Catalytic properties of ZrB$_2$–SiC–W ultra–high temperature ceramics at moderate temperatures

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Abstract. Catalytic behaviors related to recombination reactions of dissociated oxygen atoms on the surface of ZrB$_2$–SiC–W ultra–high temperature ceramic was investigated quantitatively in the temperature ranges from room temperature to 1300 K, and recombination coefficient can be obtained by the photochemical method based on spectral diagnostic techniques using microwave–discharge plasma apparatus. Oxidation of specimens even at relatively low temperature during the experiment had a significant influence on the catalytic properties of ZrB$_2$–SiC–W ultra–high temperature ceramics, and the results revealed the detectable dependence of the catalytic properties upon environment–induced surface modification. The relationship between catalytic properties of ZrB$_2$–SiC–W ultra–high temperature ceramics and surface microstructure was also discussed in detail.

1. Introduction

Transition metal diborides (MB$_2$) such as ZrB$_2$ and HfB$_2$, commonly referred to as ultra–high temperature ceramics (UHTCs), are being considered as principal candidates for the leading edges of sharp–bodied reentry vehicles. Among UHTCs, ZrB$_2$–based ceramics have received a majority of the attention due to relatively lower density and lower cost, ultra–high melting temperature (>3000°C), high electrical and thermal conductivities, excellent chemical inertness against molten metals, good thermal shock and excellent ablation/oxidation resistance [1–4].

The investigation of catalytic properties for ZrB$_2$–based ceramics are driven by the demand of developing re–usable hot structures as thermal protection systems (TPS) of space vehicles able to re–enter from Low Earth Orbit (LEO) at relatively high speed (order of 8 km/s) [5,6]. During hypersonic flight through Earth’s atmosphere, high–temperature shock waves form in front of vehicle leading edges. Molecular oxygen and nitrogen, with respective dissociation energies of approximately 5.2 eV (500 kJ/mol) and 9.8 eV (950 kJ/mol), are dissociated to atomic species in these extreme environments. If the resulting atomic species diffuse to the vehicle surface and recombine there, the energy released during atom recombination on a surface is shared between the resulting molecules and the surface. The transfer of this energy to the surface leads to its heating. The number of recombined atoms and the energy transferred depends on the nature of the surface, and the process is referred to be a catalytic atom recombination. When the recombination species are oxygen atoms, the very high sticking coefficient leads to the formation of an oxide layer on the surface. In a few milliseconds, a modification of the nature of the surface and its properties occurs. The oxidation of ceramic
accompanied with recombination reaction can result in a change of the catalytic properties. These studies are very important for the conception of catalytic materials and the qualification of materials supporting high thermal constraints. Many of these studies draw inspiration from the late Professor M. Balat–Pichelin, whose work is noted for both its high quality and enormous quantity [7–9].

The catalytic properties of ZrB$_2$–SiC–W ceramic for recombining dissociated oxygen and nitrogen is rarely investigated as one aspect of performances. In the present work, the catalytic behaviors of ZrB$_2$–SiC–W ceramic for recombining dissociated oxygen was investigated from room temperature to 1300 K, and the surface change of ZrB$_2$–SiC–W ceramic due to the plasma exposure was discussed in detail.

2. Experiment

2.1. Testing method

The atomic concentration along the surface axis is measured using spectrum accompanied with the recombination reaction on the surface of specimen, and then the recombination coefficient can be calculated based on the one–dimensional diffusion equation. This method based on the spectral diagnostic technique is referred to photometrical method, which is first proposed by M. Balat–Pichelin [7]. We further develop this method to evaluate the catalytic properties of ZrB$_2$–based ceramics quantitatively.

In the present experiment the atomic oxygen is induced by microwave generator. A small quantity of argon is introduced in the flow to correct the change in atomic oxygen concentration by spectral intensities ratio ($I_O/I_{Ar}$). The diffusion of atoms can be considered as one–dimensional steady state diffusion, which is described by diffusion equation:

$$D \frac{\partial^2 C_A}{\partial x^2} = 0 \quad (1)$$

where $D$ is the diffusion coefficient; $C_A$ is the atomic concentration; $x$ is distance from the surface of specimen.

The balance established between mass flux of atoms diffusing to surface and that of recombining atoms on surface can be given by:

$$D_{O,_{air}} \frac{\partial C_O}{\partial x} \bigg|_{x=0} = C_O(x=L) \cdot \frac{\gamma \cdot V^*}{4} \quad (2)$$

where the $V^*$ is the mean square velocity of oxygen atoms, which can be written as:

$$V^* \approx \sqrt{\frac{N_A \cdot k_B \cdot T_e}{M_O}} \quad (3)$$

Combining with the eq. (1) and eq. (2), the atomic oxygen concentration along the surface axis can be given by:

$$C_O(x) = \frac{\gamma \cdot V^* \cdot C_O(x=L)}{L \cdot \gamma \cdot V^* + 4D_{O,_{air}}} \cdot \frac{4D_{O,_{air}} \cdot C_O(x=L)}{L \cdot \gamma \cdot V^* + 4D_{O,_{air}}} \quad (4)$$

where the $C(x=L)$ means the atomic oxygen concentration at the distance of $L$.

