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Preparation and Properties of Zrb2 Composite Coatings by CVD

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Abstract. ZrB_2 has been attracted much attention for structural materials applications due to their unique combination of relative lower density, high melting point, high hardness, strong corrosion resistance, excellent thermal conductivity, good electrical conductivity and so on. However, the preparation of zirconium boride coating is difficult to realize. In this paper, zirconium boride was coated on the surface of the silicon carbide substrate by chemical vapour deposition (CVD). When the molar ratio of $ZrCl_4$ to $NaBH_4$ was 1:8, zirconium boride deposition layer was the densest. And the preparation methods, composition and microstructure of coating were investigated.

1. Introduction

Aerospace, nuclear control engineering, refractories, electrode materials and other fields are developing in a sophisticated direction, which made the urgent demands on the high temperature protective materials [1]. ZrB_2 was covalent bond compound with high melting point, excellent thermal conductivity, good electrical conductivity, strong corrosion resistance and stabilized crystal structure, making it competent for high temperature protective materials [2, 3]. However, ZrB_2 has a high melting point of 3245 °C. The uneven microstructure for ZrB_2 ceramics was easy to form during the sintering due to the grain growth, decreasing the properties seriously. It could be solved by adding one or more reinforcement phases, among which SiC was the frequently-used reinforced phase due to its relatively good high temperature resistance, excellent thermodynamic properties and high temperature strength. Research showed that adding SiC into ZrB_2 could reduce the sintering temperature and promote the densification of the coating.

ZrB_2 ceramic materials fabricated by traditional methods now have not satisfy the aerospace, electricity, biology, medicine and chemical industry and so on. Studies has showed that depositing a coating on the surface of the base material by chemical vapor deposition (CVD) could not only overcome the inherent defects of the matrix material to improve the comprehensive properties and achieve the efficacy of advanced materials, but also greatly save the cost of preparation[4,5].

In the present study, ZrB_2 was coated on the surface of the SiC substrate through CVD from $ZrCl_4$ and $NaBH_4$. The effects of different ratios and temperatures on the composition and microstructure of the coating were studied.

2. Experimental

Commercially available $ZrCl_4$ (99.0% purity, Beijing Zhongjinyan New Material Technology Co. Ltd., China) and $NaBH_4$ (99.0% purity, Tianjin Kemiou Chemical Agent Co. Ltd., China) were used as starting materials.

The fabrication of ZrB_2 composite coating mainly included the preparation of ceramic matrix and coating. In this paper, the SiC ceramic matirx was prepared by pressureless sintering. Depositing carbon fiber coating on the SiC ceramic substrate was achieved by using tetrahydrofuran (THF) as carbon source. In order to improve the bonding strength between the SiC ceramic matrix and ZrB_2 coating, ZrB_2-SiC coating was fabricated by tape casting. Finally, the ZrB_2 composite coating was prepared by CVD with $ZrCl_4$ and $NaBH_4$ as raw materials. The reaction process was that $ZrCl_4$ reacted with $NaBH_4$ to form precursor Zr $(BH_4)_4$, and then the generated precursor Zr $(BH_4)_4$ was decomposed to form ZrB_2 coating at high temperature. Ar gas was used as protective gas with a ventilation rate of 50 ml/min and the reaction temperature ranged from 400 ºC to 600 ºC. The effects of reactant composition on the phase compositions and microstructures of ZrB_2 coating were studied by XRD (D8 ADVANCE, Brucker AXS, and German) and SEM (Sirion 200, FEI, Holland) in detail.

3. Results and Discussion

3.1. XRD characterization

According to the theoretical ratio of formula (1), the molar ratio of $ZrCl_4$ and $NaBH_4$ was 1:4. However, there was no ZrB_2 in the product. Thus, investigating the ratio of $ZrCl_4$ to $NaBH_4$ was crucial to the formation of ZrB_2. In this paper, the effects of the molar ratios of 1:6, 1:8 and 1:10 on the phase composition of products were studied. The theoretical reaction was as follows.

$$ZrCl_4+4NaBH_4=Zr\ (BH_4)_4+4NaCl \ [6] \quad (1)$$

$$Zr\ (BH_4)_4=ZrB_2+2BH_3+5H_2 \quad (2)$$

Fig. 1 shows the XRD patterns of different reactant molar ratios. The diffraction peaks of the products were mainly ZrB_2 and NaCl with different reactant molar ratios. A few weak diffraction peaks might be related to impurities in raw materials. Research has showed that there were probably two kinds of reactions before and after 500 ºC in the process of preparing ZrB_2 coating by CVD [7]. When the temperature was below 500 ºC, the reaction (3) occurred.

$$ZrCl_4+2NaBH_4 \rightarrow ZrB_2+2NaCl+2HCl+3H_2 \quad (3)$$

When the temperature was above 500 ºC, $NaBH_4$ decomposed according to formula (4) with the increase of temperature. Thus, the total reaction was shown in formula (5).

$$NaBH_4 \rightarrow BH_3+NaH \quad (4)$$

$$ZrCl_4+2NaH+2BH_3 \rightarrow ZrB_2+2NaCl+2HCl+3H_2 \quad (5)$$

The results of XRD show that the deposited coating mainly included ZrB_2 and NaCl. As the molar ratio of $NaBH_4$ increased, the intensity of NaCl diffraction peaks increased. This could be attributed to the chemical balance motion. When the molar ratio of $NaBH_4$ increased, the reaction formula (1) was pushed forward in the positive direction. The product Or $(BH_4)_4$ increased and the by-product NaCl also increased.

