Improved Oxidation Resistance of Zirconium Carbide at 1500°C by Lanthanum Hexaboride Additions

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Addition of LaB₆ is adopted to improve the oxidation resistance of ZrC at 1500°C. Mixed powder of ZrC-25 vol% LaB₆ is reactively hot pressed at 1900°C for 30 min under vacuum with an applied pressure of 25 MPa. The LaB₆ reacts with ZrC to form ZrB₂ and a layered La-containing phase. ZrB₂ improves the oxidation resistance of ZrC in static air. The La-containing phase is beneficial to increasing the relative density of oxide scale during oxidation and in enhancing the oxide scale stability during exposure to thermal cycles.

I. Introduction

Z IRCONIUM carbide (ZrC) shows a number of excellent properties such as high melting temperature, high thermal and electrical conductivity, and high fracture strength.¹⁻³ It is a potential ultrahigh-temperature ceramic (UHTC) for aerospace applications.^{4,5}

Oxidation resistance is a major issue in the development of UHTCs. The ZrC has a poor high-temperature chemical stability in air, which yields a porous and non-protective oxide scale during oxidation.^{6,7} Until now, the reports on enhancing oxidation resistance of ZrC are scarce. He et al.^{8,9} prepared ternary and quaternary carbides by incorporation of Al or Al with Si into ZrC. The obtained compounds show better oxidation resistance than ZrC due to the formation of some protective products, but the oxide scale is still porous because of the inability to sinter and the formation of high vapor pressure gaseous products. Recently, Zhang et al.^{10,11} introduced 4 mol% WC into ZrB2 matrix, which promotes formation of a liquid phase during oxidation and consequently results in liquid-phase sintering of ZrO₂ scale. This increases the relative density of oxide scale and therefore decreases the rate of oxygen transport. ZrB2-4 mol% WC performs much better oxidation resistance than monolithic ZrB₂ at 1500°C and 1600°C. It is a novel and promising strategy to improve the oxidation resistance of UHTCs by forming liquid during oxidation and in turn enhancing the protective effect of oxide scale.

In a previous work, we improved the fracture toughness of ZrC by addition of LaB₆, which is attributed to the *in situ* formation of a layered La-containing compound.¹² In this article, we report the enhancement of oxidation resistance of ZrC by LaB₆ addition. It provides a new method for enhancing oxidation resistance of ZrC.

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II. Experimental Procedure

The starting powders were ZrC (mean particle size 2.1 µm, >98% purity, Changsha Wing High High-Tech New Materials Co., Ltd., Changsha, China), ZrB_2 ($D_{50} = 2.5 \mu m$, 99% purity, Northwest Institute for Non-ferrous Metal Research, Xi'an, China), and LaB₆ (-300 mesh, >99% purity, Northwest Institute for Non-ferrous Metal Research). Mixed powder of ZrC-25 vol% LaB₆ was reactively hot pressed in boron nitride-coated graphite die at 1900°C for 30 min under vacuum with an applied pressure of 25 MPa. The obtained sample is referred as CBL in this study. Monolithic ZrC and ZrC-40 vol % ZrB₂ composite were also prepared. The sintering temperature was 2000°C, holding time 60 min, and applied pressure 25 MPa. Cylindrical coupons with dimension of Φ 12.7 × 4 mm were cut from the hot-pressed plates. Static oxidation test was carried out by exposing coupons to stagnant air in a box furnace at 1500°C for 2 h or 4 h. The heating rate was 15°C/min. Cyclic oxidation test was also conducted. The coupons were exposed to stagnant air at 1500°C for 15 min and then removed quickly from the furnace, and left for cooling in air for 10 min. The total time in furnace was 2 h. After oxidation, the oxide scale was ground off and the remained thickness of coupons was measured to evaluate the oxidation degree of samples. The phase composition of oxide scale was identified using X-ray diffractometer (XRD, CuKa radiation, D/max-2200VPC, Rigaku, Tokyo, Japan). The surface and cross-section of oxidized samples were observed by scanning electron microscope (SEM, FEI Quanta 200F, Eindhoven, the Netherlands), which is equipped with an energy-dispersive spectroscopy (EDS, EDAX, NJ) system.

