influence on the size of synthesized ZrB_2 powders. The optimum processing parameters for the synthesis of ultrafine ZrB_2 powders were obtained as follows: (i) the ratio of B/Zr is 4; (ii) the solvent is pure ethanol; (iii) the condition of carbothermal reduction heat treatments is 1550°C for 20 min. The ZrB_2 powders synthesized under the optimum processing parameters have small crystallite size (100–400 nm) and high purity with sphericity. Based on the success of synthesizing ultrafine ZrB_2 powders, ZrB_2-SiC composite powders are to be synthesized by introducing silicon-bearing precursors in our next study.

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