



# Synthesis of ZrB<sub>2</sub> and ZrB<sub>2</sub>-SiC Powders Using a Sucrose-Containing System

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 $ZrB_2$  and  $ZrB_2$ -SiC powders are synthesized by a sol–gel method from zirconium *n*-propoxide, tetraethyl orthosilicate (only for  $ZrB_2$ -SiC), boric acid, and sucrose. After reduction at 1550 °C, both  $ZrB_2$  and  $ZrB_2$ -SiC are unconsolidated, soft gray powders. The  $ZrB_2$ -SiC particles have an equiaxed shape with a diameter of about 800 nm and a uniform size distribution. The SiC may be very finely distributed, because we barely find SiC among  $ZrB_2$  particles when using energy dispersive X-ray spectroscopy (EDS), although both  $ZrB_2$  and SiC are identified by X-ray diffractometry (XRD).

Keywords: Sol–Gel, Ultra-High Temperature Ceramics, Zirconium Compounds, Powders, Synthesis.

# **1. INTRODUCTION**

Because of its high melting temperature, and outstanding wear and corrosion resistance, zirconium diboride  $(ZrB_2)$ has emerged as one of the leading candidate materials for ultra-high-temperature applications.<sup>1-3</sup> However, due to the strong covalent bonds, and low bulk and grain boundary diffusivities, high purity ZrB<sub>2</sub> powder cannot be fully sintered. Therefore, various additives, especially SiC, have been employed to improve the sinterability and mechanical properties of ZrB2.3-6 To date, ZrB2-SiC ceramics are usually directly sintered from commercially available ZrB<sub>2</sub> and SiC component powders after mechanical mixing and pressing. Moreover, when making sintered bodies, it is widely believed that composite powders possess higher sinterabilities, and thus better subsequent properties, than pure component powders. Thus we sought a synthesis method to decrease the particle size and increase the uniformity of ZrB<sub>2</sub>-SiC composite powder.

In previous studies, various methods have been adopted to synthesize ZrB<sub>2</sub> powders. Mishra et al. prepared ZrB<sub>2</sub> powders by the self-propagating high-temperature synthesis process (SHS) using oxides or salts of zirconium, boric acid, and magnesium or a compound of magnesium.<sup>2</sup> Tsuchida et al. developed a technique combining mechanical activation (MA) by grinding and SHS in air, which is called MA-SHS in air to realize the simultaneous synthesis of carbide and boride of zirconium from the powder mixtures of Zr:B:C=1:1:1.7 Zhao et al. synthesized ZrB<sub>2</sub> powders by solid-state reaction with the use of ZrO<sub>2</sub>, B<sub>4</sub>C and C powders as raw materials.<sup>3</sup> In one of our previous works, a single phase of plate-like ZrB<sub>2</sub> powder was successfully synthesized by borothermal/carbothermal reduction using as-synthesized amorphous hydrous nano-ZrO<sub>2</sub>, amorphous boron and nanocarbon.<sup>8</sup> Another paper dealt with the discussion of a new sol-gel method, using AcOH as both a modifier and a unique solvent to control zirconium *n*-propoxide  $[Zr(OPr)_4]$  hydrolysis to synthesize ZrB<sub>2</sub> particles.<sup>9</sup>

Comparing with other synthetic methods, the sol-gel method is a potential method for low-temperature synthesis of fine powders. A further advantage of the sol-gel method is that high chemical and phase homogeneity can

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be achieved because the starting components interact at the molecular or colloidal level. Moreover, the powders synthesized by this method can present a relatively small particle size. Consequently, a sol–gel method may greatly improve  $ZrB_2$ -SiC ceramics. Xie et al. synthesized  $ZrB_2$ powder depending on the starting materials of  $Zr(OPr)_4$ , H<sub>3</sub>BO<sub>3</sub>, and phenolic resin by sol–gel method.<sup>10</sup> Yang et al. prepared  $ZrB_2$  powder with the starting materials of zirconium oxychloride ( $ZrOCl_2 \cdot 8H_2O$ ), H<sub>3</sub>BO<sub>3</sub>, and phenolic resin by sol–gel method.<sup>11</sup>

In the present study, sucrose  $(C_{12}H_{22}O_{11})$  was adopted as a source of pyrolyzed carbon. We conducted experiments where  $ZrB_2$ , and then  $ZrB_2$ -SiC composite powders were synthesized using a sucrose-containing sol–gel system. Under neutral conditions, a metal alkoxide reaction system with acetylacetone (acac) as the chemical modifier was investigated.

