Effects of gelation temperature, water, polyethylene glycol on morphology of ZrB₂ particles synthesized by sol-gel method

Yun Zhang* and Hong Sun
Department of applied chemistry, Yuncheng University, Shanxi, People’s Republic of China, 044000

Zirconium diboride (ZrB₂) ceramic material has many excellent properties and gains great importance in variety of applications. In the present work, the influence of the gelation temperature, H₂O, and polyethylene glycol on the morphology of ZrB₂ particles was investigated. Increasing the gelation temperature, the particle shapes changed from sphere-like particles at 65 °C to a particle chain at 75 °C, and then form rod-like particles at 85 °C. Moreover, different concentration of polyethylene glycol with 1 and 3 M was added, the morphology of ZrB₂ particles was prism and sphere-like, respectively. When the polyethylene glycol was added with 3 M, the reunion between particles was obviously lowered. Furthermore, different amount of water with 4, 6, and 10 ml was added, the shape of ZrB₂ particles was sphere-like and the average grain diameter was changed from 65, 25, to 20 nm.

Key words: Gelation temperature, Polyethylene glycol, H₂O, Morphology, Zirconium diboride.

Introduction

Zirconium diboride (ZrB₂) is one of the materials known as ultra-high-temperature ceramics. It has a series of excellent properties, such as a high melting temperature (3250 °C), high hardness (23 GPa), flexural strength (>500 MPa) [1], high thermal (60-140 W/(mK)), and electrical conductivity (~10⁷ S/m)[2] because of the coexistence of covalent and metallic bond. The unique combination of properties makes ZrB₂ a promising candidate for thermal protection materials, cutting tools, high temperature electrodes, and molten metal crucibles [3-7].

Up to now, one-dimensional (1D) materials have attracted considerable attention because of their outstanding optical, electrical, and mechanical properties. In particular, studies about the synthesis and application of 1D SiC and Si₃N₄ have been widely reported. As reported by Li [8], SiC whisker reinforced reaction bonded SiC composites with increased toughness have been developed. Likewise, Hirao et al [9], fabricated self-reinforced Si₃N₄ with a preferred orientation of elongated grains showing increased fracture toughness (1101 MPa·m¹/₂) and bending strength (1100 MPa) by seeding with rod-like β-Si₃N₄ particles. Similar to SiC and Si₃N₄, 1D ZrB₂ was recently reported to be an effective reinforcement to improve the fracture toughness of the ZrB₂-based composites, such as ZrB₂-ZrCₓ [10], ZrB₂-MoSi₂ [11], and ZrB₂-SiC-WC [12]. Therefore, 1D ZrB₂ may have great potentials for application and the synthesis of 1D ZrB₂ is attractive.

At present, several different researchers have showed interest in synthesizing ZrB₂ powders using different methods to change the sintering performance and oxidation resistance, but few literatures reported ZrB₂ shapes [13-15]. For instance, Li [16] prepared ZrB₂ with nanofibers by carbothermal reduction via electrospinning using polyzirconoxane, H₃BO₃, and polyacrylonitrile. Li et al [17], synthesized ZrB₂ with plate shapes by solid-state method using ZrO₂, H₃BO₃, and carbon. In our previous work [18], ZrB₂ particles with different shapes (equiaxed, chain, and rod) have been synthesized by sol-gel method using Zr(OPr)₄, H₃BO₃, C₁₂H₂₅O₁₁, and AcOH. In this study, the morphology of ZrB₂ with sphere-like, chain, rod-like, and prism has been synthesized by sol-gel method through changing the gelation temperature, adding polyethylene glycol (PEG), and adding different amount of H₂O.

Experimental and Method

Starting materials
Zr(OPr)₄ was supplied by the Shanghai Jingchun Reagents Co. Ltd., Shanghai, China. H₃BO₃, C₁₂H₂₅O₁₁, acetic acid (AcOH), methanol (CH₃OH), polyethylene glycol 400 (PEG), and acetylacetone (acac) were supplied by the Lanyi Reagents Co. Ltd., Beijing, China. The grade of all the above reagents was analytical.