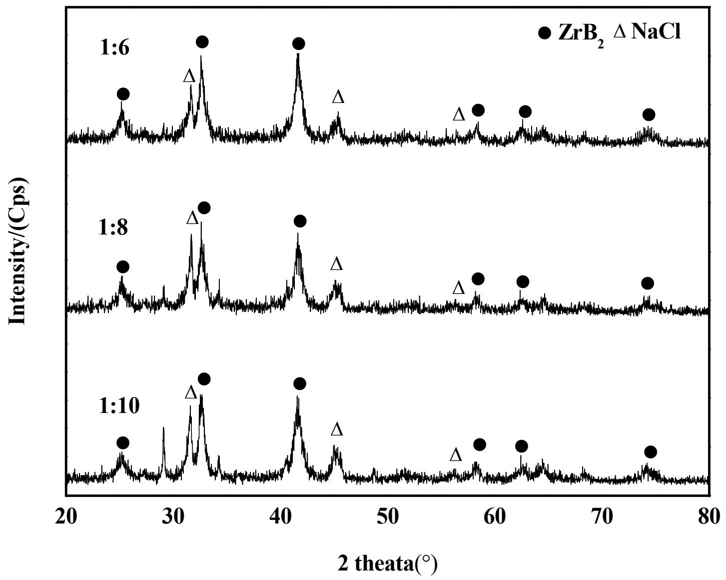

Figure 1. XRD patterns of the ZrB2 coating with different reactant molar ratios.

3.2. Microstructure Analysis

The effects of molar ratios of reactants on the microstructure of deposited ZrB_2 coating were investigated. Generally speaking, CVD reaction system was affected by temperature, gas flow rate, states of the reactants and so on. Meanwhile, the products were different in the different periods. Thus, the deposition layer on the surface of the matrix might be the different morphologies even under the same reaction condition.

Fig. 2 shows the SEM images of deposited ZrB_2 coating with the molar ratio of 1:6 between $ZrCl_4$ and $NaBH_4$, in which the microstructures were quite different. The product was irregular in shape, mainly showing the whisker and granular morphologies. As shown in Fig. 2(a), the coating showed a morphology of whisker with the length of 5 ~ 10 μm and it exhibited different orientations. In Fig. 2(b), the particles with the diameter of 1 ~ 3 μm were surrounded by glassy materials. Meanwhile, the distribution of particle was uneven and the particle surface tended to grow into whisker. Thus, it was not the ideal deposition results under the molar ratio of 1:6 between $ZrCl_4$ and $NaBH_4$.

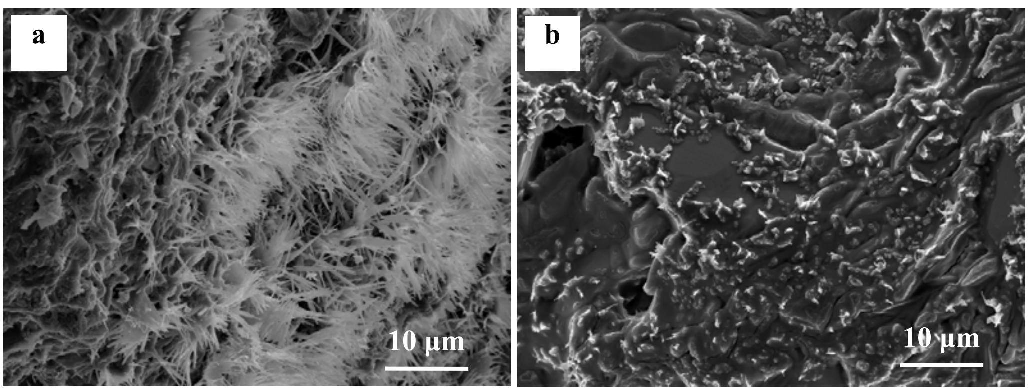

Figure 2. SEM images of ZrB_2 coating with the molar ratio of 1:6 between $ZrCl_4$ and $NaBH_4$.

