

# In Situ Synthesis of $ZrB_2$ -SiC Composite Powders by Carbothermal Reduction Method



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**Abstract**  $ZrB_2$ -SiC composite powders were synthesized in situ via carbothermal reduction using  $ZrO_2$ ,  $HBO_2$  and carbon black as the starting materials. The influences of  $HBO_2$  contents (40.6–45.5 wt%), boron sources ( $HBO_2$ ,  $H_3BO_3$  and  $B_2O_3$ ) and carbon sources (black carbon, activated carbon, graphite and petroleum coke) on phase composition and morphology of  $ZrB_2$ -SiC composite powders were analyzed. The obtained samples were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). Results showed that when the  $HBO_2$  content was 43.2 wt%, impurity-free  $ZrB_2$ -SiC composite powders could be successfully produced at 1600 °C for 90 min in argon atmosphere. Meanwhile, columnar  $ZrB_2$  and granular SiC particles were combined interactively. Compared with control groups, products fabricated via black carbon revealed the better crystallinity and finer particle size.

**Keywords**  $ZrB_2$ , SiC · Powder · Carbothermal reduction

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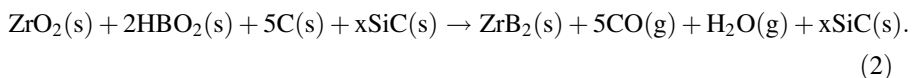
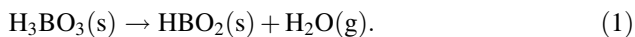
## Introduction

Carbon/carbon (C/C) composites have incomparable advantages over other materials in aerospace and other high-tech fields due to their excellent properties, such as low density, low coefficient of thermal expansion, high specific strength, and high specific modulus. Because of the internal lattice defects, C/C composites are easily oxidized at high temperature in oxidizing atmosphere, which strongly restricted their applications [1, 2]. At present, ZrB<sub>2</sub>-SiC ultra-high temperature ceramic coatings are actively used to protect C/C composites owing to the good oxidation resistance [3–5], and spraying is widely applied to prepare the coatings for its flexible operation [6, 7]. However, due to the different densities between ZrB<sub>2</sub> and SiC, the components of coatings are easy to demix during spraying, if the two powders are mixed mechanically. Therefore, the synthesis of ZrB<sub>2</sub>-SiC composite powders has become a hot issue.

There are various methods to prepare ZrB<sub>2</sub>-SiC composite powders, including self-propagation high-temperature synthesis method, sol-gel method, carbon thermal reduction method and so on [8–11]. Among different synthesis routes, carbon thermal reduction method has the advantages of simple process, short product cycle and low production costs. In this study, ZrB<sub>2</sub>-SiC composite powders were synthesized in situ by carbothermal reduction at 1600 °C for 90 min in Ar, using ZrO<sub>2</sub>, HBO<sub>2</sub>, black carbon and SiC as the starting materials. The in situ reaction could make the solidification mass transfer more fully and impede delamination effectively in spraying. The effects of HBO<sub>2</sub> content, different boron and carbon sources on phase composition and morphology of ZrB<sub>2</sub>-SiC composite powders were discussed.

## Experiment

Zirconia powders (ZrO<sub>2</sub>, ≤ 10 μm), boric acid (H<sub>3</sub>BO<sub>3</sub>, 96%, ≤ 10 μm), boron oxide (B<sub>2</sub>O<sub>3</sub>, 98%, ≤ 20 μm), carbon black (C, ≤ 10 μm), activated carbon (C, ≤ 20 μm), graphite (C, ≤ 20 μm), petroleum coke (C, ≤ 20 μm) and silicon carbide (SiC, ≤ 0.5 μm) were provided as the raw materials. Since H<sub>3</sub>BO<sub>3</sub> could volatilize easily which would do harm to the furnace owing to acid corrosion, H<sub>3</sub>BO<sub>3</sub> was put into a vacuum drying oven at 120 °C for 12 h to get HBO<sub>2</sub>, according to Eq. 1 [12]. In theory, ZrB<sub>2</sub>-SiC composite powders can be produced by Eq. 2. Because of the volatilization of HBO<sub>2</sub> during calcination, the amount of HBO<sub>2</sub> was adjusted to obtain the highly pure powders.



