

ZrB₂ Powders Synthesis by Borothermal Reduction

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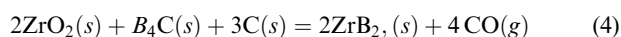
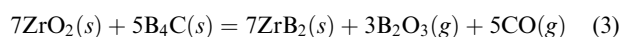
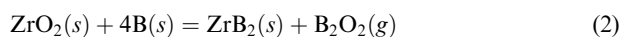
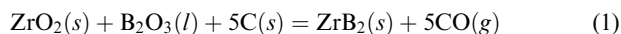
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High-purity zirconium diboride (ZrB₂) powders with sub-micrometer particle size were synthesized by borothermal reduction of nanometric ZrO₂ powders in vacuum. The reaction process was experimentally and thermodynamically assessed. B₂O₃ was identified as a possible intermediate reaction product. ZrO₂ completely converted to ZrB₂ when thermally treated at 1000°C for 2 h in a vacuum, but the removal of residual boron-related species required a temperature above 1500°C. ZrB₂ powders obtained at 1000–1200°C showed a faceted morphology, whereas those prepared above 1500°C had a nearly spherical morphology. The particle size that was calculated from the measured surface area increased with the increasing synthesis temperature from 0.15 μm at 1000°C to 0.66 μm at 1650°C. The oxygen content of the ZrB₂ powders synthesized at 1650°C was as low as 0.43 wt%.

I. Introduction

AMONG the family of ultra-high-temperature ceramics (UHTCs), ZrB₂ is thought to be one of the most attractive thermal protection materials with potential applications in aerospace due to its unique combination of physical and chemical properties, including moderate density (6.09 g/cm³), high melting point (3200°C), good chemical inertness, high thermal, and electrical conductivities.^{1–3} The strong covalent bonding, however, makes it difficult to densify ZrB₂ powders. Ultra-fine powders can increase the driving force for sintering, improve the densification behavior, and enhance the mechanical properties of the ceramics. Therefore, finding a simple and inexpensive synthesis route for ZrB₂ powders with a fine particle size is desirable because it would allow the fabrication of more cost-effective ZrB₂ ceramics.

A variety of synthesis routes have been developed to prepare ZrB₂ powders. Reduction processes,^{4,6} chemical routes,⁷ and reactive processes⁸ are the three main methods.¹ Reduction reactions are more controllable and less expensive than the other routes.^{1,6} The most common reduction reactions are:



reaction (1) is used to produce commercial ZrB₂ powders. Reactions (3) and (4) are often used under laboratory conditions.^{4,5} Reaction (2), known as borothermal reduction, on the other hand has not received much attention despite the fact it is

the simplest reaction because it has only two reactants and two products. For reactions (1), (3), and (4), carbide phases and carbon are the typical impurities in the final powder. For the borothermal reduction reaction, boron is the main expected impurity. Although carbon is present in the graphite heating element and insulation of the furnace, contamination of the final product is limited due to the activation of reaction (1) as B₂O₃ is a possible intermediate product of reaction (2) and B₂O₃ can also be introduced along with the B starting powder. A recent report showed that a proper amount of B can remove the oxygen impurities and improve the densification process of ZrB₂-SiC ceramics.⁹ Hot-pressed monolithic HfB₂ and HfB₂-20 vol% SiC ceramics based on HfB₂ powders synthesized by a borothermal reduction of HfO₂ were also reported to present good mechanical properties.¹⁰ Therefore, ZrB₂ powders prepared by borothermal reduction may have advantages in preparing ZrB₂-based ceramics.

The borothermal reaction has already been used to synthesize ZrB₂ powders. Peshev and Bliznakov⁶ reported that ≥1600°C was needed for the reaction of ZrO₂ and boron to proceed to completion. Braton and Nicholls¹¹ used the same reaction to produce BO gas and obtained ZrB₂ at 1150°C. Earlier reports focused mainly on the composition and provided no information on the reaction process, the ZrB₂ particle size, and ZrB₂ morphology.