## 2. EXPERIMENTAL DETAILS

All major chemicals were AR grade and used without further purification. Zirconium *n*-propoxide  $[Zr(OPr)_4]$ was supplied by Shanghai Jingchun Reagents Co., Ltd., Shanghai, China. Tetraethyl orthosilicate (TEOS), boric acid (H<sub>3</sub>BO<sub>3</sub>), sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>), acetic acid (AcOH), methanol (CH<sub>3</sub>OH), and acetylacetone (acac) were obtained from Lanyi Reagents Co., Ltd., Beijing, China.

A general flow diagram for the synthesis of  $ZrB_2$ -SiC composite powder is shown in Figure 1. For  $ZrB_2$  with 20 vol.% SiC, 2.5 g boric acid and 2.9 g sucrose were



Figure 1. General flow diagram for synthesis of  $ZrB_2$ -SiC composite powder (to synthesize  $ZrB_2$  powder, the step for preparing Solution 3 is skipped).

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dissolved in 45 ml acetic acid. This mixture was then heated with vigorous stirring to 80 °C, held at that temperature for 0.5 h, and then cooled to room temperature to give "Solution 1." To make "Solution 2," 6.3 ml  $Zr(OPr)_4$ was dissolved with stirring in a mixture of 25 ml methanol and 1.2 ml acetylacetone at room temperature. Thus, a B:Zr molar ratio of 2.3 was fixed. Then, 2.5 ml TEOS was added to Solution 2 with stirring, followed by dropwise addition of 10 ml distilled water; this resulting solution was continuously stirred for 0.5 h to give "Solution 3." Then Solution 3 was carefully decanted into Solution 1 to produce "Solution 4." Solution 4 was heated with vigorous stirring to 65 °C and maintained for 8 h to form a wet gel. Finally, the wet gel was dried under vacuum at 120 °C for 3 h, and then ground using a pestle and mortar.

If TEOS was not added (i.e., Solution 3 was not formed), and Solution 1 and Solution 2 were directly mixed under the same conditions, the process led to a precursor for single phase  $ZrB_2$  powder. After that, the precursor was transferred into a crucible with a cover and placed in an alumina tube furnace under an Ar atmosphere. The sample was initially heated to 800 °C at a heating rate of 5 °C/min, then from 800 to 1200 °C at a rate of 3 °C/min and held at 1200 °C for 2 h. Finally, it was heated to 1550 °C at 2 °C/min and kept for 2 h. Then, the sample was cooled to room temperature at a cooling rate of 5 °C/min. The final samples were unconsolidated, soft gray powders which did not require grinding.

Sci The crystallographic phases were identified by X-ray diffractometry (XRD, D/MAX 2200 PC, Rigaku, Japan). The morphology and distribution of elements within the particles were investigated using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM, EDS, JEOL JSM-6700F, JEOL, Japan).

## 3. RESULTS AND DISCUSSION

Metal alkoxides are known to react spontaneously with water and form precipitates resulting from successive hydrolysis and condensation reactions. To obtain a sol/gel,  $Zr(OPr)_4$  must be chemically modified using a complexing agent to decrease the alkoxide reactivity with water. Generally, inorganic acids catalyze hydrolysis reactions, whilst polycondensation is catalyzed under basic conditions. AcOH and acac are typical additives which have been reported to prevent fast hydrolysis and precipitation of transition metal oxides.<sup>12-14</sup> In this study, we used acac as a chemical modifier under neutral conditions. The effect of acac is to stabilize the alkoxide precursors by chelating (see Reaction (1)). As a consequence, it is possible to control the hydrolysis and condensation reactions that are carried out during the subsequent processing steps (see Reactions (2)–(5)). Meanwhile, the reaction of  $Zr(OPr)_4$ with water is still possible, since the Zr coordination number can increase up to 7 or 8. Upon reaction with water, OR groups are hydrolyzed first, while acac ligands are not completely removed. Zirconium diketonate  $[Zr(acac)_2]$ is more resistant to hydrolysis compared to the corresponding Zr(OPr)4;<sup>15</sup> this is advantageous for subsequent processes.



