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Thermoablative resistance of ZrB_2-SiC-WC ceramics at 2400 °C

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ABSTRACT

Although ZrB_2-SiC ceramics have been extensively researched for applications at ultra-high temperatures (>2000 °C), it is well known that at these temperatures the SiC oxidises actively yielding a gaseous sub-oxide, SiO, rather than the protective, passive oxide product, SiO_2. This limits the high-temperature range of SiC-bearing ceramics for ultra-high temperature applications. In the present work, the addition of 5 vol% WC has been shown to partially eliminate the active oxidation of SiC in ZrB_2-SiC ceramics, even when exposed to an oxyacetylene flame at 2400 °C. In contrast to the porous and fragmentary surface observed with ZrB_2-SiC ceramics tested under the same conditions, a dense oxide surface layer was observed that is believed to have resulted in decreasing pO_2 in the layers beneath. This had the effect of changing the chemistry of the system and hence the composition of the phases produced. Clear evidence of the presence of SiO_2 was observed, thus indicating that the oxidation of the SiC had been partially passive rather than active. A full volatility diagram for WB at 2400 °C was derived, and existing volatility diagrams for ZrB_2 and SiC were extended to the same temperature, in order to develop a theoretical understanding of the ablation mechanism. The significantly improved ablation resistance of ZrB_2-SiC-WC is consequently mainly attributed to a competitor transition from tungsten boride (WB) to metallic tungsten in the oxygen partial pressure range 10^{-8} Pa to 10^{-3} Pa, which retards the occurrence of the active oxidation of the SiC phase.

1. Introduction

It is well known that the efficiency of a heat engine is governed by the temperature at which it operates; the higher the temperature, the better the engine efficiency expected [1]. Whilst metals are currently used for most engines, there is an increasing desire to move to higher performing materials such as ceramics for engines that will operate under the most demanding conditions, including turbines and scramjets [2]. For example, in order to maximize performance and meet the aerodynamic shape constraints of the next generation of hypersonic vehicles, their leading edges and nose cones have to be designed into sharp profiles where active cooling using coolants is impractical. Consequently, these parts have to meet severe operating conditions, including very high heat loads and temperatures, high ablation forces and attack by atomic oxygen amongst other factors [1,3].

Ultra-high Temperature Ceramics (UHTCs) are a class of materials based on refractory metal diborides and carbides that exhibit excellent structural stability at temperatures exceeding 2000 °C. Perhaps the most widely investigated of these materials is zirconium diboride, ZrB_2, containing 20 vol% silicon carbide, SiC. Often known as ZS, these ceramics offer a trade-off between density, oxidation resistance, maximum operating temperature, thermal conductivity and mechanical performance at elevated temperature [4,5].

Many ultra-high temperature applications, however, including hypersonic flight, lead to conditions that promote active oxidation of the SiC phase in ZS ceramics. As for monolithic SiC, gaseous SiO can be formed at temperatures in excess of about 1700 °C rather than a protective SiO_2 layer, even in a stationary air atmosphere [6,7]. Under more rigorous conditions, e.g. oxyacetylene torch (OAT) testing at 2200 °C, the Si-based phase can be completely removed leaving porous monoclinic ZrO_2 ($mZrO_2$) layers on the surface of the ZS [8–11]. Although work aimed at densifying or stabilizing the porous ZrO_2 layer by incorporating rare earth oxides (e.g. SmO_2) [12] or borides (e.g. LaB_6) [13] into the ceramic matrix during processing have been shown to retard the evaporation of the borosilicate glass phase during ablation, the active oxidation of the SiC beneath this layer has not been avoided [8–13]. This then plays a key role in promoting the degradation of the ceramic [4,5,8]. The

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present work aims to solve this problem by a new approach of suppressing the active oxidation of SiC during ablation of ZS via additions of WC; the resultant ZrB_2-SiC-WC ceramics develop a dense surface oxidation layer when exposed to an oxyacetylene torch generating a heat flux of approximately 9 MW m^{-2} for 300 s. This paper presents the results of the work undertaken and offers an explanation of the mechanism underpinning the protection achieved.

2. Experimental

Powder mixtures with two different compositions, viz. ZrB_2 − 20 vol% SiC (ZS) and ZrB_2 − 20 vol% SiC − 5 vol% WC (ZSW), were prepared by mixing ZrB_2 (D_{50} = 2.1 μm, H.C. Starck, grade B, Germany), α-SiC (D_{50} = 0.5 μm, H.C. Starck, grade BF-12, Germany) and WC (D_{50} < 1 μm, Hard Alloy Co., Ltd., Zhuzhou, China) powders in appropriate amounts by wet ball mixing followed by rotatory evaporation. 3Y-ZrO_2 balls with a diameter of 10 mm and acetone were used as the mixing media and solvent, respectively. The two powder mixtures were densified in graphite dies using spark plasma sintering (SPS) to yield bodies with a diameter of 30 mm and a thickness of 12 mm. The conditions used were 1950 °C for 7 min under vacuum and a uniaxial loading of 60 MPa during the heat cycle; the heating rate was 100 °C min^{-1}.