In the present paper, ZrB₂ powders were prepared from high-purity nanometric ZrO₂ powder by borothermal reduction in vacuum. The reaction process was experimentally investigated and assessed thermodynamically. The particle size and morphology of the ZrB₂ product were characterized.

II. Experimental Procedure

Commercially available ZrO₂ (grade TZ-0, BET = 14 m²/g, Tosoh, Tokyo, Japan) and amorphous B (grade I, BET = 14.7 m²/g, H.C. Starck, Goslar, Germany) powders were used as starting materials. H₃BO₃ (grade AR, Fisher Scientific, Loughborough, U.K.) was used to increase the B₂O₃ content in the starting powder mixture. ZrO₂ and B powders were mixed in a molar ratio of 1:4 using ZrO₂ (grade TZ-3Y, Tosoh) milling balls in ethanol in a polyethylene container for 24 h on a multidirectional mixer (Type T2A, WAB, Basel, Switzerland). For the powder mixture with excess B₂O₃, 50 wt% H₃BO₃ was added to the ZrO₂-B powder mixture resulting in a ZrO₂/B₂O₃ molar ratio of 1/0.67. The slurry was dried at 60°C in a rotary evaporator and subsequently sieved with a 50 mesh sieve. Powder mixtures were dry pressed at 5 MPa into disks (20 g, Φ = 30 mm). The disks were positioned on a graphite paper in a graphite die (Φ = 65 mm) lined with graphite paper. The bottom of the disks was the only contacting surface. The thermal cycle was performed in a graphite resistance heating furnace of a hot press (W100/150-2200-50LAX, FCT Systeme, Rauenstein, Germany) in vacuum under constant evacuation at a heating rate of 10°C/min. A typical vacuum level between 10 and 20 Pa was realized before heating. After a dwell of 120 min at the predefined temperature, the furnace was naturally cooled to the room temperature. To dissolve possible boron oxides, the thermally treated disks were immersed into hot water at 90°C for 8 h. After filtration, the powders were washed three times with demineralized

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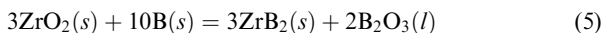
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water and two times with ethanol before drying for characterization.

The crystalline phases were determined by X-ray diffraction (XRD, 3003 TT, Seifert, Ahrensburg, Germany) using CuK α radiation with a scanning rate of 0.5°/min. The morphology of the powders was examined by scanning electron microscopy (SEM, XL30-FEG, FEI, Eindhoven, the Netherlands). The surface area of powders was determined using the BET method to analyze data collected using nitrogen adsorption analysis (Tristar 3000, Micromeritics Instrument Corp., Norcross, GA). The oxygen content was determined by a commercial hot-gas extraction analyzer (Model TC-436, LECO Co., St. Joseph, MI).

III. Thermodynamic Evaluation

For the borothermal reduction reaction, B₂O₃ is another possible product according to the following reactions^{9,10}:



Calculations indicated that reaction (5) is thermodynamically favorable above room temperature under standard state conditions ($P = 1.013 \times 10^5$ Pa). However, to the best of the authors' knowledge, there has been no report on the formation of B₂O₃ during borothermal reduction. One reason could be that the detection of boron oxides is complicated as the low atomic number of B₂O₃ relative to other species leads to a low (or no) signal when examined by EDS and a low efficiency in XRD. In addition, the use of excess B(s) can produce a reducing environment and the B(s) can react with B₂O₃(l), which is present to form boron-rich oxide gases such as B₂O₂(g), BO(g), and B₂O(g). To assess reaction (2), equilibrium calculations were conducted for the reaction of 1 mol ZrO₂(s) with 4 mol B(s) using FACTSage¹² thermochemical software, taking into account the following phases: B₂O₃(g), B₂O₂(g), BO(g), B₂O(g), BO₂(g), ZrO(g), ZrO₂(s), B(s), ZrB₂(s), and B₂O₃(l). In order to simplify the results, the products with amounts below 0.01 mol were neglected in the figures.

