Effect of carbon source on the synthesis of ZrB$_2$–SiC composite powders

X Q Lian*, X H Hua, X G Wang, L R Deng, and L Zhang

School of Materials Science and Engineering, Xi’an University of Science and Technology, Xi’an, 710054, China

E-mail: lianxiaoqing0304@126.com

Abstract. This study is aimed to synthesize ZrB$_2$–SiC composite powders by boro-carbothermal reduction of zircon using two different carbon sources, namely expanded graphite and carbon black. The effect of carbon sources on the phase composition and microstructure of composite powders was studied using an X-ray diffractometer, a scanning electron microscope, and an energy spectrum analyzer. Pure-phase ZrB$_2$–SiC composite powders were prepared in 2 h at 1550 and 1500°C using expanded graphite and carbon black, respectively. In the former case, anisotropic ZrB$_2$–SiC composite powders were synthesized. Their ZrB$_2$ phase grains had an average diameter of 2.0 μm and regular hexagonal shape, while SiC phase grains were whisker-shaped, had an average diameter of 0.15 μm and aspect ratio exceeding 20. For carbon black, finer ZrB$_2$ grains and shorter rod-shaped SiC grains were obtained.

Keywords: ZrB$_2$–SiC; carbon sources; boro-carbothermal reduction; anisotropic growth

1. Introduction

In contrast to pure ZrB$_2$ ceramics, ZrB$_2$–SiC composite ceramics have better oxidation resistance and mechanical strength [1]. This lucrative combination makes them very promising candidates for many ultra-high temperature applications, including hypersonic flights, rocket propulsion, and other re-entry space vehicles [2]. However, they are difficult to sinter and have low fracture toughness [3, 4], thereby affecting their extensive application. As key materials for preparing ZrB$_2$–SiC composite ceramics, high-purity ZrB$_2$–SiC composite powders with advanced microstructure features are urgently needed. For example, a nanometer microstructure is beneficial to promote sintering, owing to its high specific surface area. Moreover, an anisotropic microstructure is favorable to strengthening and toughening in situ through different energy dissipation mechanisms [5].

ZrB$_2$–SiC composite powders can be synthesized by various approaches, such as boro-carbothermal reduction (BCR) [6], sol–gel method [7], polymeric precursor route [8], self-propagating synthesis [9], and so on. The incomparable advantages of the BCD process over other methods were its low cost, simple operation, and easy industrialization, especially using zircon (ZrSiO$_4$) as the main source of zirconium and silicon. However, it requires high temperature and long holding time via conventional heating methods. Therefore, many combination forms such as spark plasma-assisted BCD [10] and microwave-assisted BCR [11] have been developed in recent years. In the as-prepared ZrB$_2$–SiC composite powders thus obtained, the SiC phase was mostly granular or short whisker-shaped, while and the ZrB$_2$ phase was mostly granular, plate, or short rod-shaped, and thus, not anisotropic.
Some studies on anisotropic ZrB$_2$–SiC composite powders have been reported in recent years. Song [12] designed a two-step calcination method to prepare ZrB$_2$–SiC composite powders, in which ZrB$_2$ rods with a diameter of 1–2 μm and an aspect ratio of ~8 were randomly distributed. ZrB$_2$–SiC composite powders modified using in situ grown SiC nanowires with a diameter of 200 nm were prepared by Zhong [5] via a nickel catalytic method. These studies were committed to developing new methods, but the methods were either expensive or complicated to operate to some extent. Many studies [13–15] showed that carbon sources with different morphologies would work as templates for the anisotropic growth of SiC nanowires or whiskers, indicating that carbon sources played an important role in the synthesis temperature and microstructure evolution during the preparation of SiC powders, which would be similar in preparing ZrB$_2$–SiC composite powders theoretically. Thus, a new low-cost approach in preparing anisotropic ZrB$_2$–SiC composite powders was promoted.

This study is aimed to synthesize ZrB$_2$–SiC composite powders by BCR of zircon at different temperatures using expanded graphite and carbon black as carbon sources. Expanded graphite is known to have a layered structure, and carbon black consists of spherical particles. The effect of carbon source on the phase composition and microstructure of composite powders was studied in detail.

