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Ablation resistance of ZrB_2–SiC–AlN ceramic composites

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ABSTRACT

ZrB_2–20 vol.%SiC–5 vol.%AlN ceramic composites (ZSA) were fabricated by hot pressing sintering under inert gas protected, which mechanical properties were improved obviously by introducing AlN as sintering aid. Ablation tests of ZSA were conducted with different heat flux parameters in high frequency plasma wind tunnel. The results showed that ZSA exhibited excellent ablation resistance at 2000 °C for 300 s in oxidation environment and a dense coherent scale was formed after ablation, whereas a strong degradation and mass loss were observed at 2600 °C for 300 s. The ablation behavior, microstructures evolvement and the effect of AlN were analyzed.

1. Introduction

The advanced zirconium diboride (ZrB_2) ceramic composites are candidate for thermal protection materials in both reentry and hypersonic vehicles because of their high melting points, good thermal shock and excellent ablation/oxidation resistance [1–4]. These properties may allow more advanced vehicle designs with features like sharp leading edges and sharp nosecones. The existing available thermal materials are not withstanding extreme temperatures (>2000 °C). Therefore, it is necessary to develop the thermal protection materials endowed with good ablation resistance as well as dimensional stability.

Current research activities are still facing barriers to overcome their poor sinterability that limit a feasible dense components at affordable manufacturing conditions where temperature <2000 °C [5,6]. In order to improve the powder sinterability and mechanical properties of zirconium diboride, AlN as a sintering aid was applied in fabricating ceramic composite by hot pressure sintering. The role of additives for the sintering of covalent-bonded ceramics can be regarded as not only densification aids but also key elements for the microstructural development, since the kinds and amounts of additives influence the related properties of materials. The addition of AlN as sintering aids is in function of enhancing the sinterability, reducing sintering temperature and refining grains. The introduction of AlN successfully conferred better mechanical properties, in comparison to literature data for similar materials [7,8]. In addition, the ablation resistance is a major issue in the development of ceramic composites for aero-propulsion and hypersonic flight applications. SiC as the second phase in ZrB_2 ultra high temperature ceramics (UHTCs) has succeeded in improving both the ablation resistance and mechanical properties [9–12].

The ablation behavior of the ZrB_2–SiC–AlN ceramic composites is significantly different from that at lower temperatures. However, the ablation mechanisms of these materials are still not well understood, especially for the temperature >2000 °C. The purpose of this paper is to investigate the ablation behaviors of ZrB_2–SiC–AlN ceramic composites at different heat parameters of high frequency plasma wind tunnel. The ablation behavior, microstructures evolvement and the effect of AlN were discussed.

2. Experimental procedure

The samples used here for ablation testing were fabricated from commercial ZrB_2 (Harbin Institute of Technology, China), α-SiC (Xuzhou Hongwu Nanometer Materials, China), and AlN (Fujian Sinocera Advanced Materials Co., Ltd., China). Powders containing ZrB_2–20 vol.%SiC–5 vol.%AlN were mixed by wet ball milling for 8 h in a polyethylene bottle, using WC balls and alcohol as media. After mixing, the slurry was dried in a rotating evaporator to minimize segregation. Milled powders were fabricated by hot pressing under inert gas protected in a graphite die coated boron nitride at 1850 °C for 60 min and 30 MPa of applied pressure.

ZSA samples with an Ø20 mm × 30 mm cylinder for ablation testing were cut from the billet, and all surfaces were diamond-polished to 1 μm finish. Coupons were ultrasonically cleaned successively in detergent, de-ionized water, acetone and alcohol prior to exposure. Under high frequency plasma wind tunnel, selected samples were exposed to sustained enthalpy value using an oxygen flame with high velocity gas in condition 1 (heat flux is 380 W/cm^2, enthalpy is 20.8 MJ/kg, ablation time is 300 s) and condition 2 (heat flux is 240 W/cm^2, enthalpy is 12.5 MJ/kg, ablation time is 300 s), respectively.

Bulk density and theoretical density were evaluated using the Archimedes method and the rule of mixture, respectively. The microstructure of ZSA ceramic composites was characterized using scanning electron microscopy (SEM) along with

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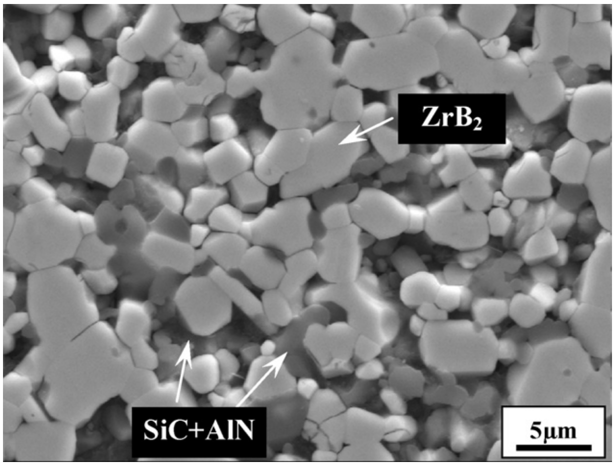

Fig. 1. SEM micrograph of as-sintered ZSA ceramic composite.

energy dispersive spectroscopy (EDS) which was used to characterize the composition and microstructure of the surface and cross-section of the samples after ablation. The different ablation layers were also investigated after removing the surface layers by polishing parallel to the original surface. The material removal was monitored using optical microscopy so that the desired region was reached. X-ray diffraction was used to identify ablation phases present after ablation.

