

Atomic oxygen adsorption and its effect on the oxidation behaviour of ZrB₂–ZrC–SiC in air

Dong Gao^a, Yue Zhang^{a,*}, Chunlai Xu^b, Yang Song^b, Xiaobin Shi^b

^a Key Laboratory of Aerospace Materials and Performance (Ministry of Education), School of Materials Science and Engineering, Beihang University, Beijing 100191, PR China

^b National Key Laboratory of Advanced Functional Composite Materials Technology, Beijing 100076, PR China

ARTICLE INFO

Article history:

Received 13 August 2010

Received in revised form 16 October 2010

Accepted 23 November 2010

Keywords:

Carbides

Ceramic

Oxidation

Adsorption

ABSTRACT

Atomic oxygen is adsorbed on the surface of the hot-pressed ZrB₂–ZrC–SiC ceramic composites, and then the ceramic composites are oxidized in air up to 1500 °C with the purpose of clarifying the effect of atomic oxygen adsorption on the oxidation behaviour of the ceramic composites. The XPS spectra are employed to identify the adsorption mechanism of atomic oxygen on the surface of the ceramic composites, and the formation of O–B, O–Zr, and O–Si bonds indicates that atomic oxygen is chemically adsorbed on the surface of the ceramic. In addition, atomic oxygen is preferred to be adsorbed on the surface of borides according to the Zr 3d core level spectrum. On the other hand, the atomic oxygen adsorption is detrimental to the oxidation resistance according to experimental results, and the porosity of the ceramic should be the major reason which provides diffusion path for the atomic oxygen. Furthermore, the structure evolution of the ceramic composites during oxidation process is analyzed.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Ceramics of borides, carbides and nitrides are referred as Ultra-High Temperature Ceramics (UHTCs) because of their high melting points (exceed 3000 °C), which makes them as potential candidates for use at extremely high temperatures [1,2]. ZrB₂ is considered as the most promising material due to its unique features, such as high melting point (exceeds 3200 °C) and hardness, excellent corrosion resistance against slags and molten iron, good thermal shock resistance and excellent oxidation/ablation resistance at elevated temperatures [3,4]. In addition, the introduction of sintering additive, such as MoSi₂ and AlN, has improved the mechanical properties significantly by inhibiting grain coarsening of ZrB₂ [5,6].

Oxidation resistance properties of the ceramic composites are the major issue for the widespread application of the material, and great efforts have been devoted to this field ever since 1960s. As reported by amounts of investigation, the introduction of second phase, such as MoSi₂ and SiC, has significantly improved the oxidation resistance property of the ceramics by forming a layer of protective silica glass on the surface when exposed to air at elevated temperatures [7,8]. And ZrB₂–SiC ceramic composites are considered as most promising materials used for thermal protective system (TPS) of re-entry vehicles due to relative lower density. Recently, the fully dense ZrB₂–SiC ceramics with addition of ZrC

additives have been prepared by hot pressing or spark plasma sintering, and the sintered ceramics show excellent high flexural strength, high fracture toughness and superior resistance to ablation or conversion than do the corresponding ZrB₂–SiC composites under arc-jet environment [9–10]. However, the oxidation behaviour of the ceramic composites is still not clearly known. Furthermore, the TPS of the re-entry vehicles servicing in the space between the low earth orbit and atmosphere layer exposes to atomic oxygen rich condition, which leads to adsorption of atomic oxygen on the surface of the material. Traditionally, the adsorption of atomic oxygen on the surface of ceramic material is omitted in comparison to those of polymers. However, the adsorption may lead to further oxidation when the aircrafts re-enter from LEO to the earth at extremely high speed. Thus the adsorption of atomic oxygen should be given thorough investigation.

In the present work, ZrB₂–ZrC–SiC ceramic composites are prepared by hot pressing method, and atomic oxygen is adsorbed on the surface of the sintered ceramic. Then the atomic oxygen adsorbed ceramic composites are oxidized in air up to 1500 °C. The adsorption mechanism on the surface of the ceramic composites is clarified according to XPS results. In addition, the effect of atomic oxygen adsorption on the oxidation behaviour of the ceramic composites at elevated temperatures in air is interpreted.