Hydrolysis:

$$\equiv Zr - OPr + H_2O \rightleftharpoons Zr - OH + PrOH$$
(2)

Condensation:

 $\equiv Zr - OPr + HO - Zr \equiv \Longrightarrow Zr - O - Zr \equiv +PrOH$ (4)

 $\equiv$  Zr - OH + HO - Zr  $\equiv \rightleftharpoons \equiv$  Zr - O - Zr  $\equiv$  +H<sub>2</sub>O (5)

A yellow solution (Solution 2 in Fig. 1) was formed after Reactions (4) and (5). This solution then reacted with Solution 1 prepared from H<sub>3</sub>BO<sub>3</sub>, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> and AcOH to form Solution 4 before a wet gel was evolved. After drying under vacuum and grinding, a powder precursor was obtained.



Figure 2. XRD patterns of synthesized precursor, and products from the precursor calcined at 1300, 1400 and 1550 °C.

Figure 2 shows XRD patterns of the synthesized precursor with a B:Zr molar ratio of 2.3. Both the raw materials and products prepared by calcining the precursor at different temperatures are included on the figure. The synthesized precursor is clearly amorphous, with no peaks in its XRD pattern. In contrast, with increasing temperature of carbothermal reduction, the precursor crystallizes in stages. In the precursor treated at 1300 °C for 2 h, m-ZrO<sub>2</sub>, t-ZrO<sub>2</sub>, and ZrB<sub>2</sub> phases are identified. With increasing temperature, the diffraction intensity of ZrB<sub>2</sub> increases; the intensities of both m-ZrO<sub>2</sub> and t-ZrO<sub>2</sub> peaks decrease at 1400 °C. Finally, an unconsolidated, soft gray powder was obtained after heating at 1550 °C for 2 h. The XRD pattern of this product shows only ZrB<sub>2</sub> phase, indicating that the carbothermal heating process is complete after treatment at 1550 °C.

Idealized reactions to produce ZrB<sub>2</sub> by carbothermal reduction are:

$$\mathrm{H}_{3}\mathrm{BO}_{3}(s) \to \mathrm{HBO}_{2}(s) + \mathrm{H}_{2}\mathrm{O}(g) \uparrow \tag{6}$$

$$2\text{HBO}_2(s) \to \text{B}_2\text{O}_3(l) + \text{H}_2\text{O}(g) \uparrow \tag{7}$$

$$C_{12}H_{22}O_{11}(s) \to 2C(s) + 11H_2O(g) \uparrow$$
 (8)

$$\operatorname{ZrO}_2(s) + \operatorname{B}_2\operatorname{O}_3(g) + 5\operatorname{C}(s) \to \operatorname{ZrB}_2(s) + 5\operatorname{CO}(g) \uparrow (9)$$

 $B_2O_3$  has an unusually low melting point (450 °C) and  $\equiv Zr - acac + H_2O \rightleftharpoons \equiv Zr - OH + acac \square (3) \qquad a high vapor pressure. The vapor pressure of B_2O_3 at$ 1527 °C reaches 344 Pa, leading to its rapid vaporization and partial loss.<sup>16</sup> Therefore, in practice, a higher B:Zr molar ratio for the starting materials is necessary, rather than the B:Zr stoichiometric proportion of 2.0, as shown in Reaction (9). In this study, as shown in Section 2, the B:Zr molar ratio is 2.3.

> As well as the formation of ZrB<sub>2</sub> as discussed above, Reactions (10) and (11) happen spontaneously if TEOS is introduced to initiate synthesis of SiC, as shown in Figure 1. Silanol groups are formed by hydrolysis and



Figure 3. XRD patterns of synthesized precursor containing silicon, before and after calcination at 1550 °C for 2 h.