**Table 1** Content of the ingredients of different groups

Group	Composition (wt%)			
	ZrO <sub>2</sub>	HBO <sub>2</sub>	C	SiC
ZS01	31.8	40.6	18.2	9.4
ZS02	30.4	43.2	17.4	9.0
ZS03	29.1	45.5	16.7	8.7

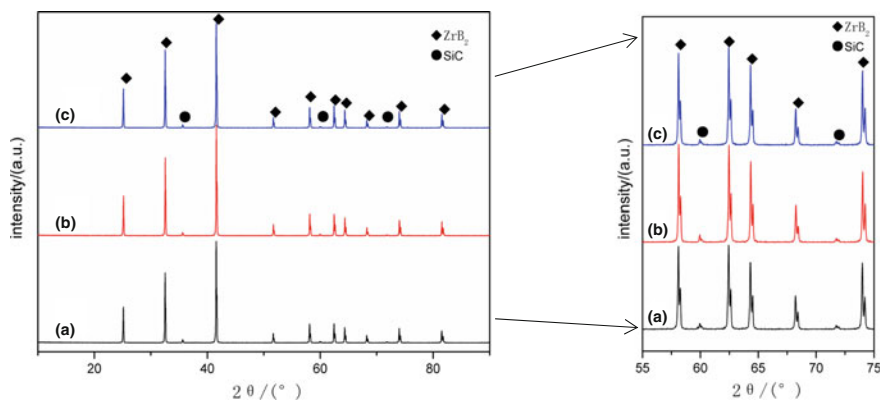
Three groups of composite powders were prepared according to the ratio of Eq. (2), referred to as ZS01, ZS02, ZS03, in which the mass fraction of SiC was 20 wt%. In order to study the impact of HBO<sub>2</sub> content, extra HBO<sub>2</sub> of 80, 100, 120 wt% were added to ZS01, ZS02, ZS03 respectively. Therefore, the content of ZrO<sub>2</sub>, HBO<sub>2</sub>, carbon black and SiC was shown as Table 1.

The three groups of powders were mixed by ball mill at 300 rpm for 20 min with ZrO<sub>2</sub> balls as the grinding media. Then, the mixed powders were put into different graphite crucibles and sealed in a graphite resistance furnace. The samples were heated to 1600 °C at a rate of 10 °C/min in argon atmosphere and then held for 90 min. After cooling to room temperature, gray powders were obtained. In addition, different boron sources were added to composite powders to compare the phase composition and morphology of the products while the mass ratio of Zr and B was constant. Further, the black carbon was replaced by activated carbon, graphite and petroleum coke to study the effect of different carbon sources. XRD (D/max-RA, Japan) was used to analyze the phase composition of ZrB<sub>2</sub>-SiC composite powders. The morphology of the products was characterized by SEM (D/max-RA, Germany).