2. Experimental procedure

2.1. Preparation of ZrB₂–ZrC–SiC ceramic composites by hot pressing method

Commercially available ZrB₂, ZrC and SiC powders with a reported purity of 99% and an average particle size of 2 μm were used. Ceramic composites containing of

* Corresponding author. Tel.: +86 10 82316976; fax: +86 10 82316976.
E-mail address: zhangy@buaa.edu.cn (Y. Zhang).

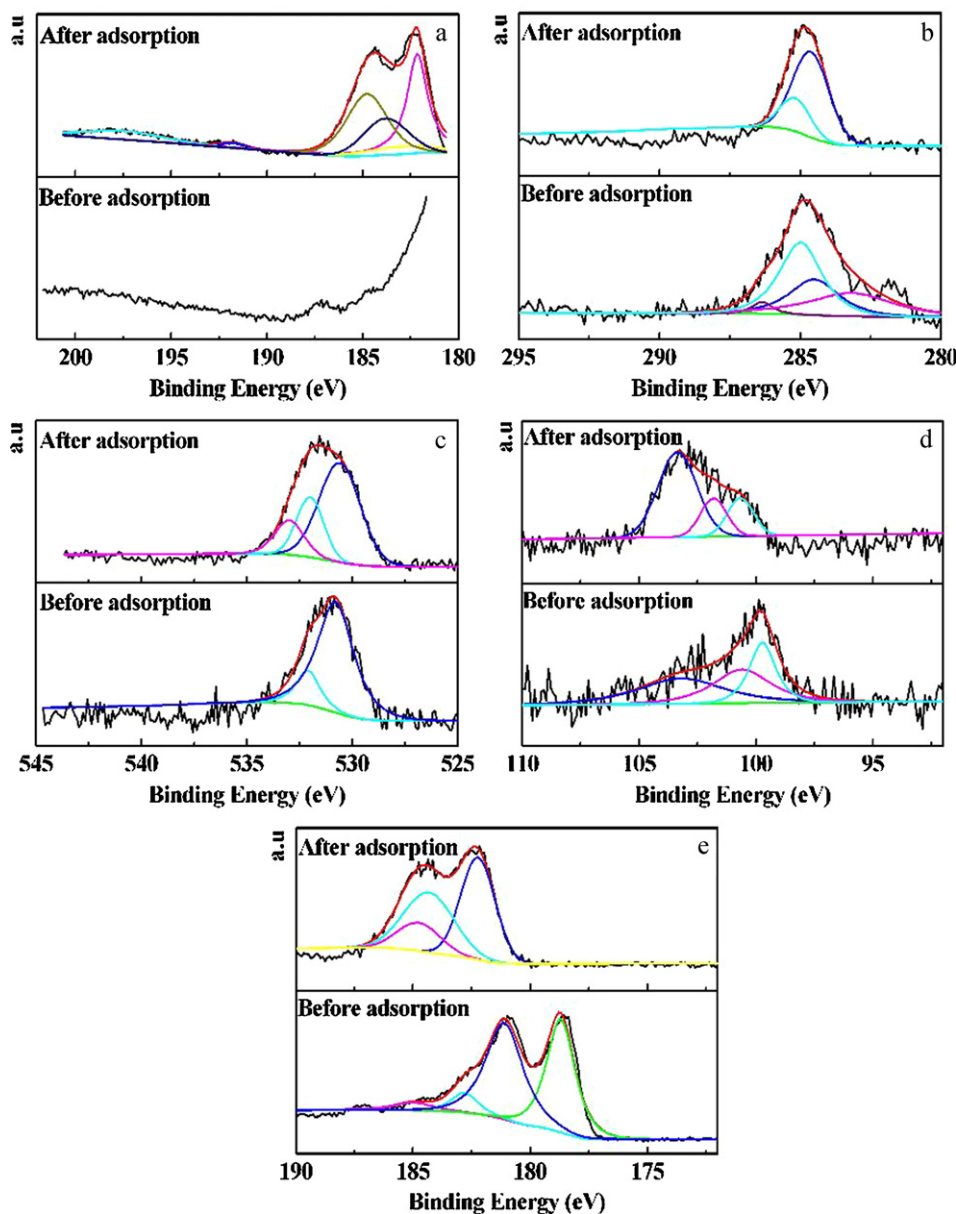


Fig. 1. XPS spectra of pre-treated and as-adsorbed $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites, (a) B 1s, (b) C 1s, (c) O 1s, (d) Si 2p and (e) Zr 3d.

