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# Atomic oxygen adsorption and its effect on the oxidation behaviour of $ZrB_2$ -ZrC-SiC in air

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### ABSTRACT

Atomic oxygen is adsorbed on the surface of the hot-pressed  $ZrB_2$ -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.

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# 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]. ZrB<sub>2</sub> 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 MoSi<sub>2</sub> and AlN, has improved the mechanical properties significantly by inhibiting grain coarsening of ZrB<sub>2</sub> [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 MoSi<sub>2</sub> 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 ZrB<sub>2</sub>–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 ZrB<sub>2</sub>–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  $ZrB_2$ –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,  $ZrB_2$ –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 ZrB<sub>2</sub>-ZrC-SiC ceramic composites by hot pressing method

Commercially available ZrB<sub>2</sub>, ZrC and SiC powders with a reported purity of 99% and an average particle size of 2  $\mu m$  were used. Ceramic composites containing of

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Table 1		
The AO exposure	experimental	condition.

Parameters	Value
Vacuum chamber pressure (Pa)	0.15
Discharging voltage	120
Discharging current (mA)	140
Exposure time (min)	30
Atomic oxygen flux (atoms $cm^{-2} s^{-1}$ )	$6.4\times10^{15}$

40 vol% ZrB<sub>2</sub>, 40 vol% ZrC and 20 vol% SiC were prepared by hot pressing method. The mixed powders were hot pressed in graphite dies lined with graphite foil and coated with BN. Then the mixtures were hot-pressed at 1900 °C for 30 min at a pressure of 30 MPa. The furnace was heated to the targeted temperature at an average rate of  $30 \circ$ C min<sup>-1</sup> after loading to the graphite dies, and argon was used as protective gas. The load was removed when the die temperature dropped below 1750 °C. The furnace was cooled to the room temperature when hot-pressing time was elapsed. Then the sintered specimens were taken out from the graphite dies. Sample coupons in the size of 10 mm × 10 mm × 5 mm were cut from sintered materials by electrical discharge machining (EDM) method, and all the surfaces of the specimens were diamond polished to 1  $\mu$ m finish. The coupons were ultrasonically cleaned successively in deionized water and ethanol before atomic oxygen adsorption. The relative density of the sintered ceramic reached to 97 vol% according to experimental results by Archimedes method.

# 2.2. Adsorption of atomic oxygen on the surface of $ZrB_2$ -ZrC-SiC ceramic composites

The specimens were pretreated in vacuum furnace at 500 °C for 2 h in order to eliminate gaseous impurities adsorbed on the surface of the ceramic. Then the atomic oxygen adsorption was carried out in the ground-based AO effect simulation facility at Beijing University of Aeronautics and Astronautics (BUAA). The facility was a filament discharge plasma-type ground-based AO effect simulation facility [11]. The atomic oxygen was the predominant component in the obtained oxygen plasma according to oxygen plasma emission spectrum, as reported elsewhere [11]. The AO exposure condition in the present research is listed in Table 1.

#### 2.3. Oxidation of atomic oxygen adsorbed ZrB2-ZrC-SiC ceramic composites

The as-adsorbed specimens were oxidized in air at 1500 °C up to 90 min. In addition, the ceramic composites without atomic oxygen adsorption were oxidized under the same condition for comparison. The weight of the specimens was measured after oxidation immediately in order to obtain curves of weight gain per unit surface area ( $\Delta W/S$ ) as a function of holding time.

#### 2.4. Characterization of as-adsorbed and oxidized ZrB2-ZrC-SiC

The chemical composition of the specimens before and after atomic oxygen adsorption was measured with a PHI Quantera X-ray photoelectron spectrometer using a monochromatic Mg X-ray source. Furthermore, the chemical structure of the specimens was deduced from the XPS spectrum of the specimens. The crystalline phase of oxidation products was determined by XRD (D-max 2200, Rigaku, Tokyo, Japan). The surface morphology and microstructure of cross section were identified by SEM (CS3400, Oxford, England), which was equipped with an EDS detector (INCAINCAPentaFET-x3, Oxford, England).