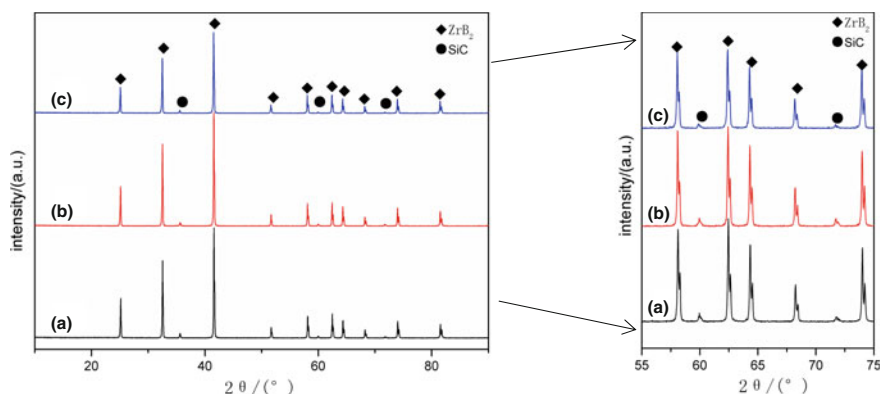
## Results and Discussion

**Effect of HBO<sub>2</sub> Content.** Figure 1 showed the XRD patterns of ZrB<sub>2</sub>-SiC composite powders prepared with different contents of HBO<sub>2</sub>. It was obvious that impurity-free ZrB<sub>2</sub>-SiC powders were synthesized. When the amount of HBO<sub>2</sub> decreased from 43.2 to 40.6 wt%, the narrowed peaks and reduced intensities of ZrB<sub>2</sub> implied the increment of grain size of the products. With extra 120 wt% HBO<sub>2</sub>, diffraction peak of ZrB<sub>2</sub> decreased while the HBO<sub>2</sub> phase was not detected in the Fig. 1c. The reason was that HBO<sub>2</sub> was converted to B<sub>2</sub>O<sub>3</sub> during heating and a part of B<sub>2</sub>O<sub>3</sub> was involved in the synthesis of ZrB<sub>2</sub> grains while the excess was present in the furnace as B<sub>2</sub>O<sub>3</sub> vapor. The partial pressure of B<sub>2</sub>O<sub>3</sub> vapor led to the change in Gibbs free energy ( $\Delta G$ ), which resulted in a slight decrease in the intensity of ZrB<sub>2</sub> phase. Meanwhile, the strongest peak of SiC appeared with 43.2 wt% HBO<sub>2</sub>. In summary, the amount of HBO<sub>2</sub> had a certain influence on the crystallinity of ZrB<sub>2</sub>-SiC composite powders.

**Effect of Different Boron Sources.** XRD patterns of ZrB<sub>2</sub>-SiC composite powders prepared with different boron sources were given in Fig. 2. As Fig. 2a, b showed,



**Fig. 1** XRD patterns of final products prepared with different contents of HBO<sub>2</sub>. **a** ZS01 **b** ZS02 **c** ZS03

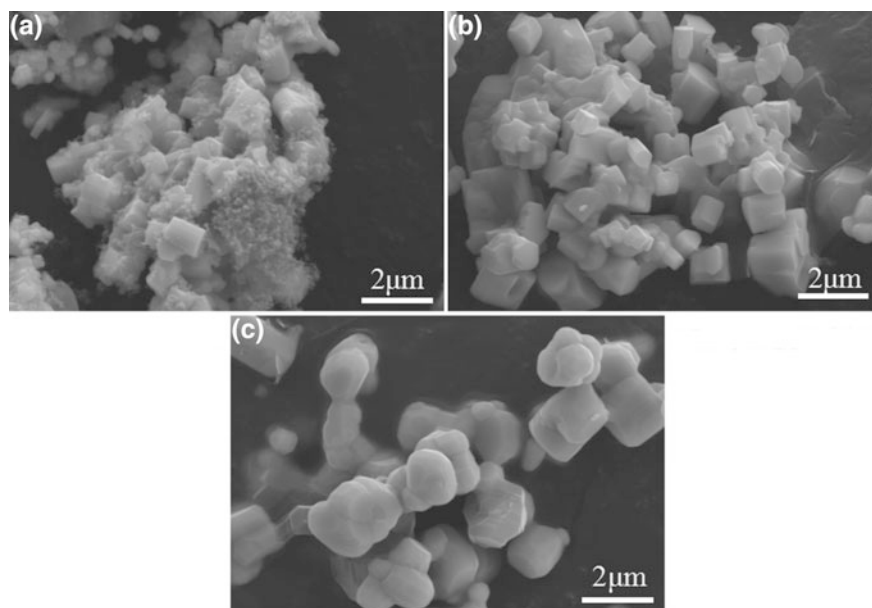


**Fig. 2** XRD patterns of final products prepared with different boron source. **a** HBO<sub>2</sub> **b** H<sub>3</sub>BO<sub>3</sub> **c** B<sub>2</sub>O<sub>3</sub>

powders with good crystallinity were successfully synthesized when HBO<sub>2</sub> or H<sub>3</sub>BO<sub>3</sub> were chosen as the boron source. However, the intensity of ZrB<sub>2</sub> peak decreased when B<sub>2</sub>O<sub>3</sub> was used instead of HBO<sub>2</sub> or H<sub>3</sub>BO<sub>3</sub>.

The resultant samples were also characterized by SEM to investigate the morphology, shown in Fig. 3. From Fig. 3a, powders synthesized by HBO<sub>2</sub> demonstrated uniform size of 1.5 μm. And columnar ZrB<sub>2</sub> and granular SiC particles were combined interactively. Grains in Fig. 3b grew larger in comparison to those in Fig. 3a, implying size increase took place with H<sub>3</sub>BO<sub>3</sub>. When the boron source was replaced by B<sub>2</sub>O<sub>3</sub>, ZrB<sub>2</sub> grains revealed poor crystallinity and irregular shapes.