after adsorption, as indicated by Fig. 1(b). Both O–Zr and O–Si bonds can be identified from O 1s spectra before and after atomic oxygen adsorption (Fig. 1(c)), the existence of oxides should be related to the EDS machined process, as reported by Alfano et al. [12]. However, the relative intensity of the O–M (M=Si, Zr) bonds increases after atomic oxygen adsorption. In addition, the formation of O–B bond after atomic oxygen adsorption confirms that atomic oxygen is chemically adsorbed on the surface of the ceramic. Si–C–O bond can be identified from the Si 2p spectra, as shown in Fig. 1(d). In addition, the relative intensity of Si–O and Si–C–O bonds shows increases significantly with atomic oxygen adsorption, which also confirms the chemical interactions between atomic oxygen and the surface of the ceramic during adsorption process. In addition, the Zr–B bond disappears from the Zr 3d spectra with atomic oxygen adsorption, while Zr–C bond can be found, as shown in Fig. 1(e), thus this phenomenon indicates that atomic oxygen is preferentially reacted with borides. The adsorption energy of atomic oxygen on the surface of (001) ZrC and (111) 3C–SiC has been calculated by Rodriguez et al. and Wang et al. respectively, as indicated by

the calculation results, the adsorption energy of atomic oxygen on the surface of ZrC is larger than that on the surface of 3C–SiC, which means that the atomic oxygen is preferred to react with ZrC in comparison to SiC [13,14]. Thus the variation of intensity of O–Zr is greater than that of O–Si with atomic oxygen adsorption, as indicated by Fig. 1.

3.2. Effect of atomic oxidation on the structure evolution of $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites

Fig. 2 shows the XRD patterns of $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites oxidized under 1500°C for 10 min, from which the effect of atomic oxygen adsorption on the oxidation products can be identified. As shown in the image, both of the ceramics with or without atomic oxygen adsorption are oxidized into monoclinic zirconia. Furthermore, as indicated by the XRD patterns, the relative intensity of monoclinic zirconia of the oxidized specimen with atomic oxygen adsorption is stronger than that without atomic oxygen

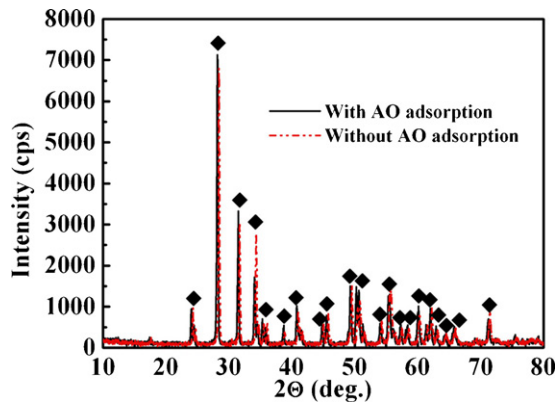


Fig. 2. XRD patterns of $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites oxidized under 1500°C for 10 min. ♦ refers to monoclinic phase zirconia.

adsorption, which indicates that the adsorption of atomic oxygen inhibits the oxidation of SiC.

The surface morphology of the $\text{ZrB}_2\text{-ZrC-SiC}$ ceramics oxidized under 1500°C for 30 min is shown in Fig. 3. As shown in the image, the surface of the specimen without atomic oxygen adsorption is covered with porous zirconia, and the gaps between the particles are filled with silica glass; while no silica glass can be observed from the surface of the ceramic with atomic oxygen adsorption. The difference indicates that atomic oxygen adsorption inhibits the oxidation of SiC, thus induces the formation of silica glass, which is consistent with the results shown in Fig. 2.