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siloxane bridges are produced by condensation polymerization during the gelating processes.

Hydrolysis:

$$Si - (OC_2H_5)_4 + 4H_2O \rightleftharpoons Si - (OH)_4 + 4C_2H_5OH$$
 (10)

Condensation:

$$2Si - OH \rightleftharpoons Si - O - Si + H_2O \tag{11}$$

Both the synthesized precursor containing silicon and the unconsolidated and soft gray powder obtained after heating 1550 °C for 2 h were characterized by XRD (Fig. 3). As before, the synthesized precursor is amorphous. The XRD pattern of the precursor reduced at 1550 °C for 2 h shows peaks for both  $ZrB_2$  and SiC phases. This means that complete disintegration of both  $ZrO_2$  and SiO<sub>2</sub> has been achieved by carbothermal reductions at 1550 °C.

In addition to Reactions (6)–(9), carbothermal reduction reactions to form SiC should also occur:

$$3C(s) + SiO_2(s) \rightarrow SiC(s) + 2CO(g) \uparrow$$
 (12)



Figure 4. SEM image (a), and EDS spectra for elements Si (b) and Zr (c) in  $ZrB_2$ -SiC composite powder calcined at 1550 °C for 2 h.

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However, some evidence from previous studies<sup>17</sup> suggests that SiC is actually produced by multi-step processes:

$$C(s) + SiO_2(s) \rightarrow SiO(g) + CO(g) \uparrow$$
 (13)

$$2C(s) + SiO(g) \rightarrow SiC(g) + CO(g) \uparrow$$
 (14)

The intermediate reactions generate SiO vapor. Transport of the SiO vapor to the carbon phase, and subsequent reaction at the carbon surface is necessary to form SiC.

In general, the morphology of particles is a comprehensive reflection of the synthesis reactions and processes. EDS reveals the distribution of elements; these distributions can be displayed as either dot maps or line profiles to distinguish particles with different chemical compositions.

Figure 4(a) shows a SEM image of ZrB<sub>2</sub>-SiC composite powder reduced at 1550 °C for 2 h. The SEM image reveals ZrB<sub>2</sub>-SiC particles with an equiaxed shape. The particle size is quite uniform, around 800 nm in diameter. The straight line in Figure 4(a) is a reference line for the EDS line scan; the signal profiles of line scans for both Si and Zr following this reference line are also shown. Figures 4(b) and (c) show the total recorded EDS line scans for Si and Zr, respectively. The EDS profiles of line scans shown in Figure 4(a) are consistent with the scans in Figures 4(b) and (c). When scanning along the reference line, the synchronized alternation of Si and Zr signals are clearly seen in Figures 4(b) and (c). That is to say, the changes in Si and Zr contents with distance across the particles are similar. Thus an area elemental analysis using EDS might be expected to show regions of different chemical composition in the ZrB2-SiC composite. However, just as for the line scans, Si and Zr showed similar behavior. To distinguish between Si and Zr by means of the dot maps was also difficult. The most likely explanation is that the SiC particles are very small, well below the spot size of the EDS method. This suggests that we have achieved our original target of high chemical and phase homogeneity by mixing the starting components at the molecular or colloidal level.

#### 4. CONCLUSIONS

Monophasic  $ZrB_2$ , and diphasic  $ZrB_2$ -SiC composite were successfully synthesized by the sol–gel method. We achieved complete disintegration of the synthesized  $ZrO_2$ and SiO<sub>2</sub> precursors by heating under argon at 1550 °C for 2 h. Soft gray  $ZrB_2$  or  $ZrB_2$ -SiC powders were obtained. SEM analysis showed that the  $ZrB_2$ -SiC composite had particles of equiaxed shape and uniform size distribution. The average particle size of the  $ZrB_2$ -SiC composite is ca. 800 nm. EDS could not find differences in the elemental distributions of Si and Zr, as would be expected for adjacent particles, although both  $ZrB_2$  and SiC were identified by XRD. This implies that the SiC particles are very small.

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