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Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Synthesis of ZrB₂ powders by carbothermal and borothermal reduction

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ARTICLE INFO

Article history: Received 20 February 2012 Received in revised form 12 May 2012 Accepted 17 May 2012 Available online 7 June 2012

Keywords: Zirconium diboride Synthesis Boron carbide Carbothermal reduction Boron carbide reduction

1. Introduction

Zirconium diboride (ZrB₂) is one of a class of materials known as ultra high-temperature ceramics (UHTCs). ZrB₂ ceramic has unique properties such as strong covalent bonding, a high melting point, good mechanical properties, chemical inertness, high thermal/electrical conductivities, and good resistance to erosion/corrosion [1,2]. Due to these properties, ZrB₂ is used in cutting tools [3], refractory linings [4,5], electrodes [6,7], and microelectronics [8]. Some structural, physical, and thermodynamic properties of ZrB₂ are summarized in Table 1 [1,2,9]. Because ZrB₂ not only has good chemical stability, but also excellent physical properties, it is considered for use in extreme chemical and thermal environments related to hypersonic flight, space shuttle use, and rocket propulsion [10–13].

Because the strong covalent bonding acts as a hindrance that makes it difficult to densify ZrB_2 , additional processes and costs are required. Therefore, there is a need to find a more cost-effective and simpler method for the synthesis of fine ZrB_2 powders in order to enhance the densification. Many synthesis routes for transition diboride (MB₂) have been researched. Among methods for the synthesis of MB₂, reduction processes [14–16], chemical routes [17], and reactive processes [18], are the three main methods, of which reduction reactions are more controllable and less expensive than the other routes [1,16,19]. Examples of reactions used to synthesize diborides are shown in Table 2 [1,20,21].

Reaction (1) is classified as a carbothermal reduction, which is used to produce ZrB₂ powders commercially [22]. Reaction (2) is

ABSTRACT

Zirconium diboride (ZrB₂) powders were synthesized using $ZrO_2 + B_2O_3 + C$ (carbothermal reduction), ZrO₂ + B₄C (boron carbide reduction), and ZrO₂ + B₄C + C (combined reduction) with various compositions at 1250 °C for 1–3 h under flowing argon. ZrB₂ powders synthesized using $ZrO_2 + B_2O_3 + C$ displayed rod shape growth. There was much residual impurity carbon in ZrB₂ powders synthesized using ZrO₂ + B₄C + C. When synthesized using ZrO₂ + B₄C, there were the residual impurity B₂O₃ and little rod shape growth. Residual B₂O₃ impurities were easily removed by washing with methanol. We concluded that the ZrB₂ powder synthesis method using boron carbide reduction is the most desirable way to produce ZrB₂ powders among the three synthesis routes. ZrB₂ powders synthesized using ZrO₂ + B₄C have a particle size of 1.1 µm and a hexagonal shape, and low oxygen content (0.725 wt.%). © 2012 Elsevier B.V. All rights reserved.

> a combined reduction using B_4C and carbon. Reaction (3) is boron carbide reduction using B_4C as a reduction agent. Fig. 1 shows thermodynamic data in the standard state Gibbs' free energy of reaction as a function of temperature for various synthesis routes for ZrB₂. While Reactions (1) and (2) become favorable above 1509 °C and 1425 °C, respectively, Reaction (3) is favorable above 1218 °C. Therefore, Reaction (3) has an advantage over the others on the synthesis temperature for ZrB₂ powders.

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The oxygen content is one of the most important factors to estimate the quality of ZrB_2 powders because it is expected that there remains synthesis impurity B_2O_3 , which hinders the densification of ZrB_2 . In this paper, a simple washing process is used to remove the residual synthesis impurity of B_2O_3 . Another possible product ZrC which can be accompanied from Reaction (1), (2), and (3) is favorable above 1550 °C [15].

We performed a comparative study on ZrB_2 synthesis using Reactions (1), (2), and (3) through various compositions to find a more effective and simple way to produce fine, purity ZrB_2 powders.