Typical microstructure of oxidation layer for the oxidized ceramic composites is shown in Fig. 4. As shown in the image, the oxidation layer can be divided into two parts for both of the ceramic composites with and without atomic oxygen adsorption after oxidation under 1500°C for 30 min. The first layer is porous zirconia and the second layer is composed of SiC depleted layer. In addition, the thickness of the oxidation layer of the ceramic with atomic oxygen layer is somewhat more than that without atomic oxygen

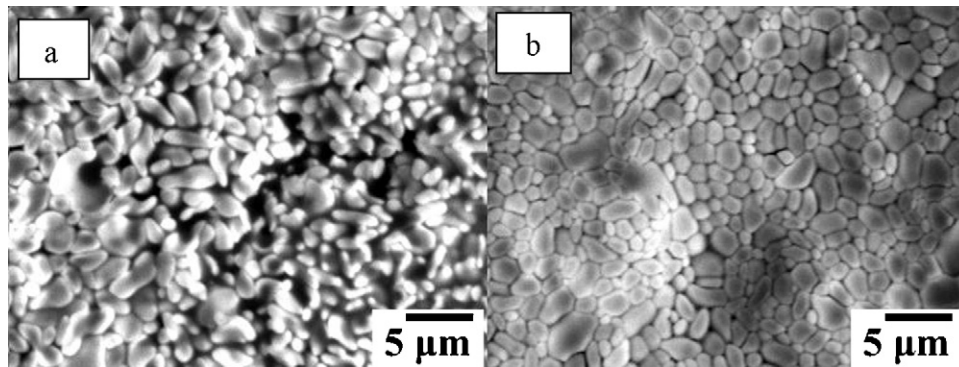


Fig. 3. Surface morphology of $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites oxidized under 1500°C for 10 min, (a) without atomic oxygen adsorption and (b) with atomic oxygen adsorption.

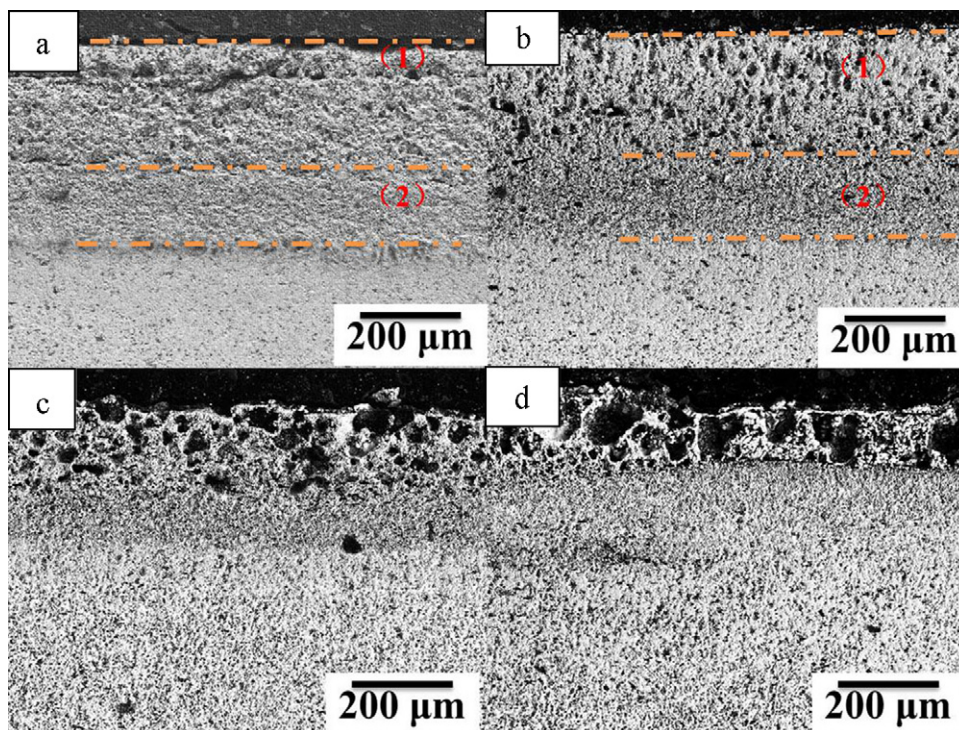


Fig. 4. Microstructure of oxidation layer for the $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites oxidized under 1500°C , (a) with AO-30 min; (b) without AO-30 min; (c) with AO-60 min; (d) with AO-90 min.