2. Materials

Commercially available powders of zircon (ZrSiO$_4$, 97.0%, 325 mesh, Chenyuan Powder, Zibo, Shandong, China), boron oxide (B$_2$O$_3$, 99.9999%, 3000 mesh, Xingye Metal, Xingtai, Hebei, China), expanded graphite (C, 99.5%, 200 mesh, Meidi Family, Shanghai, China), and carbon black (C, 99.5%, 3000 mesh, Thermax N990, Canada) were used as raw materials to synthesis ZrB$_2$–SiC composite powders according to the following reaction:

\[
\text{ZrSiO}_4(s) + \text{B}_2\text{O}_3(l) + 7\text{C}(s) = \text{ZrB}_2(s) + \text{SiC}(s) + 7\text{CO}(g)
\]  

Figure 1 shows the microstructure of expanded graphite and carbon black. Considering that boron oxide volatilized rapidly at a temperature greater than 1073 K and increasing carbon source helped to lower the reaction temperature [7], excess boron oxide and carbon black were employed and the molar ratio of raw materials was 1:1.5:8 (ZrSiO$_4$: B$_2$O$_3$:C). After dry mixing for 2 h, the powder mixture was placed in a corundum crucible and sintered at temperatures ranging from 1673 K to 1873 K at a heating rate of 5 K/min under flowing Ar (99.999%, 0.5 L/min) in a tube furnace.

The phase composition of as-prepared powders was characterized by X-ray diffraction (XRD, Shimadzu XRD-7000, Japan) with Cu-K$_{α1}$ radiation (λ = 0.154 nm). Data were selected in a range of 20°–80° (2θ) with a scan rate of 5° (2θ)/min. The microstructure of as-prepared powders was observed using a scanning electron microscope (SEM, JSM-6390A, Japan) along with X-ray energy dispersive spectroscopy (EDS).

![Figure 1. SEM photographs of carbon sources.](image-url)

3. Experimental

3.1. Phase composition analysis
Theoretically, ZrSiO$_4$ starts decomposing to m-ZrO$_2$ (monoclinic ZrO$_2$) and amorphous SiO$_2$ at 2060 K according to the ZrO$_2$–SiO$_2$ phase diagrams; however, because of the existence of liquid B$_2$O$_3$, which starts to appear at as early as 675 K (melting point), and impurities of zircon, such as Al$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$, and so on, this temperature may be lower than 1200 K practically due to the formation of low-temperature eutectic melts [16]. The main possible reactions and Gibbs free energy formulas in the ZrO$_2$–SiO$_2$–B$_2$O$_3$–C system in the present study are listed in table 1. Thermodynamic calculations were performed to predict the reaction productions at different temperatures using the enthalpy-entropy-heat capacity (HSC) chemistry 6.0 software. Considering that the reactions were performed under flowing argon gas, the partial pressure of CO was equal to atmospheric pressure. This showed that reactions (2), (3), and (4) could occur at 1776 K, 1811 K, and 1904 K, respectively, leading to the appearance of new phases ZrB$_2$, SiC, and ZrC, respectively.

**Table 1.** Main possible reactions and Gibbs free energy formulas in the ZrO$_2$–SiO$_2$–B$_2$O$_3$–C system.

| Reaction number | Reaction | Gibbs free energy $\Delta_r G$ (kJ · mol$^{-1}$) |
|-----------------|----------|--------------------------------------------------|
| (2)             | ZrO$_2$ (s) + B$_2$O$_3$ (l) + 5C (s) = ZrB$_2$ (s) + 5CO (g) | $\Delta_r G_2 = 1420.80 - 0.80T + 5RT\ln\frac{p_{CO}}{p_{CO}^0}$ |
| (3)             | SiO$_2$ (s) + 3C (s) = SiC (s) + 2CO (s) | $\Delta_r G_3 = 603.15 - 0.333T + 2RT\ln\frac{p_{CO}}{p_{CO}^0}$ |
| (4)             | ZrO$_2$ (s) + 3C (s) = ZrC (s) + 2CO (g) | $\Delta_r G_4 = 666.55 - 0.35T + 2RT\ln\frac{p_{CO}}{p_{CO}^0}$ |