**Effect of Different Carbon Sources.** XRD patterns of ZrB<sub>2</sub>-SiC composite powders produced with different carbon sources were presented in Fig. 4. As



**Fig. 3** SEM images of final products prepared with different boron source. **a** HBO<sub>2</sub> **b** H<sub>3</sub>BO<sub>3</sub> **c** B<sub>2</sub>O<sub>3</sub>

**Fig. 4** XRD patterns of final products produced with different carbon source. **a** Carbon black **b** Petroleum coke **c** Graphite **d** Activated carbon

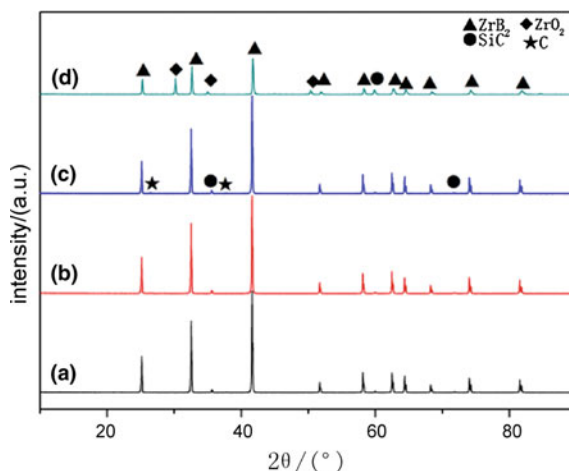
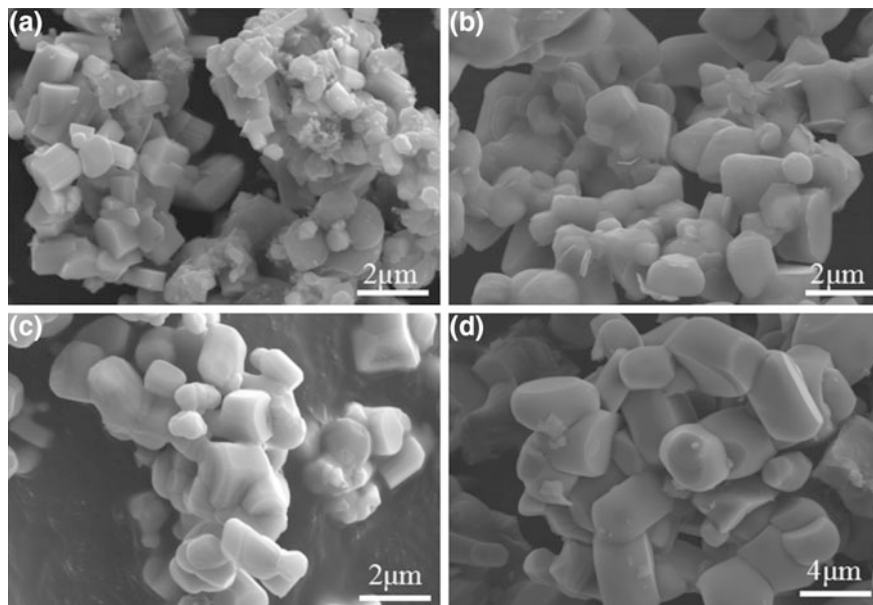


Fig. 4a, b showed, impurity-free ZrB<sub>2</sub>-SiC composite powders could be obtained with carbon black or petroleum coke. However, the faint peaks of carbon and zirconia were detected when the carbon source was replaced by activated carbon, which was probably because that activated carbon with a small specific surface area could not play a sufficient reduction effect in the reaction. Furthermore, compared



**Fig. 5** SEM images of final products synthesized with different carbon source. **a** Carbon black. **b** Petroleum coke. **c** Graphite. **d** Activated carbon

with Fig. 4a, b, the intensity of  $ZrB_2$  and SiC was reduced. From Fig. 4c, the peak of carbon was still existed when graphite was used instead of activated carbon, which could also introduce impurities.