Synthesis
According to the literature [19], the synthesis of ZrB₂
powder is shown as follows: 6.3 ml of Zr(OPr)$_4$ was dissolved in a stirred mixture solution of 25 ml CH$_3$OH and 1.2 ml $acac$ at room temperature. Then, 4.0 ml (6 ml and 10 ml were also in the final section of this paper) of distilled water was dropwise added and this resulting solution was continuously stirred for 30 min. We refer to this solution as Solution 1. On the other hand, 2.5 g of H$_2$BO$_3$ and 2.9 g of C$_2$H$_3$O$_2$CO were dissolved in 45 ml of AcOH using another beaker. Then, it was heated with vigorous stirring to 80 °C and maintained for 0.5 h. This was Solution 2. Afterwards, the Solution 1 was carefully decanted to the Solution 2 after the Solution 2 previously cooled to room temperature. This was Solution 3. The resulting Solution 3 was heated with vigorous stirring to 65 °C (This fixed temperature is so-called gelation temperature to form sol/gel. 75 °C and 85 °C were also set in the final section of this paper.) and maintained for 4 h to form a wet gel. Finally, it was dried under vacuum at 120 °C for 3 h followed by a grind process using an agate mortar and a pestle. In this way, a precursor was prepared. This synthesis powder was called Sample 1.

For purposes of comparison, when adding 4 ml of water was fixed, the gelation temperature was changed from 65, 75, to 85 °C, the synthesis powders were called Sample 2 (75 °C) and Sample 3 (85 °C), respectively. When the gelation temperature was fixed at 65 °C, the amount of H$_2$O was changed from 4, 6, to 10 ml, the synthesis powders were called Sample 4 (6 ml) and Sample 5 (10 ml), respectively. Based on Sample 1, the different concentration of PEG with 1 and 3 M was added to Solution 3, the synthesis powders were called Sample 6 (1 M) and Sample 7 (3 M), respectively.

After that, the above precursors were firstly heated to 800 °C at a heating rate of 5 °C / min, then to 1200 °C at 3 °C / min and maintained at this temperature for 2 h in argon using an alumina tube furnace. Afterwards, the precursor was continued to heat from 1200 °C to 1550 °C at a heating rate of 2 °C / min and held at this temperature for 2 h. Then, the sample was cooled to room temperature at a cooling rate of 5 °C / min. In the end, gray powders were obtained.

Characterization

The crystallographic constitution was identified by means of an X-ray diffractometer (XRD) using graphite monochromatized CuK$_\alpha$ radiation (Rigaku, D/MAX 2200 PC). Crystallite size was estimated using the Debye-Scherer equation,

$$D_{hkl} = \frac{0.9 \lambda}{\beta_{hkl} \cos \theta} \quad (1)$$

Where $D_{hkl}$ is the crystallite size, $\lambda$ is the wavelength of Cu K$_\alpha$ radiation, $\beta_{hkl}$ is the full-width at half maximum, and $\theta$ is the Bragg diffraction angle. The morphology of the final products was characterized by SEM using a JEOL JSM-6700F JAPAN microscope and TEM using a JEM-2100F microscope.

Results and Discussion

Structure and composition characterization

It is well known that the gelation temperature and the amount of H$_2$O were important factors for both nucleation and crystal feature. Moreover, surfactant can change the reunion between the particles. Here, different gelation temperatures, different amount of H$_2$O, and different concentration of PEG were fixed to synthesize ZrB$_2$ powders.

According to the literature [19], a single phase of ZrB$_2$ without residual ZrO$_2$ was evolved at 1550 °C for 2 h. Fig. 1 shows XRD patterns of the Sample 1, 2, 3, 4, 5, 6, and 7 calcined at 1550 °C for 2 h, respectively. It might be seen that all of the diffraction peaks were well assigned to a single phase of ZrB$_2$.