III. Results and Discussion

The obtained composite using ZrC and LaB₆ as raw materials is composed of three phases, namely, ZrC, ZrB₂, and a layered phase [Fig. 1(a)]. Element La mainly distributes in the layered phase [Fig. 1(b)]. The layered phase also contains elements B and C.¹²

After static oxidation at 1500°C for 4 h, CBL forms a light yellow oxide scale, and no cracking of oxide scale or edge cracking of sample is observed [Fig. 2(a)]. Some bubbles are detected on the surface of sample, suggesting formation of liquid and gaseous phases during oxidation. The remained thickness of coupon is 2.96 mm. ZrC oxidizes catastrophically in air at 1500°C. The oxide scale significantly spalls from the substrate [Fig. 2(b)], and the remained thickness of coupon is 1.67 mm. ZrC-40 vol% ZrB₂ sample exhibits severe surface and edge cracking after static oxidation at 1500°C for 4 h [Fig. 2(c)], but the remained thickness of coupon is the thickest, about 3.28 mm. After 2 h cyclic oxidation, the oxide scale of CBL appears dense and adherent [Fig. 3(a)], and the remained thickness of coupon is 3.32 mm; in contrast, the oxide scale of ZrC-40 vol% ZrB₂ is damaged seriously [Fig. 3(b)], and the remained thickness of coupon is 3.16 mm.

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Fig. 1. Microstructure analysis of CBL: (a) BSE image, (b) elemental map for the distribution of La.



Fig. 2. Macrographs of different coupons after static oxidation at 1500°C for 4 h: (a) CBL, (b) monolithic ZrC, (c) ZrC-40 vol% ZrB₂.



Fig. 3. Macrographs of CBL (a) and ZrC-40 vol% ZrB_2 (b) after cyclic oxidation at 1500°C for 2 h.

Figure 4 shows the surface SEM micrograph of different samples after static oxidation at 1500°C for 2 h. The surface of CBL appears relatively dense. The dark phase in back-scattered electron (BSE) image is ZrO_2 . Glassy phase is also observed, which mainly distributes at the boundaries of ZrO_2 grain clusters and seals the cracks at the boundaries. EDS analysis (not shown) indicates that the glassy phase contains elements La, O, and possibly B. The oxide scale on ZrC is cracked and porous while the scale on ZrC-40 vol% ZrB₂ is porous.

Introduced LaB₆ reacts with ZrC to form ZrB₂ and a layered La-containing phase. After static oxidation test, the remained coupon of CBL is thicker than that of ZrC, but thinner than that of ZrC-40 vol% ZrB₂. So, CBL has better static oxidation resistance than ZrC, but inferior static oxidation resistance compared with ZrC-40 vol% ZrB₂. Assuming that all B in the introduced LaB₆ is converted to ZrB₂, the volume ratio of ZrC to ZrB₂ in CBL is about 3:2. So, the enhancement of oxidation resistance of ZrC in static air after LaB₆ addition is attributed to the formation of ZrB₂. However, we note that the oxide scale on ZrC-40 vol% ZrB_2 is cracked macroscopically after cooling while the scale on CBL is dense and adherent. Microstructure analysis reveals that CBL has denser oxidized surface than ZrC-40 vol% ZrB₂. After 2 h cyclic oxidation at 1500°C, the remained coupon of CBL is thicker than that of ZrC-40 vol% ZrB₂, indicating the better cyclic oxidation resistance of CBL. So, the La-containing phase in CBL is beneficial to increasing the relative density of oxide scale during oxidation and enhancing the oxide scale stability during cyclic exposures.

Figure 5 shows the XRD patterns of oxide scale on CBL after static oxidation at 1500°C for 2 h and 4 h. The oxide scale formed at 1500°C for 2 h is composed of monoclinic ZrO₂ (JCPDS No. 24-1165), orthorhombic LaBO₃ (JCPDS No. 12-762), and hexagonal La₂O₃ (JCPDS No. 83-1345). Besides orthorhombic LaBO₃, another crystal form of LaBO₃ (JCPDS No. 13-571) is found in the pattern of the oxide scale formed at 1500°C for 4 h. The high background in Fig. 5(b) is consistent with the presence of glassy phase in the oxide scale. By far, it is difficult for us to clarify the oxidation mechanism of this new material. But, we believe that La₂O₃-B₂O₃ liquid formed during oxidation could play an important role in sintering of ZrO₂ scale, and the formed La₂O₃-B₂O₃ compounds are beneficial to lowering the coefficient of thermal expansion of ZrO₂ scale, ¹³⁻¹⁵ thus enhancing the damage resistance of oxide scale during cyclic exposures.

IV. Conclusions

A new approach is developed to improve the oxidation resistance of ZrC at 1500°C. A quantity of 25 vol% LaB₆ is added to ZrC before densification. After reactively hot pressing at 1900°C, introduced LaB₆ reacts with ZrC to form ZrB₂ and a layered La-containing phase. The composite prepared by ZrC with 25 vol% LaB₆ has better static oxidation resistance than ZrC at 1500°C, but shows inferior static oxidation resistance compared with ZrC-40 vol% ZrB₂. The enhancement of oxidation resistance of ZrC in static air after



Fig. 4. SEM micrographs of the surface of different samples after static oxidation at 1500°C for 2 h: (a) CBL, (b) corresponding BSE image of (a), (c) monolithic ZrC, (d) ZrC-40 vol% ZrB₂.