3. Results and discussion

3.1. Microstructure of as-sintered ZSA ceramic composite

The addition of AlN can effect on the sinterability and microstructure of the ZSA ceramic composites remarkably. The microstructure of ZrB_2–SiC–AlN ceramic composite shows equiaxed grain that the average grain size is 3–4 μm. The SEM micrograph from polished section could be clearly illustrative (Fig. 1).

3.2. Microstructure evolvement and ablation properties

The ablation properties of ZSA ceramic composite, including heat flux parameters, mass loss, ablation time, the maximum temperature, etc. are shown in Table 1. The results show that the quality ablation rate and linear ablation rate of ZSA ceramic composite under condition 1 is 0.33% and 0.006 mm/min, respectively. It is indicated that ZSA ceramic composite possesses good resistance thermal shock. When heat flow value increased to 380 W/cm^2, and enthalpy value is 20.8 MJ/kg, quality ablation rate and linear ablation rate reaches 21.23% and 099 mm/min, the property of ablation resistance for ZSA ceramic composite was decreased significantly.

Table 1
Ablation properties of ZrB_2–20 vol.%SiC–5 vol.%AlN ceramic composite.

Ablation parameters	Condition 1	Condition 2
Heat parameters		
Heat flux (W/cm^2)	238	380
Enthalpy (MJ/kg)	12.5	20.8
Pressure (KPa)	18.0	18.0
Ablation time (s)	300	300
Maximum temperature (°C)	2042	2662
Original quality (g)	49.11	48.04
Quality after ablation (g)	48.90	37.84
Mass loss (g)	0.21	10.20
Height after ablation (mm)	30.06	25.00
Quality ablation rate (%)	0.33	21.23
Linear ablation rate (mm/min)	0.006	0.990

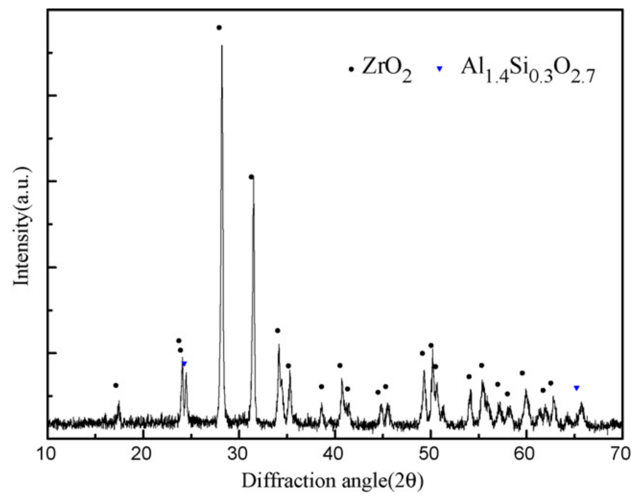

Fig. 3. XRD of ZSA samples after ablation for 300 s.

Fig. 2 shows the surface appearance photos of ZSA ceramic composite at different ablation parameters. A continuous ablation layer was found to form on the surface for ZSA at condition 1, while a discontinuous ablation layer was formed at the outside scale of the surface for ZSA under condition 2. Fig. 2 (b) also shows that a number of cracks were also observed on the surface of ZSA. The formation of the cracks was attributed to the formation of large amounts of high pressure gaseous ablation products (i.e., B_2O_3, SiO and CO, etc.) and the desquamation in function of the high frequency plasma arc. Because the formed ablatant is mainly melted zirconium silicate at extreme high temperature.

The X-ray diffraction analysis of ZSA samples after ablation is shown in Fig. 3. The result showed that the component of com-

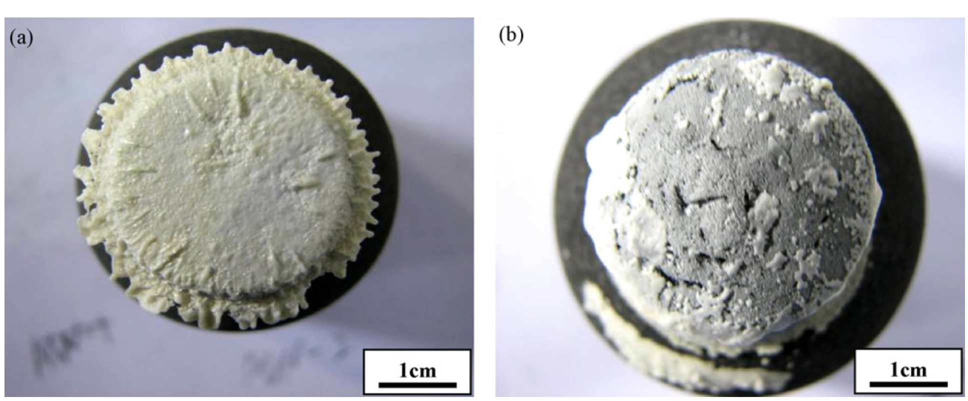

Fig. 2. Surface appearance photos at different ablation parameters (a) condition 1 and (b) condition 2.