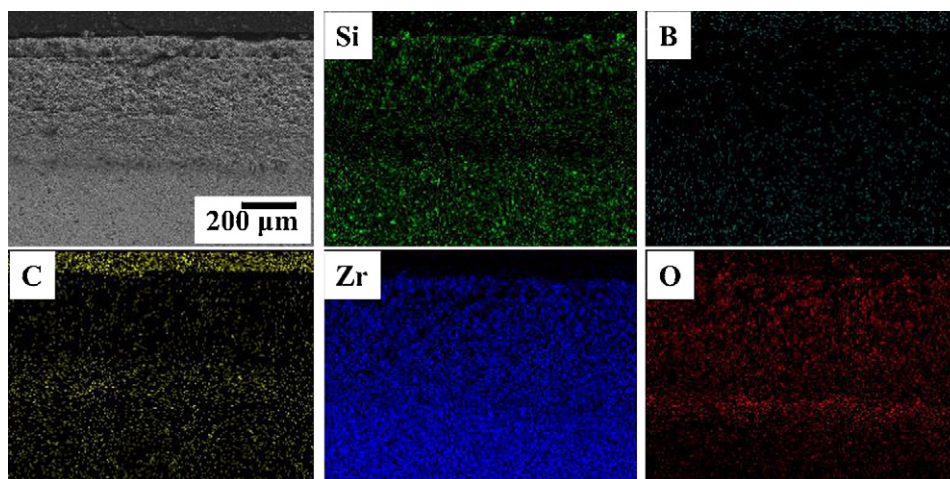


Fig. 5. Elemental distribution of Si, B, C, O and Zr on the surface of atomic oxygen adsorbed $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites oxidized under 1500°C for 30 min.

adsorption. However, the SiC depleted layer of the atomic oxygen adsorbed specimen is a little thinner than that without atomic oxygen adsorption, as can be identified from the image. As reported by Fahrenholtz et al., the formation of SiC depleted layer is related to the active oxidation of SiC, and the formation of protective and continuous oxidation layer on the surface is necessary [15]. In the present work, the surface of the ceramic composites is covered by dense layer of zirconia particles, and silica glass distributes in the grain boundary, thus the oxygen partial pressure in the inner part of the ceramic is lowered. The elemental distribution of Si, Zr, O, B and C on the oxidation layer can be identified from Fig. 5, which confirms the formation of SiC depleted layer.

The thickness of oxide scale and SiC depleted layer of the oxidized ceramics is measured from the SEM images of their cross section, and the variation of oxidation layer and SiC depleted layer with holding time can be identified from Fig. 6. An interesting phenomenon can be observed from the image, i.e., both of the thickness of oxide scale and SiC depleted layer for the oxidized ceramic composites increases at first and then decreases. The ceramic composites with atomic oxygen adsorption show more serious oxidation according to thicker oxide scale and SiC depleted layer, which indicates that atomic oxygen adsorption is detrimental to the oxidation resistance performance of the ceramic composites. The variation of the thickness of the oxide scale and SiC depleted layer should be related to the formation and flow of silica glass during oxidation process. In the present work, the oxidation of ZrC

produces amounts of pores in the oxidation layer during the initial 30 min and emits gaseous CO, thus the oxidation layer is loose. Then the pores are filled with silica glass with further oxidation, and porous zirconia is sintered with crystal growth of zirconia particles, which leads to volumetric shrinkage. Thus the oxidation layer is thinner. On the other hand, the emission of CO lowers oxygen partial pressure and leads to active oxidation of SiC, which results in formation and growth of SiC depleted layer in the initial oxidation. Then the SiC depleted layer is filled with silica glass with further oxidation, and detailed microstructure of the SiC depleted layer for the ceramic composites oxidized at 1500°C for 90 min is shown in Fig. 7, from which the assumption can be confirmed.