2. Experimental procedure

Commercially available ZrO₂ (purity 99 + %, main impurities include HfO₂ 2%, bulk density 5.89 g/cm³, particle size -325 mesh, Alfa Aesar), B₂O₃ (purity 99%, bulk density 2.46 g/cm³, Alfa Aesar), boron carbide (B₄C, density 2.52 g/cm³, particle size about 1-7 µm, Alfa Aesar), and carbon black (S.A. 75 m²/g, bulk density 0.0945–0.1025 g/cm³, Alfa Aesar) powders were used as starting materials. The ZrO₂, B₂O₃, B₄C, and carbon powders were weighed according to Table 3, using an electronic balance with an accuracy of 0.0001 g. Powders were mixed in a polypropylene bottle for 48 h with Co-bonded WC balls used as milling medium. 1 g powder mixtures were pressed into a pellet with 12 mm diameter under uni-axial pressure of 0.54 ton/cm² in order to promote synthesis reaction by increasing contact surface of particles. Then, the pressed pellet 2 mm in height was placed in a graphite

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^{0925-8388/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jallcom.2012.05.076

Table 1Properties of zirconium diboride (ZrB2).

Property	ZrB ₂
Crystal system space group Density (g/cm ³) Melting temperature (°C) Young's modulus (GPa)	Hexagonal 6.119 3246 489
Hardness (GPa) Coefficient of thermal expansion (K^{-1}) Electrical conductivity (S/m) Thermal conductivity ($W \cdot (m K)^{-1}$) Free energy of formation at 25 °C (kJ)	$\begin{array}{c} 23 \\ 5.9 \times 10^{-6} \\ 1.0 \times 10^{7} \\ 60 \\ -318.2 \end{array}$

Table 2

Reduction reactions generally used to synthesize borides and free energy.

	Reaction	React. temp. expected	$\Delta G^{\circ}_{rxn} \left(kJ \right)$
(1)	$ZrO_2(s) + B_2O_3(l) + 5C(g)$ $\rightarrow ZrB_2(s) + 5CO(g)$	1509 °C	1431–0.803 T
(2)	$2ZrO_2(s) + B_4C(s) + 3C(s)$ $\rightarrow 2ZrB_2(s) + 4CO(g)$	1425 °C	1134–0.668 T
(3)	$7\text{ZrO}_2(s) + 5\text{B}_4\text{C}(s) \rightarrow 7\text{ZrB}_2(s) + 3\text{B}_2\text{O}_3(g) + 5\text{CO}(g)$	1218 °C	1378–0.924 <i>T</i>



Fig. 1. Thermodynamic data in the standard state Gibbs' free energy of various reactions as a function of temperature.

crucible and thermally treated over the temperature range of 1150–1450 °C in an atmosphere tube furnace with 60 mm inner diameters. A heating rate was maintained at 10 °C/min and was held for 1–3 h at the desired temperatures under flowing argon (purity 99.9%, 2 L/min). Then, the pressed pellet was crushed into powders for characterization. The residual synthesis impurities B_2O_3 and carbon were removed using methanol or deionized water by centrifuging.

The phase analysis of the synthesized powders was carried out by X-ray diffraction (XRD, UltimalV, Rigaku, Japan) using CuK α radiation (λ = 1.54178 Å). The samples were scanned over the range of 2θ = 20°–80° with a scanning rate of 3°/min. From the 2θ values, the *d* values were calculated and the data were compared with the standard values from the JCPDS diffraction files (PDF) to identify the phase. The morphology of the powders was observed by means of a field emission scanning electron microscope (FESEM, JSM-6330F, JEOL, Japan). Particle size distribution was analyzed by laser particle size analysis (PSA, LS230, Beckman Coulter, USA). Oxygen content of the synthesized powders was examined by using the combustion gas hot extraction method (Model TC-600, LECO Co., USA).

Table 3	
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Compositions of raw materials.	
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Sample	Raw materials (molar ratio)		atio)	Note	
	ZrO_2	B_2O_3	B ₄ C	С	
Z1BO5C	1	1	0	5	Stoichiometric
Z3BO5C	1	3	0	5	Excess 2 mol B ₂ O ₃
Z5BO5C	1	5	0	5	Excess 4 mol B ₂ O ₃
Z5BO10C	1	5	0	10	Excess 4 mol B ₂ O ₃ , 5 mol Carbon
Z0.5B1.5C	1	0	0.5	1.5	Stoichiometric
Z0.6B1.5C	1	0	0.6	1.5	Excess 0.1 mol B ₄ C
Z0.7B1.5C	1	0	0.7	1.5	Excess 0.2 mol B ₄ C
Z0.8B1.5C	1	0	0.8	1.5	Excess 0.3 mol B ₄ C
Z0.714B	1	0	0.714	0	Stoichiometric
Z0.72B	1	0	0.72	0	Excess 0.006 mol B ₄ C
Z0.73B	1	0	0.73	0	Excess 0.016 mol B ₄ C
Z0.75B	1	0	0.75	0	Excess 0.036 mol B ₄ C