Figure 2a and 2b shows the XRD patterns of as-prepared powders sintered at various temperatures using expanded graphite and carbon black, respectively. For expanded graphite, the peaks of ZrB$_2$ and β-SiC appeared at 1725 K, but m-ZrO$_2$ peaks still remained a major phase, indicating that reaction (2) was still not complete. No SiO$_2$ peaks were seen; however, it was hard to confirm that reaction (3) was complete because SiO$_2$ itself was amorphous as the decomposition product of ZrSiO$_4$. As temperature increased to 1775 K, m-ZrO$_2$ peaks gradually weakened, while ZrB$_2$ and β-SiC peaks gradually strengthened. Hence, ZrB$_2$ and β-SiC were the major phases. At 1825 K, m-ZrO$_2$ peaks disappeared, and phase pure ZrB$_2$–SiC composite powders were obtained. The phase composition transformation results from XRD analysis were in agreement with thermodynamic calculations.

![XRD patterns](image1)

**Figure 2.** XRD patterns of as-prepared powders using different carbon sources.

For carbon black, similar to expanded graphite, the main products were ZrB$_2$, β-SiC, and m-ZrO$_2$ at 1725 K. ZrO$_2$ peaks disappeared at 1775 K. Little changes were observed in the peaks at 1775 K and 1825 K, which showed that reactions (1) and (2) were completed at 1775 K, which was 50 K lower than that using expanded graphite. Due to the advantages of amorphous nature and high reactivity,
carbon black was helpful in reducing the reaction temperature compared with expanded graphite, which was of great significance to energy saving.

3.2. Microstructure analysis

SEM photographs and EDS spectra of as-prepared powders were obtained at 1825 K using expanded graphite and carbon black as shown in Figures 3 and 4, respectively. For expanded graphite, regular hexagonal sheets and whiskers were mixed together. The average particle size of regular hexagonal sheets was about 2.0 μm. The spectra at 001 showed the existence of elements Zr and B. The mean diameter of whiskers was 0.15 μm, and the aspect ratio was more than 20. The spectra at 002 showed the existence of elements Si and C. The unmarked peaks belonged to Pt sprayed on the surface of samples to enhance electrical conductivity. Therefore, the regular hexagonal sheets were ZrB₂ phase and the whisker grains were SiC phase.

The microstructure of powders using carbon black was obviously different from that of expanded graphite. Grains in final powders were mainly granular and short rod shaped. The particle size of grains ranged from 0.2 μm to 0.6 μm, which was finer than that of grains obtained from expanded graphite. Therefore, it was concluded by EDS analysis that the granular- and short rod–shaped grains were ZrB₂ and SiC, respectively, which were consistent with those prepared via the sol–gel method [7].

![Figure 3](image1.png)

(a) SEM photographs. (b) EDS spectra at 001. (c) EDS spectra at 002.

**Figure 3.** SEM photographs and EDS spectra of as-prepared powders using expanded graphite.

![Figure 4](image2.png)

(a) SEM photographs. (b) EDS spectra 003. (c) EDS spectra 004.

**Figure 4.** SEM photographs and EDS spectra of as-prepared powders using carbon black.

While the carbon source was expanded graphite, powders presented anisotropic growth behavior, especially for the SiC phase. As no catalyst was added, SiC whiskers could be formed by the following reactions [17]:

\[
\begin{align*}
\text{SiO}_2 (s) + C (s) &= \text{SiO} (g) + CO (g) \\
\text{SiO} (g) + 2C (s) &= \text{SiC} (s) + CO (g) \\
\text{SiO} (g) + 3CO (g) &= \text{SiC} (s) + 2\text{CO}_2 (g)
\end{align*}
\]

The gas–solid reaction (6) was dominant, and studies showed that it always occurred along with gas–gas reaction (7) [18]. The expanded graphite would expand to dozens or hundreds of times in
volume at elevated temperature, which applied enough growth space for whiskers; meanwhile, it provided channels for CO to overflow, further promoting the reaction process.

