

Influence of SiC on phase and microstructure of ZrB₂ powders synthesized via carbothermal reduction at different temperatures

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ABSTRACT

ZrB₂ powders were successfully prepared via carbothermal reduction of ZrO₂ with H₃BO₃ and carbon black under flowing argon. By introducing SiC species into reaction mixtures, the effects of SiC addition on phase composition and morphology of ZrB₂ powders thermally treated at different temperatures were investigated. The resultant samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive spectrometer (EDS). The highly pure ZrB₂ with the mean size of 5 μm could be obtained at 1600 °C for 90 min and the grains presented columnar shapes. After addition of SiC, ZrB₂ revealed relatively better crystallinity and finer particle size. Regular columnar ZrB₂ grains ranging from 1 to 2 μm were seen existing after reaction at 1500 °C for 90 min.

1. Introduction

ZrB₂ is actively applied to ultra-high temperature materials, refractory materials and electronic components owing to its excellent properties, such as high melting point, high hardness, good electrical conductivity and low thermal expansion coefficient [1–3]. Currently ZrB₂ powders can be produced by various methods, including self-propagating high temperature synthesis [4], sol-gel method [5], direct molten salt reaction [6], carbothermal reduction [7], borothermal reduction [8,9] and boro/carbothermal reduction method [10]. Among multiple techniques for powder synthesis, carbothermal reduction method has received widespread attention due mainly to the simple manufacturing process and low cost. Based on this approach, previous researchers have successfully obtained the ZrB₂ powders and achieved some remarkable results. Li et al. reported that ZrB₂ nanofibers could be synthesized by combination of solution based carbothermal reduction and electrospinning technique, in where polyzirconoxane (PZO), polyacrylonitrile (PAN) and boric acid were provided as the zirconia, carbon and boron sources, respectively [11]. A.I. Karasev prepared ZrB₂ powders through the reduction of mixtures of ZrO₂ and B₂O₃ with carbon, and indicated that excess B₂O₃ was indispensable to obtain highly pure ZrB₂. The influences of temperature, holding time, and ambient atmosphere on the fabrication process of ZrB₂ were also discussed in the paper [12].

Earlier studies demonstrated that the addition of SiC could improve the oxidation resistance, as well as lead to considerable increment in the strength of ZrB₂ due to the changes in grain size and microstructure [13–18]. A study by Xie et al. on the effect of SiC addition on the formation of ZrB₂ showed adding SiC improved the morphology and affected the growth mechanism of ZrB₂ particles [19]. Besides, Shahedi Asl et al. discovered that the presence of SiC could inhibit the grain growth of ZrB₂ matrices during calcination [20].

In our study, ZrB₂ powders were synthesized by carbothermal reduction, using ZrO₂, H₃BO₃ and carbon black as the raw materials. By adding 30 vol% SiC into reaction mixtures, the effects of SiC on phase composition and microstructural development of ZrB₂ were analyzed at different heating temperatures.

2. Materials and methods

Starting materials used in this paper were ZrO₂ (particle size ≤ 10 μm, purity 99%), H₃BO₃ (particle size ≤ 20 μm, purity 96%), carbon black (particle size ≤ 10 μm) and SiC (particle size ≤ 0.5 μm, purity 96%). The chemical composition of SiC starting powder was listed in Table 1. The powder mixtures of ZrO₂, H₃BO₃ and carbon black should have reacted according to the stoichiometric proportion of Eq. (1). Excess H₃BO₃ was added to ingredients, however, to avoid the loss of boron source owing to the poor viscosity and significant vaporization

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Table 1
Chemical composition of SiC starting powder (wt%).

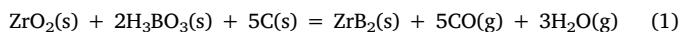
Total Si	Total C	Total O	Al ₂ O ₃	Fe ₂ O ₃
69.09	29.34	1.74	0.11	0.06

Table 2
Composition of the raw materials.

Sample no.	Content(molar ratio)		
	ZrO ₂	H ₃ BO ₃	C
ZB1	1	3.2	5
ZB2	1	3.6	5
ZB3	1	4	5

of B₂O₃ above 1373 K. ZrO₂, H₃BO₃ and carbon powders were weighed according to Table 2.

The powders were ball-milled at 300 rpm for 20 min in an alumina pot with zirconia balls as grinding body. As H₃BO₃ was easy to evaporate during heat treatment, thus doing harm to furnace in virtue of acid corrosion, the mixed powders were placed in a vacuum oven at 120 °C for 12 h to obtain HBO₂ via Eq. (2) [21,22]. After that, the preheated powders were filled into graphite crucibles and sealed in a pressureless furnace safely. The powder samples were heated at 10 °C/min up to 1400–1700 °C and then held for 90 min. After cooling to room temperature, gray powders with good dispersibility were fabricated for each temperature. During the cycle, argon gas was kept flowing through the chamber of furnace at a rate of 35 sccm (standard cubic centimeter).

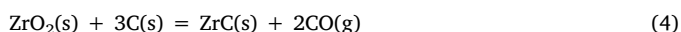


Further, 30 vol% SiC was added to the reaction powder mixtures with optimal H₃BO₃ content to investigate the influences of SiC addition on composition and microstructure of ZrB₂. The volume ratio of SiC to the products obtained according to Eq. (1) was maintained at 3: 7, which was calculated based on the densities of 6.09 g/cm³ for ZrB₂ and 3.21 g/cm³ for SiC.