Morphology characterization

Influence of gelation temperature on morphology of ZrB$_2$

According to the literature [18], it was observed that the morphology of ZrB$_2$ has changed with different gelation temperature from sphere-like at 65 °C to particle chain at 75 °C, and rod-like at 85 °C. Here, the influence of the gelation temperature on the morphology of the samples was also investigated, and the SEM images of the as-calcined samples are shown in Fig. 2. It is observed that the morphology of the samples was affected by the gelation temperature. For the ZrB$_2$ sample gelated at 65 °C, the SEM revealed a sphere-like morphology of ZrB$_2$ nanoparticles (see Fig. 2(a)). At 75 °C, the morphology showed a particle chain (see Figs. 2(b) and 3(a)). With the increasing of the temperature to 85 °C, the morphology of the ZrB$_2$ particles evolved to a rod-like shape (see Figs. 2(c) and 2(d)).
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Additionally, the size of ZrB$_2$ particle also increased notably with the increasing of the gelation temperature.

To explain the morphology influenced by the gelation temperature requires a multidisciplinary knowledge. According to the literature [18], a further investigation, a high-resolution TEM (HRTEM), was conducted to clarify the microstructure and crystal feature of the ZrB$_2$ particles. At a lower temperature, the rate of nucleation was faster than that of growth, whereas the monomer concentration was sharply decreased [20]. Such slow growth conditions favored the formation of a sphere-like shape (see Fig. 2(a)). With increasing the gelation temperature, Figs. 2(b) and 3(a) show that a particle chain of ZrB$_2$ was evolved at 75 °C. The HRTEM image of ZrB$_2$ particle chain revealed that each unique particle chain was composed of several sphere-like particles. These sphere-like particles aligned one by one to form a polycrystalline particle chain of ZrB$_2$ and shared a quasi-parallel crystal orientation at the grain interfaces (see Figs. 3(a, b)). It is notable that the interface between the two grains in the rectangle region (magnified in Fig. 3(b)) involved edge dislocations (arrowhead). With the temperature further increased, adjacent particles fused together to form strong links resulting in the evolution of ZrB$_2$ rods (see Figs. 2(c) and 3(c, d)). In the same way, the adjacent grains shared a common crystallographic orientation, followed by joining of these grains at a planar interface with edge dislocations (arrowhead) (see Fig. 3(d)). It also may be found from the HRTEM image that these particle chain/rod shared {001} lattice fringes with interplanar spacings of 0.35 nm.

From a crystallography perspective, according to the “oriented attachment mechanism”, which was first explored by Banfield [21], adjacent particles share a common crystallographic orientation, followed by joining of these particles at a planar interface. Bonding between adjacent nanoparticles reduces the overall energy by removing the surface energy associated with unsatisfied bonds. Clearly, this attachment mechanism is reflected by the results in Fig. 3. The ZrB$_2$ nanoparticles connected with each other via the “oriented attachment mechanism” and a reduction in surface free energy was achieved by the complete removal of pairs of surfaces. Imperfect oriented attachment of nanocrystals can generate dislocations. Any defects observed by HRTEM can be attributed to the growth process.

Table 1. The morphology and phase composition of powder with different amount of H$_2$O and the corresponding gelation time.

<table>
<thead>
<tr>
<th>Amount of H$_2$O (ml)</th>
<th>4</th>
<th>6</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gelation temperature (°C)</td>
<td>65</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Gelation time (h)</td>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>Calcination temperature (°C)</td>
<td>1550</td>
<td>1550</td>
<td>1550</td>
</tr>
<tr>
<td>Morphology</td>
<td>sphere-like</td>
<td>sphere-like</td>
<td>sphere-like</td>
</tr>
<tr>
<td>Average grain diameter (nm)</td>
<td>62</td>
<td>25</td>
<td>20</td>
</tr>
</tbody>
</table>

Influence of the amount of H$_2$O on morphology of ZrB$_2$

Theoretically, metal organic compounds forming process of sol and gel is essentially a hydrolysis process. The speed of formation sol-gel, the growth of crystal, and the morphology of ZrB$_2$ particles may be influenced by the different amount of H$_2$O. In the present work, when the gelation temperature was fixed at 65 °C, adding the different amount of H$_2$O from 4, 6, to 10 ml was investigated, respectively. From Fig. 1 (4) and Fig. 1(5), all of the diffraction peaks were well assigned to a single phase of ZrB$_2$. Moreover, when the gelation temperature and the calcination temperature
were fixed, adding the amount of H$_2$O from 4, 6, to 10 ml, the gelation time was changed from 4, 6, to 8 h, and the average grain diameter was changed from 65, 25, to 20 nm, respectively (see Tab. 1).