Therefore, the atomic oxygen concentration at surface of specimen ($C(x=0)$) is represented as:

$$C_O(x=0) = \frac{4D_{O,_{air}} \cdot C_O(x=L)}{L \cdot \gamma \cdot V^* + 4D_{O,_{air}}} \quad (5)$$
Based on the actinometry, the ratio of the concentration is proportional to the intensity ratio of emitted lines,

$$\frac{C(x=L)}{C(x=0)} = \frac{(I_O/I_{Ar})_{x=L}}{(I_O/I_{Ar})_{x=0}} = \frac{R_L}{R_0}$$

with the $(I_O/I_{Ar})_{x=0}$ and $(I_O/I_{Ar})_{x=L}$ as the intensity ratio at surface and the distance of $L$, respectively.

The recombination coefficient can be calculated finally,

$$\frac{C(x=L)}{C(x=0)} = \frac{(I_O/I_{Ar})_{x=L}}{(I_O/I_{Ar})_{x=0}} = \frac{R_L}{R_0}$$

where $\gamma$ is the recombination coefficient, which can be further rewritten as:

$$\gamma = \frac{1}{R_0} \cdot \frac{4 \cdot D_{O,air}}{V^*} \cdot \tan \alpha$$

where the $\tan \alpha$ is the slope of the curve of intensity ratio versus distance.

2.2. Experimental process

Commercially available ZrB$_2$ powder (2μm, >99.5%, Northwest Institute for non–ferrous metal research, China), SiC powder (1μm, >99.5%, Weifang Kailhua Micro–powder Co., Ltd., China) and W powder (5 μm, >99.0%, Zhuzhou Cemented Carbide Group Co. Ltd., China) were used as raw powders. The powder mixtures of ZrB$_2$ plus 15vol% SiC and 5vol% W were ball–mixed for 20h in a polytetrafluoroethylene bottle using ZrO$_2$ balls and ethanol as the grinding media. After mixing, the slurry was dried in a rotary evaporator and screened. The resulting powder mixtures were hot–pressing at 1900 °C for 1 h under a uniaxial load of 30 MPa in Ar atmosphere. The bulk density of the specimens was measured by the Archimedes method. Specimens with Ø24 mm × 3 mm were cut from the billet, and then polished to 1 µm finish.

The test was carried out using a microwave–discharge plasma apparatus, which was described in detailed elsewhere [10]. Specimen was placed on the alumina rod inside the quartz tube, the flow rates of oxygen and argon were controlled at 60 and 20 ml/min, respectively. The pressure regulated by the pressure regulator and vacuum pump was 50 Pa. The temperature of specimen was measured with optical pyrometer and thermocouple. The test temperatures of specimens were room temperature (~300 K), 500, 1100 and 1300 K, respectively. The flow was discharged by microwave generator, and the anode current was fixed at 350 mA. The recombination coefficients of specimens were tested at a constant testing temperature for ~90 min.

The microstructural features of the specimen were observed by scanning electron microscopy (SEM, FEI Sirion, USA) with simultaneous chemical analysis by energy dispersive spectroscopy (EDS, EDAX Inc). The phase composition was determined by X–ray diffraction (XRD; Rigaku, Dmax–rb, CuKa = 1.5418 Å).

3. Experiment

The testing for catalytic properties of ZrB$_2$–SiC–W ceramic was carried out twice in the temperature range from room temperature to 1300K. During the first test run, the specimens were tested from room temperature to 1300 K. During the second test run, the measurements of the specimens tested at 1300 K in the first test run were repeated again. The recombination coefficients of the ZrB$_2$–SiC–W ceramic after testing are summarized in Figure 1. It is obviously that the catalytic properties of specimens between two test runs are different under the same condition. In the first test run, the recombination coefficient of ZrB$_2$–SiC–W ceramic at room temperature is calculated as $9.58 \times 10^{-4}$. The recombination coefficient at 500 K as $7.03 \times 10^{-3}$ is significantly higher than that at room temperature. As the temperature increases to 1300 K, the recombination coefficient increases slightly to $7.82 \times 10^{-3}$. 
Similarly, as the temperature increases from room temperature to 1300 K in the second test run, the recombination coefficient increases gradually from $9.00 \times 10^{-4}$ to $7.44 \times 10^{-3}$. It should be noted that the catalytic reaction activity of specimen increases with temperature, and the recombination coefficient in second test run is lower than that in first test run. The change in catalytic properties of ZrB$_2$–SiC–W ceramic can be attributed mainly to the surface component and microstructures.

