Oxidation Behavior of Zrb2 Composite Coating

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Abstract. ZrB2 composite coating was prepared by CVD and tape casting in order to realize the low cost and ultra-high temperature performance of SiC ceramics. The oxidation behavior of the as-prepared ZrB2 composite coating was studied. The results show that the oxidation of ZrB2 occurred at relatively low 800 °C. With the increase of temperature, the content of glassy phase increased. When oxidized at 1600 °C, the microcracks were evident in the SiO2 glassy phase because of the thermal expansion coefficient mismatch between ZrO2 and ZrB2.

1. Introduction
ZrB2 ultra-high temperature ceramics was one of the most potential materials for high temperature structural applications due to their high melting point, high hardness, high stability, corrosion resistance, good thermal conductivity, and they were an effective barrier for oxygen to enter the materials[1-2]. In order to realize the low cost and ultra-high temperature performance of ordinary ceramics, new ZrB2 coating fabrication technology has been developed, including brushing sintering, vapor deposition, thermal spraying, high temperature cladding and tape casting process and so on [3].

SiC ceramic matrix composites have been proved the potential structural materials in the aerospace field. However, intolerance to high temperature has not met the requirements in the hypersonic flight [4]. In the present study, according to the bonding ability between coating and SiC substrate, thermal expansion coefficient of raw materials and high temperature protection performance of materials, the carbon fiber deposition layer, ZrB2-SiC tape casting layer and ZrB2 deposition layer were fabricated by chemical vapor deposition and tape casting on the surface of SiC substrate from the bottom to top. The microstructure and phase composition of the ZrB2 composite coating were investigated. Moreover, the oxidation behavior of the ZrB2 composite coating was studied in detail.

2. Experimental
Commercially available ZrB2 (~ 2 μm, Dandong Chemical Research Institute Co. Ltd., China), SiC (~ 5 μm, Henan Xinxiang Micro-powder Co. Ltd., China), ZrCl4 (99.0% purity, Beijing Zhongjinian New Material Technology Co. Ltd., China) and NaBH4 (99.0% purity, Tianjin Kemiou Chemical Agent Co. Ltd., China) and tetrahydrofuran (AR, Tianjin Jinfeng Chemical Industry Co. Ltd., China) were used as starting materials.

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The preparation for ZrB₂ composite coating included the preparation of carbon fiber coating by vapor deposition, ZrB₂-SiC coating by tape casting and ZrB₂ coating by CVD shown in Fig. 1. The oxidation behavior of the ZrB₂ composite coating was examined in air at 800 °C, 1200 °C and 1600 °C for 0.5h with a heating rate of 5/min. The phase composition of the as-prepared ZrB₂ composite coating was investigated by XRD (D8 ADVANCE, Brucker AXS, Germany). The Microstructure and elemental composition of the ZrB₂ composite coating after oxidation were investigated by SEM (Sirion 200, FEI, and Holland) and EDS (INCA Energy, Oxford, England) in detail.

3. Results and Discussion

3.1. Microstructure and composition of ZrB₂ composite coating

The photos of ZrB₂ composite coating after CVD were shown in Fig.2, in which the deposition products obtained from different ratios were quite different. The quartz glass with the same dimension was used as matrix. When the molar ratio of ZrCl₄ to NaBH₄ was 1:6, uneven black particles were deposited on the surface of the quartz glass shown in Fig. 2(a). In Fig. 2(b), the relatively dense and uniform black particles were deposited on the surface of the quartz glass. The surface of the quartz glass was also covered with a layer of black particles in Fig. 2(c). However, the growth of the black particles was uneven accompanied by the formation of large particles as well as particles exfoliation. Thus, the microstructure and elemental composition of the ZrB₂ composite coating with the molar ratio of 1:8 between ZrCl₄ and NaBH₄ after oxidation at different temperature were mainly investigated in detail.

![Figure 1. Schematic diagram of the preparation for ZrB₂ composite coating.](image)

Fig. 3 shows the XRD pattern of ZrB₂ composite coating with the molar ratio of 1:8 between ZrCl₄ and NaBH₄. The diffraction peaks of the products were mainly ZrB₂ and NaCl. A few weak diffraction peaks might be related to impurities in raw materials.