Figure 5 showed the SEM images of  $ZrB_2$ -SiC composite powders synthesized with different carbon sources. From Fig. 5a, columnar  $ZrB_2$  and granular SiC particles were combined interactively and the particle size of  $ZrB_2$  was estimated to 1.5  $\mu m$ . When the carbon source was replaced by petroleum coke or graphite,  $ZrB_2$  grains which were distributed on the surface of SiC increased to about 2  $\mu m$  in size. Furthermore, the grain boundaries of  $ZrB_2$  began to melt and the morphology became irregular, shown in Fig. 5b, c. As Fig. 5d showed,  $ZrB_2$  particles with the size of 4  $\mu m$  could be produced by activated carbon. The different specific surface area of carbon materials might be the reason for the influences of carbon source on the fabrication of  $ZrB_2$ . Based on above results, it could be concluded that the grains of powders prepared by carbon black possess relatively finer particle size and better crystallinity compared with control groups.

## Conclusion

Impurity-free  $ZrB_2$ -SiC composite powders were successfully produced from  $ZrO_2$ ,  $HBO_2$ , SiC and carbon black by in situ carbothermal reduction method. Effects of  $HBO_2$  content, various carbon and boron sources on the phase composition and

morphology of ZrB<sub>2</sub>-SiC composite powders were investigated. When the HBO<sub>2</sub> content was 43.2 wt%, the highly pure composite powders with regular shapes could be synthesized at 1600 °C for 90 min in Ar and ZrB<sub>2</sub> was estimated to 1.5 μm in particle size. Compared with samples prepared by petroleum coke, graphite or activated carbon, the composite powders fabricated by black carbon possessed relatively better crystallinity and finer particle size.

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## References

1. J. Wang, K. Li, W. Li et al., The preparation and mechanical properties of carbon/carbon composite joints using Ti-Si-SiC-C filler as interlayer. *Mater. Sci. Eng., A* **574**, 37–45 (2013)
2. M.P. Bacos, J.M. Dorvaux, O. Lavigne et al., C/C composite oxidation model: I. Morphol. Exp. Invest. Carbon **38**, 77–92 (2000)
3. Y. Zhang, H. Hu, J. Ren et al., Effect of the surface microstructure of SiC inner coating on the bonding strength and ablation resistance of ZrB<sub>2</sub>-SiC coating for C/C composites. *Ceram. Int.* **42**, 18657–18665 (2016)
4. X. Zou, Q. Fu, L. Liu et al., ZrB<sub>2</sub>-SiC coating to protect carbon/carbon composites against ablation. *Surf. Coat. Technol.* **226**, 17–21 (2013)
5. D. Wang, Y. Zeng, X. Xiong et al., Ablation behavior of ZrB<sub>2</sub>-SiC protective coating for carbon/carbon composites. *Ceram. Int.* **41**, 7677–7686 (2015)
6. M. Tului, G. Marino, T. Valente, Plasma spray deposition of ultra high temperature ceramics. *Surf. Coat. Technol.* **201**, 2103–2108 (2006)
7. C. Bartuli, T. Valente, M. Tului, Plasma spray deposition and high temperature characterization of ZrB<sub>2</sub>-SiC protective coatings. *Surf. Coat. Technol.* **155**, 260–273 (2002)
8. Y. Yan, Z. Huang, S. Dong et al., New route to synthesize ultra-fine zirconium diboride powders using inorganic-organic hybrid precursors. *J. Am. Ceram. Soc.* **89**, 3585–3588 (2006)
9. Y. Li, W. Han, H. Li et al., Synthesis of nano-crystalline ZrB<sub>2</sub>/ZrC/SiC ceramics by liquid precursors. *Mater. Lett.* **68**, 101–103 (2012)
10. R.V. Krishnarao, Preparation of ZrB<sub>2</sub> and ZrB<sub>2</sub>-SiC powders in a single step reduction of zircon (ZrSiO<sub>4</sub>) with B<sub>4</sub>C. *Ceram. Int.* **43**, 1205–1209 (2017)
11. R.V. Krishnarao, MdZ Alam, D.K. Das et al., Synthesis of ZrB<sub>2</sub>-SiC composite powder in air furnace. *Ceram. Int.* **40**, 15647–15653 (2014)
12. J. Yu, L. Ma, Y. Zhang et al., Synthesis of TiB<sub>2</sub> powders via carbothermal reduction of TiO<sub>2</sub>, HBO<sub>2</sub> and carbon black. *Ceram. Int.* **42**, 5512–5516 (2016)