Cylinders with diameters of 10 mm were prepared by electrical discharge machining the as-sintered discs. After cleaning successively using deionized water and ethanol, the cylinders were fully dried before being subject to oxyacetylene torch (OAT) testing; the latter facility has been described previously [9]. An oxidizing flame was achieved by using an oxygen: acetylene ratio of 1.35: 1; the pressure was regulated at 0.083 MPa for both gases whilst the flow rates were 0.8 m^3 h^{-1} for the acetylene and 1.1 m^3 h^{-1} for the oxygen. The samples were held in a water-cooled graphite holder and the distance between the flame tip and the sample was set as 25 mm; this yielded a heat flux of ~9 MW m^{-2}. Details of how the heat flux was obtained have been reported elsewhere [14]. All OAT tests were undertaken for a fixed ablation time of 300 s since ablation is a dynamic process. The temperature was recorded using a two-colour infrared pyrometer (Raytek GmbH, Berlin, Germany) focused on the centre of the hot face of each sample. Meanwhile, the temperature distribution across the samples was also measured using an infrared thermal imaging camera (Thermovision A40, FLIR Systems AB, Sweden).

The surface and cross section of the as-sintered and each as-ablated specimen were characterized using scanning electron microscopy, SEM (JEOL 7000, Tokyo, Japan) equipped with energy-dispersive spectroscopy (EDS). To resolve the overlapping of the kα line between silicon and zirconium from EDS, wavelength dispersive spectroscopy (WDS) was also used via the same SEM; the latter allowed the light elements such as boron and oxygen to be mapped across the polished cross sections. Detailed microstructures for the ZSW after OAT testing were further characterized using transmission electron microscopy, TEM (JEOL 2100, Tokyo, Japan), also with EDS capability, and operated at 200 keV. TEM thin foils were extracted from key locations in the oxidized layers by an *in situ* lift-out technique using a gallium ion focused ion beam (FIB, Quanta 3D FEG, FEI, Eindhoven, Netherlands). In each case, secondary electron images (SEIs) were collected from the SEM with the sample tilted at 52°. Electron and X-ray diffraction (XRD, Bruker, D8 Advance) were combined to identify the phase assemblage in the oxidized layers in the ZSW. For the XRD measurements, a series of patterns were taken from sections at different depths by dry grinding the ablated surface gently using 1200-grit SiC sandpaper.

3. Results and discussion

3.1. Density, microstructure and phase assemblages before ablation

The measured bulk densities for the two compositions were 5.45 g cm^{-3} and 5.95 g cm^{-3} for ZS and ZSW respectively, which correspond to 98.7% and 99.1% of their theoretical values. The microstructures are shown in Fig. 1. ZrB_2 grains, which appear grey, may be seen to form a continuous matrix with mean grain sizes of 2.8 μm and 2.5 μm in the ZS and ZSW respectively. The SiC phase appears black and is present in both ceramics as an isolated phase, although some elongated SiC grains form agglomerates in the ZS. As expected, the ZSW revealed the presence of reaction-generated phases that were randomly but well distributed, these include ZrC (labelled 'Z' and appearing light grey) and WB (labelled 'W' and appearing white), Fig. 1b. The reaction paths of WC in the ZrB_2-SiC system with and without the presence of oxygen have been well documented [15,16]. No obvious porosity was observed in either ceramic in accordance with the density measurements and thus will not have played a part in the resulting ablation performance.

3.2. Temperature response during OAT

Fig. 2a shows the temperature/time curves for the thermo-ablative assessment undertaken using the OAT tests. Compared with ZS, it was observed that the ZSW heated faster and achieved a higher maximum temperature, ~2400 °C after 100 s. One possible reason is the incorporation of WC into the composition reduced the thermal conductivity compared to the ZS ceramics as a result of enhanced phonon scattering through solid solution and phase boundary in ZSW [17]. An alternative explanation is that the emissivity of the oxide layer was changed due to the presence of the W; rare-earth species have been shown to alter the emissivity of zirconia-based scales [12]. Whatever the explanation, as may be observed, this resulted in a maximum temperature difference of up to 400 °C between the two samples during OAT testing. It should also be noted that at elevated temperatures, the thermal conductivity of these ceramics is mainly dominated by the electron contribution. This means that the thermal conductivities will approach a constant value for both ZS and ZSW, regardless of their composition [18]. This could well explain why, ultimately, both ceramics achieved a similar maximum temperature during OAT testing; ~2400 °C for ZSW and 2350 °C for ZS.

Fig. 2b shows how the flame played across the samples during OAT testing. The oxyacetylene flame is normally constituted by an inner cone and an outer feather; however, in this work most of the feather parts of the flame were blocked by the sample under testing and flowed in radial directions, Fig. 2b. Since the distance between the sample and nozzle tip was 25 mm, which is 10 mm larger than that for previous testing [9], the flame covered the sample fairly uniformly and hence the temperature distribution from centre to edge of each sample was limited to less than 150 °C according to measurements made using the thermal camera, as shown in Fig. 2e and f. Nevertheless, all of the analyses presented here were performed in the central region of the sample surface where the temperature was well defined.

Fig. 2 c and d show images of ZS and ZSW samples after 300 s of OAT testing. Extensive damage can be seen for the ZS sample with the oxide film formed cracking and detaching readily from the sample surface and damage being clearly visible on the layer below. The primary location of the flame is also easily identified and numerous macroscopic bubbles were observed on the ZS surface after ablation, implying large quantities of gas were generated during the test. In contrast, the yellowish coloured oxidation layer for the ZSW was much more adherent. It is worth noting that the