According to the calculations, ZrO₂(s) can be completely consumed to produce ZrB₂(s) above room temperature at an ambient pressure of 20 Pa, but the amount of residual boron and related oxide products vary with temperature. The yield of boron oxides as a function of temperature is graphically presented in Fig. 1. When reacting 1 mol ZrO₂(s) with 4 mol B(s), 0.667 mol B₂O₃(l) is produced and the same amount of B(s) is left at and below 1200°C. Above 1200°C, the amount of B(s) and B₂O₃(l) start to decrease with formation of B₂O₂(g) and BO(g). B(s) and B₂O₃(l) can be completely consumed above 1600°C.

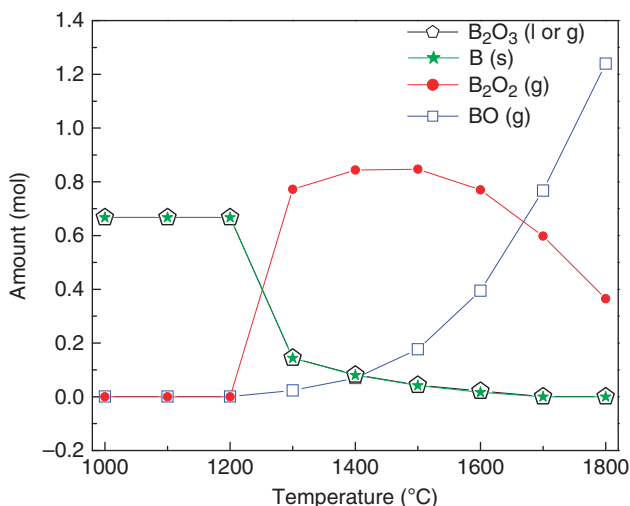


Fig. 1. Calculated yield of boron-related products as a function of temperature at 20 Pa for the reaction of 1 mol ZrO₂ with 4 mol B.

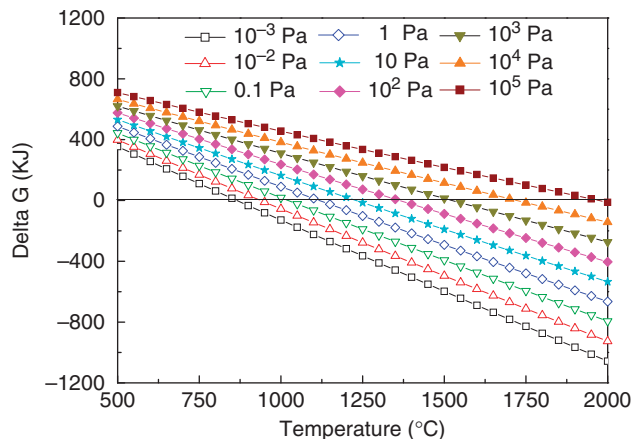
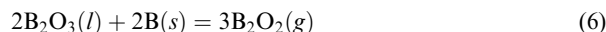


Fig. 2. Gibbs free energy of reaction (6) as a function of temperature and partial pressure of B₂O₂(g).

These results imply that ZrO₂(s) initially reacts with B(s) to form B₂O₃(l) according to reaction (5) and subsequently B₂O₃(l) reacts with the residual B(s) at a higher temperature to produce B₂O₂(g) according to reaction (6). BO(g) may be formed by a direction reaction between B₂O₃(l) and B(s) (reaction (7)) or by the gas-phase decomposition of B₂O₂(g).¹³



The temperature for the appearance of B₂O₂(g) is determined by the favorability of reaction (6). The Gibbs free energy of reaction (6) is plotted as a function of temperature and partial pressure of B₂O₂(g) in Fig. 2. The ambient pressure affects the onset temperature for gas-forming reactions. For example, the onset temperature for reaction (6) decreases from 1950°C in the standard state ($P_{\text{B}_2\text{O}_2} = 1.013 \times 10^5$ Pa) to 850°C at 10^{-3} Pa. In our experiments, the partial pressure of B₂O₂(g) was assumed to be the furnace pressure (between 10 and 120 Pa), implying that the favorable temperature for reaction (6) under the experimental conditions was between 1250° and 1350°C.

