Preparation and Properties of Zrb2 Composite Coatings by CVD

Lijuan Zhou1*, Kaili Yin1,a, Tianqi Wang2,b, Shengjun Liao1,c, Yunxia Zhao1,d
1School of Materials Science and Engineering, Shandong University of Technology, Zibo 255200, China
2The Four Prospecting Team of Shandong Coal Geology Bureau, Weifang 261000, China

*Corresponding author e-mail: zhouljuan@sdut.edu.cn, a18353360973@163.com, btankeywang@163.com, c351942480@qq.com, dhaoyunxia@sdut.edu.cn

Abstract. ZrB2 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 ZrCl4 to NaBH4 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]. ZrB2 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, ZrB2 has a high melting point of 3245 °C. The uneven microstructure for ZrB2 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 ZrB2 could reduce the sintering temperature and promote the densification of the coating.

ZrB2 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, ZrB2 was coated on the surface of the SiC substrate through CVD from ZrCl4 and NaBH4. The effects of different ratios and temperatures on the composition and microstructure of the coating were studied.
2. Experimental
Commercially available ZrCl4 (99.0% purity, Beijing Zhongjinyan New Material Technology Co. Ltd., China) and NaBH4 (99.0% purity, Tianjin Kemiou Chemical Agent Co. Ltd., China) were used as starting materials.

The fabrication of ZrB2 composite coating mainly included the preparation of ceramic matrix and coating. In this paper, the SiC ceramic matrix 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 ZrB2 coating, ZrB2-SiC coating was fabricated by tape casting. Finally, the ZrB2 composite coating was fabricated by CVD with ZrCl4 and NaBH4 as raw materials. The reaction process was that ZrCl4 reacted with NaBH4 to form precursor Zr (BH4)4, and then the generated precursor Zr (BH4)4 was decomposed to form ZrB2 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 °C to 600 °C. The effects of reactant composition on the phase compositions and microstructures of ZrB2 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 ZrCl4 and NaBH4 was 1:4. However, there was no ZrB2 in the product. Thus, investigating the ratio of ZrCl4 to NaBH4 was crucial to the formation of ZrB2. 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.

\[
\text{ZrCl}_4 + \text{NaBH}_4 \rightarrow \text{Zr (BH}_4\text{)}_4 + 4\text{NaCl} \quad [6]
\]

\[
\text{Zr (BH}_4\text{)}_4 \rightarrow \text{ZrB}_2 + 2\text{BH}_3 + 5\text{H}_2
\]

Fig. 1 shows the XRD patterns of different reactant molar ratios. The diffraction peaks of the products were mainly ZrB2 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 °C in the process of preparing ZrB2 coating by CVD [7]. When the temperature was below 500 °C, the reaction (3) occurred.

\[
\text{ZrCl}_4 + 2\text{NaBH}_4 \rightarrow \text{ZrB}_2 + 2\text{NaCl} + 2\text{HCl} + 3\text{H}_2
\]

When the temperature was above 500 °C, NaBH4 decomposed according to formula (4) with the increase of temperature. Thus, the total reaction was shown in formula (5).

\[
\text{NaBH}_4 \rightarrow \text{BH}_3 + \text{NaH} \quad (4)
\]

\[
\text{ZrCl}_4 + 2\text{NaH} + 2\text{BH}_3 \rightarrow \text{ZrB}_2 + 2\text{NaCl} + 2\text{HCl} + 3\text{H}_2
\]

The results of XRD show that the deposited coating mainly included ZrB2 and NaCl. As the molar ratio of NaBH4 increased, the intensity of NaCl diffraction peaks increased. This could be attributed to the chemical balance motion. When the molar ratio of NaBH4 increased, the reaction formula (1) was pushed forward in the positive direction. The product Or (BH4)4 increased and the by-product NaCl also increased.
3.2. Microstructure Analysis

The effects of molar ratios of reactants on the microstructure of deposited ZrB₂ 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 ZrB₂ coating with the molar ratio of 1:6 between ZrCl₄ and NaBH₄, 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 ZrCl₄ and NaBH₄.

Fig. 3 shows the SEM images of deposited ZrB₂ layer with the molar ratio of 1:8 between ZrCl₄ and NaBH₄. 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 ZrB₂, respectively. Thus, it was the relatively ideal deposition results under the molar ratio of 1:8 between ZrCl₄ and NaBH₄.

![Figure 3. SEM images of ZrB₂ coating with the molar ratio of 1:8 between ZrCl₄ and NaBH₄.](image)

Fig. 4 shows the SEM images of deposited ZrB₂ layer with the molar ratio of 1:10 between ZrCl₄ and NaBH₄, 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 ZrCl₄ to NaBH₄ was 1:10, the products were ZrB₂ and NaCl. However, excessive NaBH₄ decomposed to form BH₃ gas and NaH, thus resulting in the formation of a large number of pores, thereby reducing the coating densification.

![Figure 4. SEM images of ZrB₂ coating with the molar ratio of 1:10 between ZrCl₄ and NaBH₄.](image)

4. Conclusion
The ZrB₂ composite coating was fabricated by CVD method. The main products of gas phase reaction between ZrCl₄ and NaBH₄ were ZrB₂ and NaCl. The microstructures of the products were different with the different molar ratios between ZrCl₄ and NaBH₄. When the molar ratio of ZrCl₄ to NaBH₄ was 1:6, the products showed the whisker and granular morphologies. When the molar ratio of ZrCl₄ to NaBH₄ was 1:8, the products showed the granular and tetragonal morphologies. When the molar ratio of ZrCl₄ to NaBH₄ 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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References
[1] C. C. Wei, C. S. Ye, Mechanical properties and thermal shock behavior of bionic laminated ZrB$_2$-SiC-G ceramics, Int. J. Refract. Met. Hard Mater. 51 (2015) 233-238.
[2] B.S. Xu, S.B. Zhou, C.Q. Hong, J.C. Han, X.H. Zhang, Mechanical enhancement of lightweight ZrB$_2$-modified carbon-bonded carbon fiber composites with self-grown carbon nanotubes, Carbon 102 (2016) 487-493.
[3] M.S. Asl, M.G. Kakroudi, S. Noori, Hardness and toughness of hot pressed ZrB$_2$-SiC composites consolidated under relatively low pressure, J. Alloy. Compd. 619 (2015) 481-487.
[4] B. S. Xu, Amazing Surface Engineering, Tsinghua University Press, Beijing, 2000.
[5] T. Q. Wang, L. J. Zhou, Y. C. Zhang, Research Progress of Zirconium Boride Coating Material, Chinese Ceramic. 49 (2013) 5-8.
[6] J. X Zheng, Borohydride, Chemical Industry Press, Beijing, 2011.
[7] L. Y. Chen, Y. L. Gu, Z. H. Yang, L. Shi, J. H. Ma, Y. T. Qian, Preparation and some properties of nanocrystalline ZrB$_2$ powders, Scripta. Metall. 50 (2004) 959-961