![Figure 2. The photos of ZrB₂ composite coating after CVD with different reactant molar ratios of (a)1:6, (b)1:8 and (c)1:10.](image)
3.2. Microstructure and composition of ZrB2 composite coating after oxidation

In order to separate the ZrB2 from the products, the water-dissolving method was used to remove the by-product NaCl. Then, the oxidation of the samples was conducted at the temperature of 800 °C, 1200 °C, and 1600 °C for 0.5 h. The following reactions could occur during the oxidation:

\[ \text{ZrB}_2(s) + \frac{5}{2} \text{O}_2(g) \rightarrow \text{ZrO}_2(s) + \text{B}_2\text{O}_3(l) \]  
\[ \text{B}_2\text{O}_3(l) \rightarrow \text{B}_2\text{O}_3(g) \]  
\[ \text{SiC}(s) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{SiO}_2(l) + \text{CO}(g) \]

Fig. 4 shows the SEM images for the ZrB2 composite coating with the molar ratio of 1:8 between ZrCl4 and NaBH4 after oxidation at 800 °C for 0.5 h. The ZrB2 composite coating had a larger number of pores. The research has showed that ZrB2 was oxidized into B2O3 and ZrO2 at 800 °C under an oxidizing atmosphere (Eq. (1)) [5]. The ZrB2 particles and white ZrO2 particles were evident in Fig. 4(a). In addition, there was no obvious glassy phase after oxidation at 800 °C. In Fig. 4(b), the large particle was SiC according to the EDS analysis results.

The SEM images and the corresponding EDS analysis results for the ZrB2 composite coating with the molar ratio of 1:8 between ZrCl4 and NaBH4 after oxidation at 1200 °C for 0.5 h are shown in Fig. 5. After oxidation, the ZrB2 composite coating was not dense and the pores were obvious. The morphology of particles surrounded by SiO2 glassy phase (as illustrated in Fig. 5(b)) could be clearly seen. According to the EDS patterns in Fig. 5(a), the compositions of the ZrB2 composite coating after oxidation at 1200 °C were SiO2 and ZrO2. Moreover, no B2O3 was present. B2O3 had a low melting point (450 °C) and high vapor pressure [6], resulting in the easy volatilization at high temperature (Eq. (2)). In addition, the SiC was oxidized into SiO2 at 1200 °C (Eq. (3)) [7], which led to a viscous SiO2 glassy phase on the sample surface after oxidation.
Figure 4. SEM images for the ZrB2 composite coating with the molar ratio of 1:8 between ZrCl4 and NaBH4 after oxidation at 800 °C for 0.5 h.

Figure 5. SEM images for the ZrB2 coating with the molar ratio of 1:8 between ZrCl4 and NaBH4 after oxidation at 1200 °C for 0.5 h.

Fig. 6 shows the SEM images for the ZrB2 composite coating with the molar ratio of 1:8 between ZrCl4 and NaBH4 after oxidation at 1600 °C for 0.5 h. After oxidation, the microstructure of the ZrB2 composite coating was not compact and there were a few pores. ZrO2 particles were surrounded by SiO2 glassy phase could be clearly seen in Fig. 6(a). In comparation with Fig. 5, there was more viscous SiO2 glassy phase ((as illustrated in Fig. 6(b)) on the surface of the samples when heated at 1600 °C. This partly hindered the oxygen entering into the samples. Moreover, the microcracks were evident in the SiO2 glassy phase because of the thermal expansion coefficient mismatch between ZrO2 and ZrB2.
Figure 6. SEM images for the ZrB$_2$ coating with the molar ratio of 1:8 between ZrCl$_4$ and NaBH$_4$ after oxidation at 1600 °C for 0.5 h.

4. Conclusion
The ZrB$_2$ composite coating was fabricated by CVD and tape casting method, and the oxidation behavior of samples were investigated in detail. The main products were ZrB$_2$ and NaCl after CVD by using ZrCl$_4$ and NaBH$_4$ as raw materials. The oxidation of ZrB$_2$ first occurred at relatively low 800 °C. With the increase of temperature, the glassy phase increased, contributing to hindering the oxygen entering into the samples partly. After oxidation at 1600 °C, there were microcracks in the SiO$_2$ glassy phase, which resulted in the thermal expansion coefficient mismatch between ZrO$_2$ and ZrB$_2$.

Acknowledgments
This work was financially supported by “Shandong Province Natural Science Foundation (ZR2016EMM19)”.

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