Fig. 5. XRD patterns of the oxide scale on CBL after static oxidation at 1500°C for 2 h (a) and 4 h (b).

LaB₆ addition is attributed to the formation of ZrB₂. Microstructure analysis and cyclic oxidation test indicate that the formed La-containing phase in the composite prepared by ZrC with 25 vol% LaB₆ is beneficial to increasing the relative density of oxide scale during oxidation and in enhancing the oxide scale stability during cyclic exposures. Combining our previous results that the layered La-containing phase can enhance fracture toughness of ZrC, addition of LaB₆ has important significance for application of ZrC as UHTCs.

References

¹M. M. Opeka, I. G. Talmy, E. J. Wuchina, J. A. Zaykoski, and S. J. Causey, "Mechanical, Thermal, and Oxidation Properties of Refractory Hafnium and Zirconium Compounds," *J. Eur. Ceram. Soc.*, **19**, 2405–14 (1999).

²A. Krajewski, L. D'Alessio, and G. De Maria, "Physico-Chemical and Thermophysical Properties of Cubic Binary Carbides," *Cryst. Res. Technol.*, **33**, 341–74 (1998).

³H. O. Pierson, *Handbook of Refractory Carbides and Nitrides*. William Andrew Publishing/Noyes, Westwood, NJ, 1996, 68pp.

⁴H. Wiedemeier and M. Singh, "Thermochemical Modelling of Interfacial Reactions in Molybdenum Disilicide Matrix Composites," *J. Mater. Sci.*, **27**, 2974–8 (1992).

⁵M. M. Opeka, I. G. Talmy, and J. A. Zaykoski, "Oxidation-Based Materials Selection for 2000°C+ Hypersonic Aerosurfaces: Theoretical Considerations and Historical Experience," *J. Mater. Sci.*, **39**, 5887–904 (2004).

⁶R. F. Voitovich and E. A. Pugach, "High-Temperature Oxidation of ZrC and HfC," *Powder Metall. Met. Ceram.*, **12**, 916–21 (1973).

⁷S. Shimada, M. Nishisako, M. Inagaki, and K. Yamamoto, "Formation and Microstructure of Carbon-Containing Oxide Scales by Oxidation of Single Crystals of Zirconium Carbide," *J. Am. Ceram. Soc.*, **78** [1] 41–8 (1995).

⁸L. F. He, Z. J. Lin, Y. W. Bao, M. S. Li, J. Y. Wang, and Y. C. Zhou, "Isothermal Oxidation of Bulk $Zr_2Al_3C_4$ at 500 to 1000°C in Air," *J. Mater. Res.*, 23, 359–66 (2008).

Res., 23, 359–66 (2008). ⁹L. F. He, Y. W. Bao, M. S. Li, J. Y. Wang, and Y. C. Zhou, "Oxidation of $Zr_2[Al(Si)]_4C_5$ and $Zr_3[Al(Si)]_4C_6$ in Air," *J. Mater. Res.*, 23, 3339–46 (2008). ¹⁰S. C. Zhang, G. E. Hilmas, and W. G. Fahrenholtz, "Improved Oxidation

¹⁰S. C. Zhang, G. E. Hilmas, and W. G. Fahrenholtz, "Improved Oxidation Resistance of Zirconium Diboride by Tungsten Carbide Additions," *J. Am. Ceram. Soc.*, **91** [11] 3530–5 (2008).

¹¹S. C. Zhang, G. E. Hilmas, and W. G. Fahrenholtz, "Oxidation of Zirconium Diboride with Tungsten Carbide Additions," *J. Am. Ceram. Soc.*, **94** [4] 1198–205 (2011).

^{1198–205} (2011). ¹²L. Y. Zhao, D. C. Jia, Y. J. Wang, J. C. Rao, Z. H. Yang, X. M. Duan, and Y. Zhou, "ZrC-ZrB₂ Matrix Composites with Enhanced Toughness Prepared by Reactive Hot Pressing," *Scripta Mater.*, **63**, 887–90 (2010).

¹³I. N. Chakraborty, J. E. Shelby, and R. A. Condrate, "Properties and Structure of Lanthanum Borate Glasses," *J. Am. Ceram. Soc.*, **67** [12] 782–5 (1984).
¹⁴I. N. Chakraborty and D. E. Day, "Effect of R³⁺ Ions on the Structure

¹⁴I. N. Chakraborty and D. E. Day, "Effect of R³⁺ Ions on the Structure and Properties of Lanthanum Borate Glasses," *J. Am. Ceram. Soc.*, **68** [12] 641-5 (1985).

¹⁵I. N. Chakraborty, D. E. Day, J. C. Lapp, and J. E. Shelby, "Structure-Property Relations in Lanthanide Borate Glasses," *J. Am. Ceram. Soc.*, **68** [7] 368–71 (1985).