The ambient pressure, i.e. the furnace pressure in the experiment, also has a significant effect on the type and amount of B-O species, as summarized in Fig. 3. At 1650°C, BO(g) is the only boron oxide product below 10^{-2} Pa whereas B(s) and

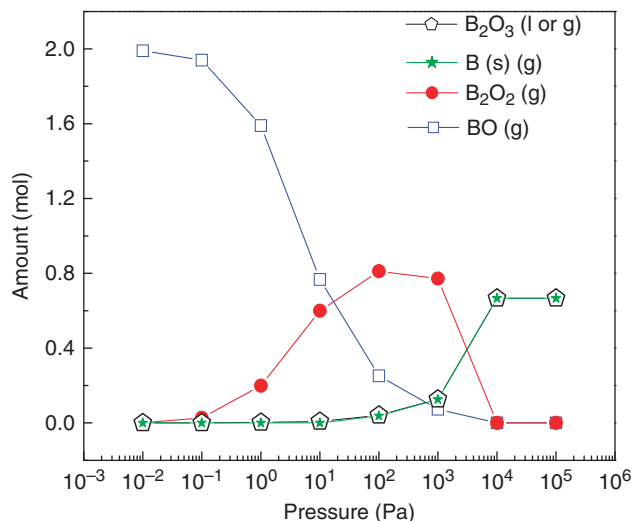


Fig. 3. Calculated yield of boron-related products as a function of ambient pressure at 1650°C for the reaction of 1 mol ZrO₂ with 4 mol B.

$B_2O_3(l)$ are the only products above 10^4 Pa. $BO(g)$, $B_2O_2(g)$, $B_2O_3(g)$, and $B(s)$ coexist at pressures between 10^{-2} and 10^4 Pa.

IV. Results and Discussion

The XRD analysis results of the powder compact prepared at 1000°C are presented in Fig. 4. Owing to the low atomic number, B_2O_3 is difficult to detect by XRD. However, as B_2O_3 was liquid at 1000°C , it accumulated at the bottom of the powder compact due to a gravity-induced flow. As a result, the most intense XRD peak of B_2O_3 ($2\theta = 27.77^\circ$) could be detected at the bottom part of the powder compact whereas no evidence for B_2O_3 was found in the upper part. Although there was no other evidence to support the presence of the B_2O_3 phase, the current experimental result is consistent with the thermodynamic analysis, shown in Fig. 1. ZrO_2 and B were initially batched in a 1:4 molar ratio according to reaction (2); processing at 1000°C , however, produced liquid B_2O_3 . This process is more accurately described by reaction (5), which requires a 3:10 ZrO_2 :B ratio, and therefore consumes only part of the $B(s)$. Hence, some residual B was likely to be present in the powder compact treated at 1000°C .

ZrB_2 powders were prepared by borothermal reduction at different temperatures for 2 h. To assess the reaction process, the weight loss of the reaction products was measured as a function of the synthesis temperature and the vacuum level was recorded during the thermal treatment at 1650°C , as presented in Fig. 5. With the as-pressed ZrO_2 -B powder disks as reference, the weight loss of the reaction products increased with the increasing synthesis temperature. At 1500°C , the weight loss reached a maximum of 32.6% and no additional mass loss was measured at higher temperatures, indicating that all volatile products had been removed from the system when heating at $\geq 1500^\circ\text{C}$ for 2 h. This weight loss is comparable with a theoretical value of 32.2%, calculated for the loss of $B_2O_2(g)$ by reaction (2). As shown in Fig. 5, the furnace pressure sharply increased above 1200°C , which is in agreement with the thermodynamic calculations indicating that reaction (6) begins to proceed above 1200°C at a pressure of 20 Pa (see Fig. 1). At 1580°C , the furnace pressure reached a maximum of 113 Pa, revealing a maximum in the rate of production of volatile species.