3.3. Atomic oxygen adsorption on the oxidation kinetics of $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites

The weight gain per unit surface area ($\Delta W/S$) of the oxidized ceramic composites is measured by analytical balance immediately after oxidation, and the variation of $\Delta W/S$ as a function of holding time for the ceramic composites can be identified from the curves, as shown in Fig. 8. As can be seen from the image, both of the ceramic composites with and without atomic oxygen adsorption follow near parabolic relation to holding time when oxidation under 1500°C in air. In addition, the weight gain of the ceramic composites with atomic oxygen adsorption is obviously

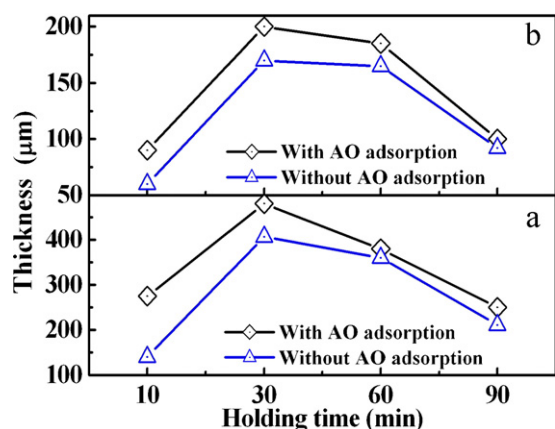


Fig. 6. Variation of thickness of oxide scale (a) and SiC depleted layer (b) for $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites oxidized under 1500°C .

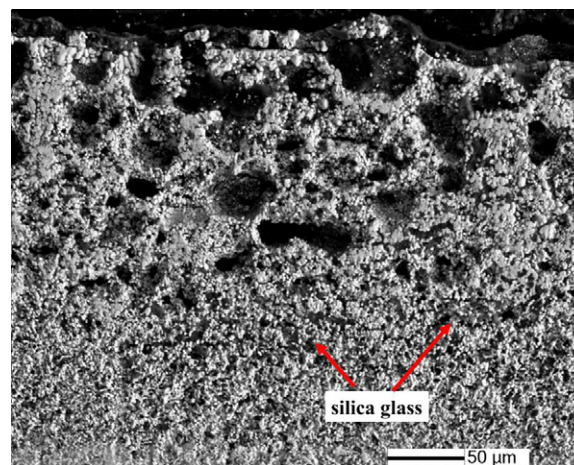


Fig. 7. Microstructure of oxidation layer for the atomic oxygen adsorbed $\text{ZrB}_2\text{-ZrC-SiC}$ ceramic composites oxidized under 1500°C for 90 min.

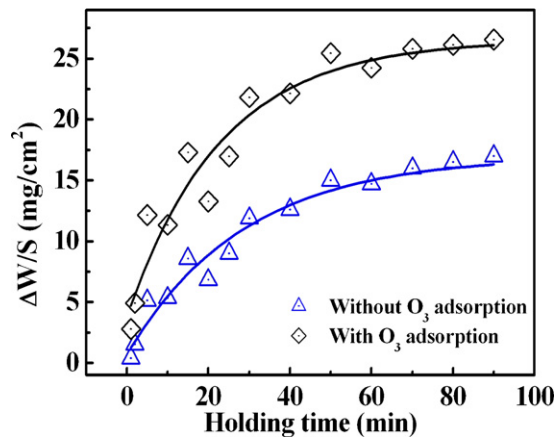


Fig. 8. Weight gain per unit surface area of the $\text{ZrB}_2\text{--ZrC--SiC}$ ceramic composites oxidized under 1500°C in air.

Table 3

Oxidation kinetics parameters of $\text{ZrB}_2\text{--ZrC--SiC}$ ceramic composites oxidized under 1500°C in air.

Samples	n	R^2 value for n	k_p
With AO adsorption	1.257	0.9534	0.7404
Without AO adsorption	1.371	0.9528	0.6407

larger than that without atomic oxygen adsorption, which indicates that atomic oxygen adsorption results in worse oxidation resistance performance for $\text{ZrB}_2\text{--ZrC--SiC}$ ceramic composites. The oxidation kinetics parameters, n and k_p , can be determined according to Eq. (1).

$$\left(\frac{\Delta W}{S}\right)^n = k_p t \quad (1)$$

Herein, n refers to oxidation exponent, and k_p means oxidation rate constant. The values of n and k_p can be determined from the slope and intercept of the plot showing the variation of the logarithm of weight gain per unit surface area versus logarithm time. Table 3 records the value of n and k_p , which reflects the difference of oxidation kinetics between specimens with and without atomic oxygen adsorption. As indicated by oxidation kinetics parameters, the oxidation exponent of the ceramic with atomic oxygen adsorption is smaller than that without atomic oxygen adsorption, while the oxidation rate constant is larger, which refers to worse oxidation resistance performance.