3. Results and discussion

With reference to thermodynamic data, it is expected that the synthesis reaction of ZrB_2 is set off at a temperature between 1200 °C and 1500 °C (Fig. 1). XRD analysis results of thermally treated Z5BO10C as a function of the synthesis temperature are shown in Fig. 2-a. The presence of ZrO_2 was confirmed at the holding temperature below 1150 °C, but ZrO_2 peaks disappeared when heated above 1250 °C for 3 h. The synthesis temperature of this result is lower than the thermodynamically calculated value of 1509 °C, and this is considered to be due to the effect of excess B_2O_3 and





Fig. 2. X-ray diffraction patterns of (a) Z5B010C thermally treated at different temperatures for 3 h, (b) powders thermally treated at 1250 °C for 3 h with different amounts of B_2O_3 and carbon in excess.



Fig. 3. X-ray diffraction patterns of (a) Z0.8B1.5C thermally treated at different temperatures for 1 h, (b) powders thermally treated at 1250 °C for 1 h with different amounts of B_4C in excess.

carbon. Fig. 2-b shows the XRD pattern of powders thermally treated at 1250 °C for 3 h with different amounts of B_2O_3 and carbon in excess. The intensity of ZrO_2 peaks decreased according to an increase of excess B_2O_3 and carbon. ZrO_2 was totally converted to ZrB_2 when 4 mol of excess B_2O_3 and 5 mol of excess carbon were added to the stoichiometric composition. However, the purity was adversely affected by residual impurity B_2O_3 and carbon resulting from excess B_2O_3 and carbon, which was difficult to remove.

XRD analysis results of thermally treated Z0.8B1.5C are shown in Fig. 3-a as a function of synthesis temperature. Similar to Reaction (1), ZrO₂ peaks disappeared when heated above 1250 °C for 1 h. The XRD patterns of powders thermally treated at 1250 °C for 1 h with different amounts of B₄C and carbon in excess, on the basis of Reaction (2), are presented in Fig. 3-b. When using ZrO₂, B₄C, and carbon, the procedure of the synthesis reaction is as follows. First, ZrO₂ and B₄C were reacted and ZrB₂ was produced. At the same time, ZrO₂, B₂O₃, and carbon were reacted and ZrB₂ was produced. Reaction (1) is only favorable above 1509 °C thermodynamically and it is expected that B₂O₃ and carbon had little effect on the ZrB₂ synthesis. Therefore, ZrO₂ did not react with the B₂O₃ and carbon at 1250 °C and was completely converted to ZrB₂ by adding 0.2 mol of B₄C in excess of the stoichiometric composition.

Fig. 4-a shows the XRD pattern of Z0.75B powders thermally treated at different temperatures for 1 h. ZrB_2 and m- ZrO_2 phases are found at 1150 °C, but only the ZrB_2 peak is observed above 1250 °C. Fig. 4-b gives the XRD pattern of powders thermally treated using B₄C according to compositions in Table 3 at 1250 °C. All



Fig. 4. X-ray diffraction patterns of (a) Z0.75B thermally treated at different temperatures for 1 h, (b) powders thermally treated at 1250 °C for 1 h with different amounts of B_4C in excess.

XRD analysis was conducted after a washing process. Peaks of m-ZrO₂ were confirmed in the XRD pattern of Z0.714B composed of a stoichiometric amount of ZrO₂ and B₄C. There is no B₄C present in Z0.714B up to the XRD resolution. Experiments for several compositions containing different amounts of B₄C in excess (0.016 mol, 0.036 mol, and 0.086 mol, more than the stoichiometric composition of 0.714 mol of B₄C) were conducted to convert all unreacted ZrO₂ to ZrB₂. No evidence of ZrO₂ or any additional phase different than ZrB₂ was found for Z0.73B (excess 0.016 mol of B₄C) and



Fig. 5. X-ray diffraction patterns of Z0.73B thermally treated at $1250 \degree C$ for 1 h before and after washing.



Fig. 6. Oxygen content of Z0.73B before and after washing (a) by methanol and (b) by deionized water.

Z0.75B (excess 0.036 mol of B_4C). Therefore, when adding more than 0.016 mol of excess B_4C compared with the stoichiometric composition, ZrO_2 can be completely converted to ZrB_2 .

Among the various compositions, Z0.73B synthesized powder contained the minimum excess of B_4C while still show complete conversion from ZrO_2 to ZrB_2 . Fig. 5 shows the XRD pattern of Z0.73B before and after the washing process. Besides the peaks of ZrB_2 , a peak related to B_2O_3 was observed at $2\theta = 27.77^\circ$ (JCPDS 13-0570) from the as-synthesized powders [19]. Residual synthesis impurity B_2O_3 was removed using methanol or deionized water by centrifuging. After washing, there was no B_2O_3 peak observed in the XRD pattern.