The XRD pattern of the starting powder mixture is compared with those of the demineralized water-washed reaction products as a function of the synthesis temperature in Fig. 6. Clear ZrB_2 peaks begin to appear at 900°C and ZrB_2 is the only crystalline product above 1000°C , indicating that phase-pure ZrB_2 can be produced by borothermal reduction at 1000°C . Carbothermal and boro/carbothermal reduction were claimed to be thermodynamically favorable below 1000°C in vacuum (about 10 Pa).⁵ However, experimental results showed that unreacted ZrO_2 and

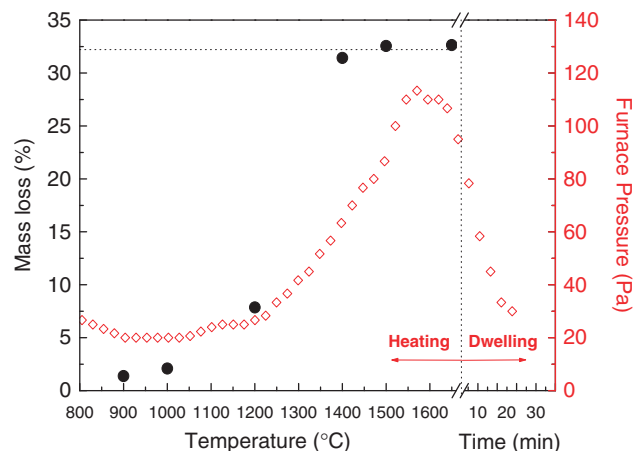


Fig. 5. Mass loss after synthesis at different temperatures and vacuum-level evolution during synthesis at 1650°C .

undesired reaction products such as ZrC and C could not be removed completely below 1500°C even with an excess of B_4C .^{4,5} For borothermal reaction, $B_2O_3(s)$ and $B(s)$ are the likely impurities in the final products. $B_2O_3(s)$ can be removed by washing with hot water or vaporization above 1500°C in vacuum. With the presence of residual $B_2O_3(l)$, residual amorphous $B(s)$ can also be eliminated at temperatures above 1500°C according to reaction (6). Although $B_2O_3(l)$ has a high vapor pressure, the equilibrium vapor pressure at 1200°C is only 0.5 Pa.¹⁴ The calculations and experimental results were consistent with reaction (6) starting above 1200°C .

Oxygen contents of the powders synthesized at different temperatures were measured. The powders obtained at 1000° and 1500°C were washed with hot demineralized water before measurements to remove soluble boron oxides. The measured oxygen content was 2.30, 0.66, and 0.43 wt% for the powders produced at 1000° , 1500° , and 1650°C , respectively. Therefore, there will be nearly no residual oxides present in the final ZrB_2 product when thermally treated above 1500°C . In addition, according to reaction (5), 3.33 moles B is enough to convert 1 mole of ZrO_2 to ZrB_2 . Considering the oxidation of amorphous B, keeping the molar ratio of B and ZrO_2 between 3.33 and 4 is helpful to ensure the complete consumption of ZrO_2 and decrease possible residual B in the products. It should be pointed out that any residual B is difficult to be distinguished because of its low atomic number and the fact that amorphous B was used in the experiments. Residual $B(s)$ is expected to be eliminated by reaction (6) with the B_2O_3 present in the starting powder compacts. Both the starting and completion temperature of the

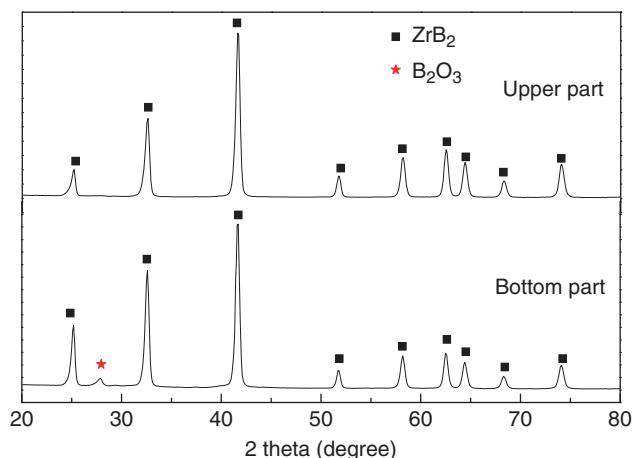


Fig. 4. X-ray diffraction patterns of the upper and bottom part of the ZrB_2 powder compact synthesized at 1000°C for 2 h in vacuum.