Fig. 3 shows the SEM images of deposited ZrB_2 layer with the molar ratio of 1:8 between $ZrCl_4$ and $NaBH_4$. The products were mainly composed of two sizes of particles. As shown in Fig. 3(a), the large particles with the diameter of 5 ~ 15 μm showed a tetragonal morphology. The small particles with the diameter of 0.1 ~ 2 μm had a tight combination and there was no glassy materials in Fig. 3(b). According to the XRD patterns shown in Fig. 1, the compositions of the large and small particles were NaCl and ZrB_2, respectively. Thus, it was the relatively ideal deposition results under the molar ratio of 1:8 between $ZrCl_4$ and $NaBH_4$.

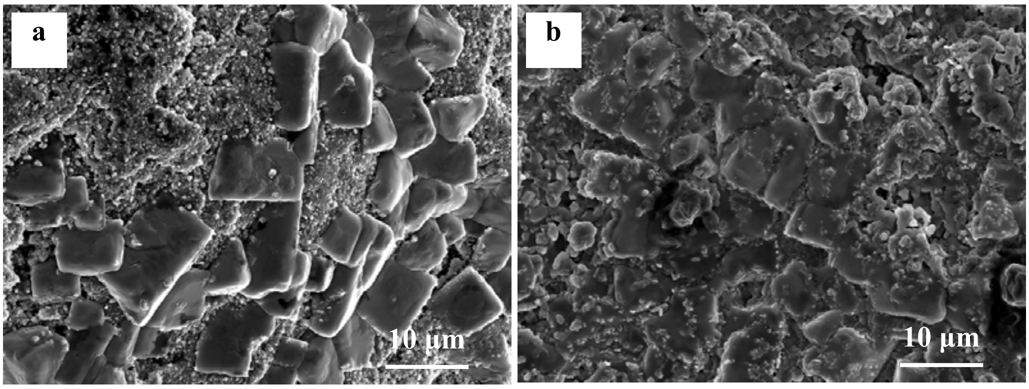

Figure 3. SEM images of ZrB_2 coating with the molar ratio of 1:8 between $ZrCl_4$ and $NaBH_4$.

Fig. 4 shows the SEM images of deposited ZrB_2 layer with the molar ratio of 1:10 between $ZrCl_4$ and $NaBH_4$, in which two kinds of coating morphologies could be seen clearly. In Fig. 4(a), the diameter of the particles was 0.5 ~ 2 μm and there were a large quantity of pores between particles. The microstructure in Fig. 4(a) was similar to the porous ceramics. As shown in Fig. 4(b), there were a large number of tetragonal particles with good crystallinity. The size of the particles was 2 ~ 10 μm and the composition of the tetragonal particles was NaCl according to the XRD patterns. When the molar ratio of $ZrCl_4$ to $NaBH_4$ was 1:10, the products were ZrB_2 and NaCl. However, excessive $NaBH_4$ decomposed to form BH_3 gas and NaH, thus resulting in the formation of a large number of pores, thereby reducing the coating densification.

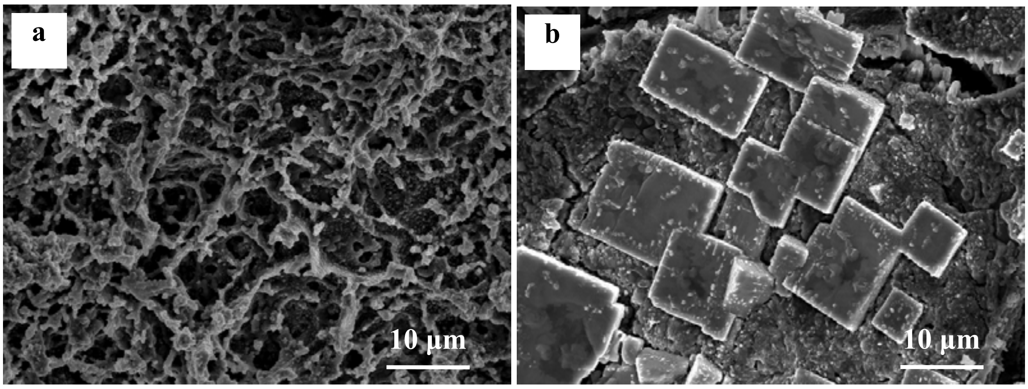

Figure 4. SEM images of ZrB_2 coating with the molar ratio of 1:10 between $ZrCl_4$ and $NaBH_4$.

4. Conclusion

The ZrB_2 composite coating was fabricated by CVD method. The main products of gas phase reaction between $ZrCl_4$ and $NaBH_4$ were ZrB_2 and NaCl. The microstructures of the products were different with the different molar ratios between $ZrCl_4$ and $NaBH_4$. When the molar ratio of $ZrCl_4$ to $NaBH_4$ was 1:6, the products showed the whisker and granular morphologies. When the molar ratio of $ZrCl_4$ to $NaBH_4$ was 1:8, the products showed the granular and tetragonal morphologies. When the molar ratio of $ZrCl_4$ to $NaBH_4$ was 1:10, there was a large amount of tetragonal NaCl and the coating showed the porous morphologies. The damage of NaCl to the coating remained to be solved.

Acknowledgments
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