X-ray diffractometer (XRD: D/max-RA, Japan) was utilized to analyze the phases. The morphology was characterized by Scanning electron microscope (SEM: D/max-RA, Germany) using both secondary electron (SE) and backscattered electron (BSE) imaging. Energy dispersive spectrometer (EDS: D/max-RA, Germany) was used to investigate element contents of the products.

3. Results and discussion

Fig. 1 showed the X-ray diffraction patterns of powders synthesized by ZB2 at different temperatures. Weak peaks of ZrB₂ were detected while unreacted ZrO₂ phase was remained in Fig. 1(a), implying that ZrO₂ had not been totally converted to ZrB₂ at 1400 °C. Besides, the track of C was not observed in XRD pattern owing to its amorphous property. As seen from Fig. 1(b), X-ray pure ZrB₂ was successfully obtained. With increase in temperature to 1600 °C, the increased intensities and broaden peaks of ZrB₂ indicated better crystallinity and finer particle size. Since B₂O₃, the product of HBO₂ dehydration at above 400 °C (Eq. (3)), volatilized more easily at relatively high temperature and the remaining ZrO₂ could react with carbon black via Eq. (4), ZrC phase appeared in Fig. 1(d).



The SEM images of powders derived from ZB2 at different

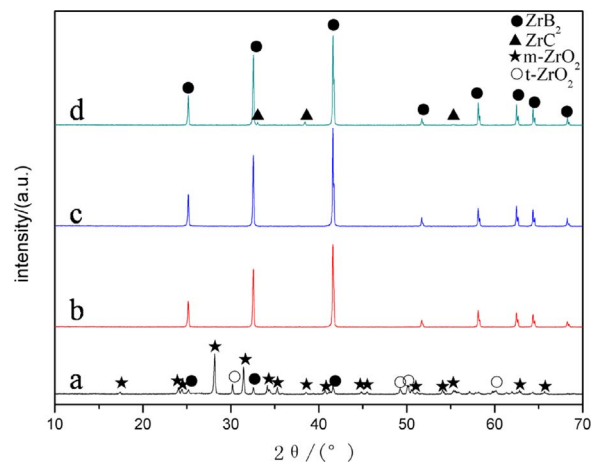


Fig. 1. X-ray diffraction patterns of powders synthesized by ZB2 at different temperatures. (a) 1400 °C; (b) 1500 °C; (c) 1600 °C; (d) 1700 °C.

temperatures were given in Fig. 2. From Fig. 2(a), since the calcination temperature was not sufficient to provide rapid diffusion required for the completed reaction, particle aggregates could be intuitively observed. Rod-like ZrB₂ grains possessing a mass of structural defects had been identified when heated at 1500 °C, though, there were small-sized irregular particles with inhomogeneous distribution in Fig. 2(b) indicating no sufficiently high temperature for the formation of fully crystallized grains. When the temperature rose up to 1600 °C, the obtained ZrB₂ powders with the mean size of 5 μm presented an columnar shape with minor defects, showing a more accomplished reaction process, which was in accordance with the XRD results. The melting of grain boundaries was clearly observed in Fig. 2(d), illustrating the existence of oversintering with the increase of calcination temperature.

Fig. 3 showed the XRD patterns of powders thermally treated at 1600 °C for 90 min with different amounts of H₃BO₃ in excess. Peaks of m-ZrO₂ and t-ZrO₂ were confirmed in the XRD analysis result of ZB1, implying the lack of boron source. From Fig. 3(b), phase pure ZrB₂ could be obtained when 80 mol% of excess H₃BO₃ was added to the stoichiometric composition. Owing to the low atomic number and amorphous property, B₂O₃ was not detected in Fig. 3(c). Based on above results, it could be confirmed that highly pure columnar ZrB₂ grains had been produced with 80 mol% H₃BO₃ in excess after calcined at 1600 °C for 90 min in argon.

In order to study the role of SiC in synthesizing ZrB₂ powders, 30 vol% SiC was introduced into the reaction mixtures of ZB2. The XRD patterns of products with 30 vol% SiC prepared at different temperatures were displayed in Fig. 4. From Fig. 4(a), (b) and (c), the obtained powders were composed of SiC and ZrB₂. Broad diffraction peaks and high intensities of ZrB₂ at 1500 °C revealed the best crystallinity and finest grain size. Except for ZrB₂ and SiC phases, weak track of ZrC was also identified in Fig. 4(d).

Fig. 5 presented the SEM micrographs of products with 30 vol% SiC synthesized at different temperatures. Some of the grains with poor crystallinity and inhomogeneous distribution were observed in Fig. 5(a). The regular columnar ZrB₂ powders thermally treated at 1500 °C reduced to 1 μm in terms to grain size. Compared to Fig. 2, it was intuitive that the growth of ZrB₂ received inhibition of SiC particles, and the difference in grain size could be attributed to the grain-boundary pinning of SiC, in where SiC limited the grain boundary migration rate as a grain growth inhibitor [17–20,23]. On further increasing the temperature to 1600 °C, ZrB₂ powders had no obvious change in size while some of the grain boundaries began to melt, resulting in a rod-like structure. Besides, oversintering happened in Fig. 5(d), leading to agglomeration of the particles. Based on the previous XRD and SEM results, it could be concluded that the optimal calcination temperature for the formation of ZrB₂ powders decreased to

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