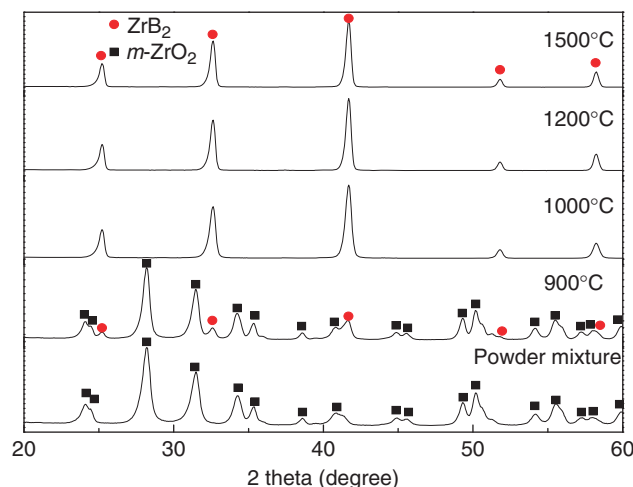


Fig. 6. X-ray diffraction patterns of the starting powder mixture and thermally treated powders after washing with hot demineralized water.

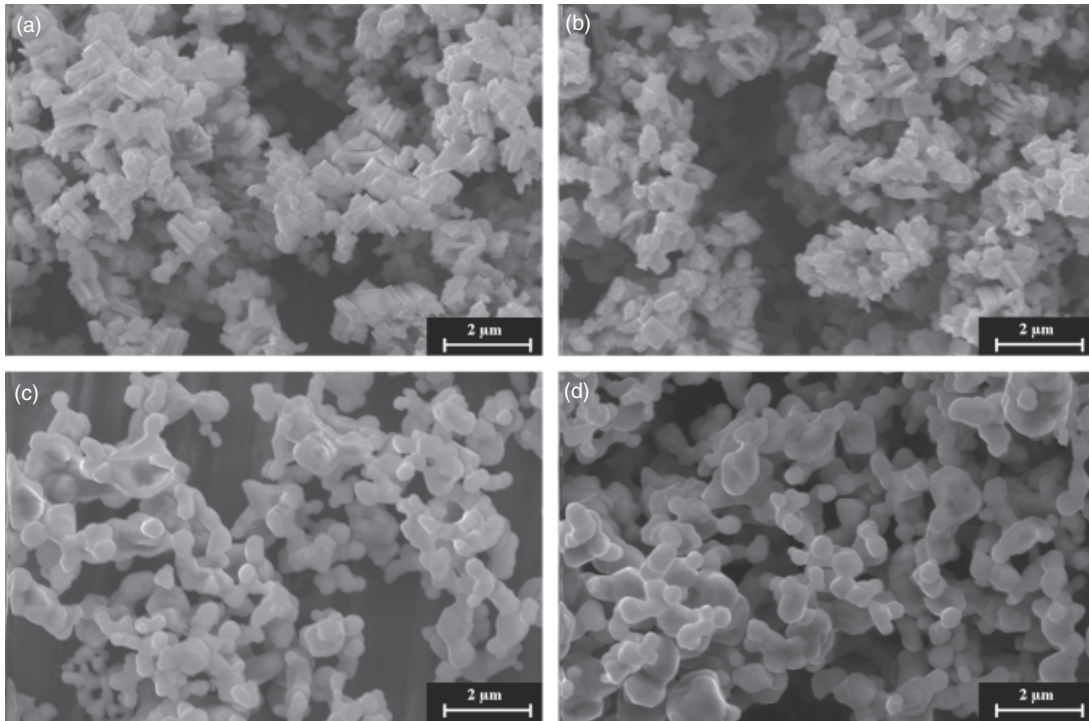


Fig. 7. Scanning electron micrographs of the ZrB₂ powders synthesized at 1000°C (a), 1200 °C (b), 1500 °C (c), and 1650°C (d).

borothermal reaction in this study are lower than the 1200° and 1600°C respectively reported in the literature.⁶ This may be due to the use of nanometric ZrO₂ starting powder as the raw material and a higher homogeneity of the ZrO₂ and B powder mixture.