**Figure 1.** The recombination coefficients of ZrB$_2$–SiC–W ceramic tested at different temperature.

Figure 2 shows the XRD patterns of specimens tested under different temperature. It is evident that the specimen at room temperature is mainly composed of ZrB$_2$ and SiC, and some weak peaks corresponding to WB can be identified that could result from the reaction during hot-pressing. After testing at 500 K, Aside from ZrB$_2$ and SiC, ZrO$_2$ and WO$_3$ can be found at the surface, which indicates that the specimen is oxidized slightly even at low temperature. When the specimen is tested at 1100 K, only a small amount of ZrB$_2$ is identified, because the substrate of specimen is covered with oxide scale. Monoclinic ZrO$_2$, tetragonal ZrO$_2$ and WO$_3$ as the oxidation products can be found. The main components at surface of specimen tested at 1300 K are not fundamentally different from those at 1100 K.

**Figure 2.** XRD patterns of ZrB$_2$–SiC–W ceramic tested at different temperature.
Figure 3a shows the surface SEM image of the specimen tested at room temperature. There is no detectable change in surface morphology between this specimen and the original specimen. The surface is mainly composed of ZrB$_2$, SiC and WB. After testing at 500 K, the surface of specimen is relatively rough owing to the slight oxidation during testing. WB is oxidized to WO$_3$, while obvious oxidation is not observed in ZrB$_2$ and SiC, which is consistent with the result of XRD (Figure 3b). As the temperature increases to 1100 K, the oxidation of SiC is much slower than that of ZrB$_2$ in this temperature regime [11], and the surface is incompletely covered with glass resulting from the oxidation of ZrB$_2$ (Figure 3c). Similarly, the surface morphology of specimen tested at 1300 K is not different from that at 1100 K except for the amount of glass (Figure 3d).

![Figure 3. Surface morphology of ZrB$_2$–SiC–W ceramic at different temperature: (a) room temperature, (b) 500 K, (c) 1100 K and (d) 1300 K.](image)

The catalytic properties are significantly related to the surface microstructure and testing environment. The recombination coefficient of ZrB$_2$–SiC–W ceramic increases with temperature that is consistent with other reports in the open literature [9]. In addition, under the same condition, the recombination coefficient calculated in the second test run is lower than that in the first test run. This can be attributed to that the surface of specimen tested in the second test run is covered with glass. The literatures [12, 13] have reported that the glass has a relative low catalytic reaction activity compared with metal oxide. The material surface changed by interactions with the environment has a significantly influence on the catalytic properties of ZrB$_2$–SiC–W ceramic.

4. Summary
The catalytic properties of ZrB$_2$–SiC–W ultra–high temperature ceramic have been investigated quantitatively in the temperature ranges from room temperature to 1300 K, and the recombination coefficient can be calculated by the photochemical method based on spectral diagnostic techniques
using microwave–discharge plasma apparatus. The catalytic reaction activity of ZrB$_2$–SiC–W ceramic increases with temperature. The recombination coefficient in the first test run is lower than that in the second test run under the same condition, which can be related to surface component and microstructure. The surface that was changed by interactions with the environment at a relatively low temperature had a significantly influence on the catalytic properties of ZrB$_2$–SiC–W ceramic.

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References
[1] Monteverde F 2005 Corros. Sci. 47 2020-33
[2] Fahrenholtz WG, Hilmas GE, Talmy IG and Zaykoski JA 2009 Mater. Sci. Eng. A 516 297-301
[3] Okamoto NL, Kusakari M, Tanaka K, Inui H, Yamaguchi M and Otani S 2007 J. Am. Ceram. Soc. 90 1347-64
[4] Du BH, Li N, Ke B, Xing PF, Jin XX, Hu P and Zhang XH 2016 Ceram. Int. 42 14292-7
[5] Venkatapathy E, Laub B, Hartman GJ, Arnold JO, Wright MJ and Allen Jr GA 2009 Adv. Space. Res. 44 138-50
[6] Parmenter KE, Shuman K, Milstein F, Szalai CE, Tran HK and Rasky DJ 2001 J. Spacecraft Rock. 38 231-6
[7] Balat M, Czerniak M and Badie JM 1997 Appl. Surf. Sci. 120 225-38
[8] Balat–Pichein M, Badie JM, Berjoan R and Boubert P 2003 Chem. Phys. 291 181-94
[9] Bedra L and Balat–Pichelin M 2005 Appl. Surf. Sci. 9 318-28
[10] Li N, Hu P, Zhang XH and Han WB 2013 Mater. Sci. Forum 745-746 636-41
[11] Hu P, Wang GL and Wang Z 2009 Corros. Sci. 51 2724-32
[12] Balat M, Czerniak M, Badie JM and Olalde G 1999 J. Spacecraft Rocket 36 273-9
[13] Alfano D, Scatteia L, Cantoni S and Balat M 2009 J. Eur. Ceram. Soc. 29 2045-51