# 3. Results and discussion

# 3.1. Adsorption of atomic oxygen on the ZrB<sub>2</sub>–ZrC–SiC ceramic composites

The adsorption mechanism of atomic oxygen on the surface of  $ZrB_2$ -ZrC-SiC ceramic composites can be deduced from the XPS spectra of as adsorbed ceramic composites, as shown in Fig. 1. In addition, the XPS spectra of specimens pre-treated in vacuum tabular furnace was offered for comparison, thus the chemical shift of chemical bonds before and after atomic oxygen adsorption can be identified, as listed in Table 2. As can be seen from Fig. 1(a), obvious chemical shift between B-Zr and B-O can be identified after atomic oxygen adsorption, and the B-Zr bond cannot be identified from the B 1s spectrum of as-adsorbed ceramic composites, which is also confirmed by the O 1s spectra (shown in Fig. 1(c)). In addition, the bond of C-Si can disappear from the C 1s spectrum with atomic oxygen adsorption, while the relative intensity of C-Zr bond is lowered

omponent posi omposites.	ions (±0.1 e\	V), nature of	the chemic	al bonds me	asured from	i deconvolutec	i photoelect	ron peaks (E	3 1S, C 1S, U	1s, sı 2p an	d Zr 3d <sub>3/2,5/2</sub> )	collected for	the pre-treated	l and as-adsor	oed ZrB2-ZrC-	SIC CERAMIC
Sample	Compone	ents position	ts (±0.1 eV) a	and nature of	f main chem	ical compositi	on									
	0 1s			B 1s		C 1s			Si 2p		Zr 3d <sub>3/2, 5/2</sub>					
											Zr 3d <sub>3/2</sub>	Zr 3d <sub>5/2</sub>	Zr 3d <sub>3/2</sub>	Zr 3d <sub>5/2</sub>	Zr 3d <sub>3/2</sub>	Zr 3d <sub>5/2</sub>
Pre-treated	I	532.1	530.8	I	187.5	286.1	283.3	282.9	103.2	100.6	185.0	182.8	181.2	178.7	183.5	181.1
	I	0-Si	0-Zr	I	B–Zr	C-Si-O	C–Si	C-Zr	Si-O	Si-C	Zr-0		Zr-B		Zr-C	
As-adsorbed	533.2	532.1	530.8	192.8	187.5	I	I	282.9	103.2	100.6	185.0	182.8	I	I	183.5	I
	0-B	0-Si	0-Zr	0-B	B-Zr	I	I	C-Zr	Si-O	Si-C	Zr-0		I		Zr-C	



Fig. 1. XPS spectra of pre-treated and as-adsorbed ZrB2-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 ZrB<sub>2</sub>–ZrC–SiC ceramic composites

Fig. 2 shows the XRD patterns of  $ZrB_2$ –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  $ZrB_2$ –ZrC–SiC ceramic composites oxidized under 1500 °C for 10 min.  $\blacklozenge$  refers to monoclinic phase zirconia.

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

The surface morphology of the  $ZrB_2$ -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  $ZrB_2$ -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  $ZrB_2$ -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 ZrB2–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



**Fig. 6.** Variation of thickness of oxide scale (a) and SiC depleted layer (b) for  $ZrB_2$ -ZrC-SiC ceramic composites oxidized under 1500 °C.

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 ZrB<sub>2</sub>–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. 7. Microstructure of oxidation layer for the atomic oxygen adsorbed  $ZrB_2$ -ZrC-SiC ceramic composites oxidized under 1500 °C for 90 min.



Fig. 8. Weight gain per unit surface area of the  $ZrB_2$ -ZrC-SiC ceramic composites oxidized under 1500 °C in air.

#### Table 3

Oxidation kinetics parameters of  $ZrB_2-ZrC-SiC$  ceramic composites oxidized under 1500  $^\circ\text{C}$  in air.

Samples	n	$\mathbb{R}^2$ 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  $ZrB_2$ –ZrC–SiC ceramic composites. The oxidation kinetics parameters, n and  $k_p$ , can be determined according to Eq. (1).

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

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 ZrB2-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  $0 \leftrightarrow B$ ,  $0 \leftrightarrow Zr$  and  $O \leftrightarrow Si$  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.

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