The reaction products in the powder compacts heat treated at 1000° and 1200°C were hard to crush, whereas the ZrB₂ reaction products obtained above 1400°C were loosely packed and easy to crush by hand. According to Fig. 5, the weight loss was only 7.9% at 1200°C, which is far below the theoretical value of 32.2%, implying a substantial amount of residual B(s) and B₂O₃(l) when thermally treated at temperatures up to 1200°C. When the powder compacts were cooled to room temperature, liquid B₂O₃ would solidify and act as a binding agent for ZrB₂ particles. At higher temperatures, B₂O₃(l) was completely consumed by reaction (6) and converted into fugitive B₂O₂(g) and BO(g), resulting in a loosely packed powder.

Figure 7 presents the SEM micrographs of ZrB₂ powders synthesized at different temperatures. The powders obtained at 1000°, 1200°, and 1500°C were washed with hot demineralized water before the SEM investigation. The ZrB₂ powders obtained at 1000° and 1200°C showed a faceted morphology, whereas the powders thermally treated at 1500° and 1650°C have a nearly

spherical morphology. As discussed above, there was a liquid B₂O₃ phase existing in the system when the synthesizing temperature was 1000°C. The condition was same as that for molten salt method (MSS) in which the crystalline habit of a certain orientation (depending on relative surface energies) can be obtained.¹⁵ The crystal structure of ZrB₂ is hexagonal with anisotropy in the *a*-axis (*a* = 0.3168 nm) and *c*-axis (*c* = 0.3530 nm).¹ Preferential growth of ZrB₂ grains in ZrB₂-MoSi₂ composites was claimed recently to be due to the formation of liquid phases.¹⁶ Similarly, the faceted morphology of ZrB₂ in this study may be attributed to the presence of liquid B₂O₃. Although the same amount of B₂O₃(l) is formed during the reaction process at any reaction temperature, the thermodynamic analysis summarized in Fig. 1 reveal that the amount of B₂O₃(l) that evaporates increases with the increasing temperature. At 1000°C, all formed B₂O₃(l) was present during the whole duration of the dwell period, providing enough time for the ZrB₂ grains to grow. With the increasing synthesis temperature, the B₂O₃(l) in the system was consumed both by the evaporation and reaction (6). As a result, little or no liquid phase was present in the system at temperatures above 1200°C. Analysis by SEM showed the grain morphology changed from faceted at 1000°C to spherical at 1500°C, which is the same temperature range over

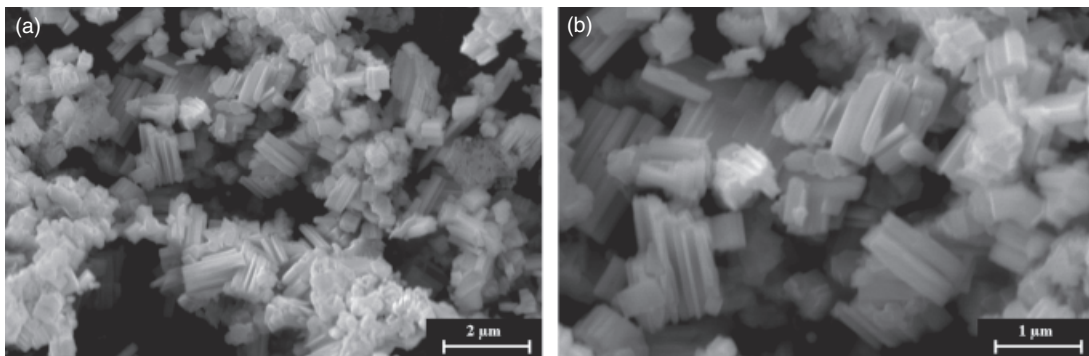


Fig. 8. Low- (a) and high-magnification (b) scanning electron micrographs of the ZrB₂ powders synthesized at 1000°C with 50 wt% H₃BO₃ addition to the starting powder mixture.