Furthermore, the morphology of Sample 1, 4 and 5 were sphere-like (see Fig. 2(a) and Fig. 4). Here, adding the different amount of H$_2$O has not changed the morphology of ZrB$_2$, but the average grain diameter became smaller and the reunion of particles was serious. In order to explain the phenomenon of reunion, Ready [22] thought that the hydrogen bonds from H$_2$O molecules with the hydroxyl from the particles of the surface formed the bridge bonds. Those bridge bonds determined the size of reunion force between particles. When the particle was close to another particle, through the interaction of the hydrogen bonds and hydroxyl, and when the powder was dry, the H$_2$O molecules took off, and because of the close to each other to form chemical bonds between particles, eventually the hard reunion was produced [23].

Influence of the polyethylene glycol on morphology of ZrB$_2$

In the synthesis process, the morphology and size of particles were influenced by its environment. To stabilize the particles dispersed in the liquid system mainly reduced attractive force and increased the repelling force to control the particle / liquid bead forming gathered or flocculation. That process could be achieved by using nonionic surfactants or polymeric surfactants. Here, PEG was used to change the reunion between particles.

Fig. 1(6) and (7) show that all of the diffraction peaks were well assigned to a single phase of ZrB$_2$ and Fig. 5 shows that the morphology of ZrB$_2$ was prism and sphere-like. Obviously, the reunion was lowered between the particles by adding 3 M of PEG (see Fig. 5(b)), but the average grain diameter became bigger.

To explain the mechanism of forming different morphology of ZrB$_2$ was that PEG was a kind of nonionic surfactant and did not exist in the form of ions in the solution, therefore, its stability was very high. In the anhydrous state, polyoxyethylene chain of PEG was in zigzag state, when it was soluble in water, the weak hydrogen bonds were formed though the oxygen atoms of ether bond with the hydrogen of H$_2$O, and the molecular chains were twists and turns. The oxygen atoms of hydrophilic were located in the outer edge of the chain and ethenyl (-CH$_2$CH$_2$-) was located in the inner edge of the chain, thus, the chain around was just a hydrophilic entirety [24, 25]. In the crystal growth process, the hydrophilic group of PEG interacted with different crystal face of ZrO$_2$ particles lead to changing the growth speed of different crystal directions of ZrO$_2$ particles. Because of the different concentration of PEG, the number of PEG adsorbed around the ZrO$_2$ particles and the interfacial tension were different. Generally, the morphology of particles with the increasing of surfactant concentration more tended to form the rules of the morphology. Therefore, there were two shapes of ZrB$_2$ particles.

After adding PEG, ZrO$_2$ particles were parcel by PEG and formed the space barriers because of the adsorption. That is to say, that space barriers could prevent the collisions and union each other between particles, therefore, the reunion between particles could be lowered (see Fig. 5(b)).

Conclusions

In summary, sphere-like, particle chain, rod-like, and prism ZrB$_2$ particles could be obtained through different gelation temperatures (65, 75, and 85°C), different concentration of PEG (1 and 3 M), and different amount of H$_2$O (4, 6, and 10 ml). In an effort to understand the mechanism of morphology evolution at different gelation temperatures, the “oriented attachment mechanism” might explain the crystalline processes of ZrB$_2$ particles based on the HRTEM observation. Moreover, the reunion between particles was obviously lowered by adding 3 M of PEG. Furthermore, the amount of H$_2$O with 4 and 6 ml was added, the average grain diameter was 25 and 20 nm, respectively.

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