The difference between oxidation kinetics of the specimens with and without atomic oxygen adsorption should be related to the

porosity of the sintered ceramic, which provides diffusion path for the atomic oxygen when exposed to the AO rich environment. Thus the atomic oxygen adsorbs on the inner part of the ceramic and induces to inner oxidation of the ceramic when exposed to elevated temperatures, which results in significant decay of oxidation resistance property of the ceramic composites.

4. Conclusion

Ceramic composites of $\text{ZrB}_2\text{--ZrC--SiC}$ were prepared by hot pressing method, and the atomic oxygen adsorption behaviour and its effect on the oxidation behaviour of the sintered ceramic composites at elevated temperature were analyzed. The atomic oxygen was preferred adsorbed on the surface of the borides according to experimental results. The interactions between $\text{O} \leftrightarrow \text{B}$, $\text{O} \leftrightarrow \text{Zr}$ and $\text{O} \leftrightarrow \text{Si}$ were identified from the XPS spectra, which confirmed the chemical adsorption of atomic oxygen on the surface of the material and the formation of oxides after adsorption. The adsorbed ceramic composites were oxidized in air, and the structure evolution of the oxidized ceramic was analyzed in order to clarify the effect of atomic oxygen on the oxidation behaviour of the material. The experimental results indicated that atomic oxygen adsorption was detrimental to the oxidation resistance performance of the ceramic, and the porosity of the sintered ceramic provided diffusion path for the atomic oxygen during adsorption and resulted in inner oxidation when exposed to high temperatures. The variation of $\Delta W/S$ as a function of holding time confirmed the difference in oxidation kinetics caused by the adsorption of atomic oxygen.

References

- [1] M.M. Opeka, I.G. Talmy, J.A. Zaykoski, J. Mater. Sci. 39 (2004) 5887.
- [2] K. Upadhyay, J.M. Yang, W.P. Hoffmann, Am. Ceram. Soc. Bull. 76 (1997) 51.
- [3] S.-Q. Guo, J.-M. Yang, H. Tanaka, Y. Kagawa, Compos. Sci. Technol. 68 (2008) 3033.
- [4] M.M. Opeka, I.G. Talmy, Wuchina, Mech. J. Eur. Ceram. Soc. 19 (1999) 2405.
- [5] D. Sciti, C. Melandri, A. Bellosi, Adv. Eng. Mater. 6 (2004) 775.
- [6] A. Balbo, D. Scit, Mater. Sci. Eng. A 475 (2008) 108.
- [7] T. Zhu, W. Li, W. Zhang, P. Hu, C. Hong, L. Weng, Mater. Chem. Phys. 116 (2009) 593.
- [8] A. Rezaie, W.G. Fahrenholtz, G.E. Hilmas, J. Eur. Ceram. Soc. 27 (2007) 2495.
- [9] V. Medri, F. Monteverde, A. Balbo, A. Bellosi, Adv. Eng. Mater. 7 (2005) 159.
- [10] Q. Qu, J. Han, W. Han, X. Zhang, C. Hong, Mater. Chem. Phys. 110 (2008) 216.
- [11] X. Wang, X. Zhao, M. Wang, Z. Shen, Nucl. Instrum. Methods Phys. Res. B 243 (2006) 320.
- [12] D. Alfano, L. Scatteia, S. Monteverde, E. Bêchem, M. Balat-Pichelin, J. Eur. Ceram. Soc. 30 (2010) 2345.
- [13] J.A. Rodriguez, P. Liu, J. Gomes, K. Nakamura, F. Viñes, C. Sousa, F. Illas, Phys. Rev. B: Condens. Matter 72 (2005) 075427.
- [14] J. Wang, L. Zhang, Q. Zeng, G.L. Vignoles, L. Cheng, A. Guette, Phys. Rev. B: Condens. Matter 79 (2009) 125304.
- [15] W.G. Fahrenholtz, J. Am. Ceram. Soc. 90 (2007) 143.