The fracture toughness of common ZrB$_2$–SiC composite ceramics was only 3–4 MPa m$^{1/2}$, and added short SiC fibers made it possible to achieve toughness above 6 MPa m$^{1/2}$ [19]. Bai [20] introduced SiC whiskers to laminated ZrB$_2$–SiC/BN ceramics, whose fracture toughness increased from 11.29 ± 0.42 MPa m$^{1/2}$ to 13.31 ± 0.33 MPa m$^{1/2}$ through toughening mechanisms, including crack deflection, delamination, whiskers bridging pullout, and so on. However, the fibers or whiskers are easy to fracture in ball mill process if directly added. Therefore, the synthesis of anisotropic ZrB$_2$–SiC composite powders is an effective way to increase the fracture toughness of ZrB$_2$–SiC composite ceramics, similar to the as-prepared ZrB$_2$–SiC composite powders in this study, in which SiC-phase grains were whisker-shaped with a mean diameter of 0.15 μm and aspect ratio exceeding 20. Many studies [5, 12] on anisotropic ZrB$_2$–SiC composite powders are still at the stage of preparing powders and are not concerned with the performances of ceramics, which is the focus of our follow-up study.

4. Conclusions

The effect of carbon sources on the phase composition and microstructure of ZrB$_2$–SiC composite powders was investigated based on XRD, SEM, and EDS analyses. Carbon black was found to be helpful in reducing the reaction temperature, and phase pure ZrB$_2$–SiC composite powder could be prepared at 1773 K for 2 h, which was lower by 50 K than that using expanded graphite. However, ZrB$_2$–SiC composite powders prepared using expanded graphite differed from those produced by conventional techniques by their anisotropic morphology, including regular hexagonal ZrB$_2$ sheets with a mean size of 2.0 μm and SiC whiskers with a mean diameter of 0.15 μm and aspect ratio of more than 20.

Acknowledgment

This study was financially supported by the Natural Science Foundation of Shaanxi Province for Youth (No. 2017JQ5100) and the Special Scientific Research Project of Shaanxi Education Department (No. 18JK0498).

References

[1] Ryu H Y, Nersisyan H H and Lee J H 2012 Int. J Refra Met H. 30 133
[2] Lin Y H, Liu J H, Song S L, Li J B, Bashirc S, Guo Y and Zhen Q 2018 Ceram. Int. 11 80
[3] Parvisi S, Ahmadi Z, Zamharir M J and Asl M S 2018 Int. J. Refra. Met H.75 10
[4] Asl M S and Kakroudi M G 2015 Mat. Sci. Eng. A 625 385
[5] Zhong Z X, Yan L W, Liu L and Xu B S 2017 Ceram. Int. 43 3462
[6] He J B, Gao Y, Wang Y G, Fang J Y and An L N 2017 Ceram. Int. 43 1602
[7] Li F L, Cao Y N, Liu J H, Zhang H J and Zhang S W 2017 Ceram. Int. 43 7743
[8] Xie B Y, Ma L, Lin X, Liu Y, Zhang Y J, Gong H Y and Zhang W M 2018 Ceram. Int. 44 19525
[9] Zhang S W, Khamano M K, Zhang H J and Yeprem H A 2014 J. Am. Ceram. Soc. 1-3 1
[10] Emami S M, Salehine Zakeri M and Tayebifard S A 2015 Ceram. Int. 42 6581
[11] Deng X G, Du S, Zhang H J, Li F L, Wang J K, Zhao W G, Liang F, Huang Z and Zhang S W 2015 Ceram. Int. 41 14419
[12] Song S L, Lin Y H, Fan Y L, Li R, Hu P F and Zhen Q 2019 J. Solid. State. Chem. 273 101
[13] Liang J J, Guo W M, Liu J X, Qin H and Gao P Z 2019 J. Alloy. Compd. 797 101
[14] Maity A, Das H, Kalita D, Kayal N, Goswami T and Chakrabarti O 2014 J. Eur. Ceram. Soc. 34 3499
[15] Luo Y, Zheng S L, Ma S H, Liu C L, Ding J and Wang X H 2018 Ceram. Int. 44 10585
[16] Krishnarao RV 2017 Ceram. Int. 43 1205
[17] Chen J J, Ding L J, Xin L P, Zeng F and Chen J 2017 J. Solid. State. Chem. 253 282
[18] Chen X Y, Qin Y M, Jia Q L, Zhang Q, Zhou Y and Liu X H 2019 Mater. Lett. 234 187
[19] Sciti D, Guicciardi S and Silvestrini L 2014 Mater. Des. 55 82
[20] Bai Y H, Sun M Y, Li M X, Fan S W and Cheng L F 2018 Ceram. Int. 44 8890