The oxygen content of the powders synthesized from Z0.73B was examined to determine the effect of the washing process. Oxygen content data of powders as-synthesized from Z0.73B before and after the washing process by methanol and deionized water are presented in Fig. 6. Through the washing process using methanol and deionized water, the oxygen content is reduced from 14.4 wt.% to 0.725 wt.% and 0.733 wt.%, respectively. Therefore, it was confirmed that most of the B_2O_3 was removed.

Fig. 7 shows SEM images of powders synthesized by different reactions. Fig. 7-a provides an SEM image of commercially available ZrB_2 powders (98%, 1.5–2.5 μ m, Grade: ZrB_2 -F, Japan New Metals) and Fig. 7-b is that of powders synthesized using ZrO_2 ,



Fig. 7. Scanning electron microscopy morphologies of (a) commercial ZrB₂ powders and ZrB₂ powder synthesized from (b) ZrO₂ + B₂O₃ + C (Z5BO10C), (c) ZrO₂ + B₄C + C (Z0.7B1.5C), and (d) ZrO₂ + B₄C (Z0.73B).



Fig. 8. Particle size distribution of synthesized ZrB_2 powders from Z0.73B at 1250 °C for 1 h after washing.

B₂O₃, and carbon (Z5BO10C) at 1250 °C for 3 h. ZrB₂ powders obtained from Z5BO10C showed rod shape growth. Its growth mechanism is unclear, but it is probably related to the presence of liquid B₂O₃ [19]. ZrB₂ has hexagonal crystal structure with anisotropy in the *a*-axis (3.17 Å) and *c*-axis (3.53 Å) [1]. Preferential growth of ZrB₂ grains in ZrB₂-MoSi₂ composites was recently claimed to be due to the formation of liquid phase [23]. Similarly, the rod shape morphology of ZrB₂ in this study may be attributed to B₂O₃ existing in a liquid phase [19,23]. Fig. 7-c shows the morphology of powders using ZrO₂, B₄C, and carbon (Z0.7B1.5C) thermally treated at 1250 °C for 1 h. Compared with powders synthesized using ZrO_{2} , B₂O₃, and carbon (Fig. 7-b), not only does Z0.7B1.5C have a smaller particle size, but there is little rod shape growth. However, there is much residual impurity carbon, which was not easy to remove and additional processes were needed. Fig. 7-d provides an SEM image of powders synthesized using ZrO_2 and B_4C (Z0.73B) at 1250 °C for 1 h. These powders have $D_{50} = 1.1 \,\mu\text{m}$ in terms of particle size (Fig. 8) and have a hexagonal shape. Further there is little rod shape growth compared with powders synthesized using ZrO₂, B₂O₃, and carbon.

4. Conclusions

ZrB₂ powders were synthesized by adjusting the amounts of reactants with reference to thermo-gravimetric/differential thermal analysis, thermodynamic data, and reaction formulas used for the synthesis of ZrB₂ powders.

ZrB₂ powders were synthesized by:

(i) Using ZrO₂, B₂O₃, and carbon at 1250 °C for 3 h under flowing argon of 2 L/min. Although the synthesis temperature was low compared with the thermodynamically calculated value, there were residual impurities of which carbon was especially difficult to remove. Synthesized ZrB_2 powders have a particle size of $3-4 \mu m$, and there is rod shape growth due to B_2O_3 existing in a liquid phase.

- (ii) Using ZrO₂, B₄C, and carbon. All ZrO₂ was converted to ZrB₂ by an excess of 0.2 mol of B₄C more than the stoichiometric composition at 1250 °C for 1 h under flowing argon of 2 L/ min. These powders have a smaller particle size and there is less rod shape growth than powders synthesized using B₂O₃ and carbon. However, there is much residual impurity carbon, which is not easy to remove.
- (iii) Using ZrO₂, B₄C. ZrO₂ was completely converted to ZrB₂ through an additional 0.016 mol of B₄C over the stoichiometric composition at 1250 °C for 1 h under flowing argon of 2 L/min. Residual impurity B₂O₃ in the as-synthesized ZrB₂ powders was easily removed by a washing process using methanol or deionized water. Finally, prepared ZrB₂ powders have a particle size of 1.1 μ m, hexagonal shape, the least rod shape growth compared with synthesis methods (i) and (ii), and low oxygen content (0.725 wt.%).

Acknowledgments

This research was supported by the National Research Foundation of Korea.

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