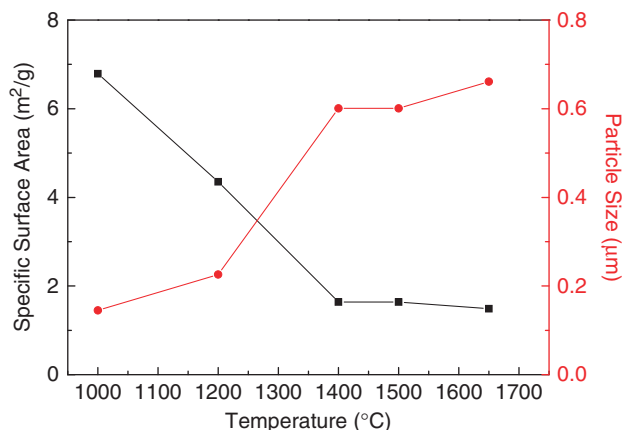


Fig. 9. Specific surface area and equivalent calculated particle size of the ZrB_2 powder as a function of the synthesis temperature.

which the B_2O_3 is removed from the system. Therefore, the change in grain morphology could be due to stabilization of the faceted morphology by the liquid phase or temperature-induced coarsening. Although it is difficult to separate the influence of the temperature from that of liquid B_2O_3 , the effect of the latter could be intensified by adding B_2O_3 in the form of H_3BO_3 to the starting powder mixture. With extra liquid B_2O_3 at 1000°C, the faceted morphology of the ZrB_2 grains was more prominent, as illustrated in Fig. 8.

The specific surface area and equivalent average particle size of the synthesized powders, as calculated from the BET value assuming a spherical particle shape, are graphically presented as a function of the synthesis temperature in Fig. 9. The specific surface area decreased from 6.79 to 1.49 m^2/g whereas the average particle size increased from 0.15 to 0.66 μm with the increasing synthesis temperature from 1000° to 1650°C. It should be noted that the change is most pronounced in the 1200°–1400°C range. Below 1200°C, residual B(s) could separate the ZrB_2 grains, inhibiting fast crystal growth. At 1400°C, reaction (6) was nearly complete and adjacent ZrB_2 particles could coagulate to form larger particles. Because of the evaporation of $B_2O_2(g)$ and $BO(g)$, however, the powders were relatively loosely packed and there was no evident increase in particle size above 1400°C.

V. Conclusions

Thermodynamic and experimental assessment of the borothermal reduction of ZrO_2 nanopowders with amorphous B revealed that $ZrO_2(s)$ initially reacts with B(s) to form $B_2O_3(l)$ and $ZrB_2(s)$. $B_2O_3(l)$ is subsequently consumed by the residual B(s) to produce fugitive $B_2O_2(g)$ and $BO(g)$. The ambient pressure strongly influences the onset temperature and relative amount of boron oxide products of the reaction between $B_2O_3(l)$ and B(s).

Full conversion of ZrO_2 into ZrB_2 could be obtained after 2 h at 1000°C in a vacuum of 10–20 Pa, but the complete removal of residual boron-related species requires a temperature above 1500°C. The morphology of the ZrB_2 powders obtained changed from faceted at 1000°C to spherical at 1500°C, which could be due to the presence of $B_2O_3(l)$ or grain coarsening induced by the temperature. The faceted shape obtained at 1000°C was even more pronounced upon the addition of B_2O_3 in the form of H_3BO_3 to the starting powder. The calculated equivalent BET particle size increased from 0.15 to 0.66 μm with the increasing synthesis temperature from 1000° to 1650°C. The oxygen content of the ZrB_2 powders synthesized at 1650°C was 0.43 wt%.

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