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Original Article

Influence of SiC content on the oxidation of carbon fibre reinforced ZrB_2/SiC composites at 1500 and 1650 °C in air

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ABSTRACT

The microstructure and the oxidation resistance in air of continuous carbon fibre reinforced ZrB_2–SiC ceramic composites were investigated. SiC content was varied between 5–20 vol.%, while maintaining fibre content at ~40 vol.%. Short term oxidation tests in air were carried out at 1500 and 1650 °C in a bottom-up loading furnace. The thickness, composition and microstructure of the resulting oxide scale were analysed by SEM-EDS and X-Ray diffraction. The results show that contents above 15 vol.% SiC ensure the formation of a homogeneous protective borosilicate glass that covers the entire sample and minimizes fibre burnout. The scale thickness is ~90 µm for the sample containing 5 vol.% SiC and decreases with increasing SiC content.

1. Introduction

The borides of early transition metals are covalent compounds characterized by melting points exceeding 3000 °C and are part of a class of materials called Ultra High Temperature Ceramics (UHTCs). They display high thermal and electrical conductivity and good ablation resistance [1–3] Among UHTCs, ZrB_2 has been extensively studied as a potential candidate for the fabrication of reusable Thermal Protection Systems (TPS) for aerospace applications or for use in hypersonic aircrafts [4,5] owing to its high thermal conductivity and relatively low density [1,6,7]. The main drawbacks of these materials are their low fracture toughness and poor thermal shock resistance which constitute major problems to their implementation [8]. Moreover, the oxidation resistance of monolithic ZrB_2 is low at temperatures above 1200 °C due to the formation of volatile oxides (B_2O_3) and of a porous ZrO_2 scale which does not provide protection against further oxidation [9]. The addition of silicides, such as SiC or $MoSi_2$, has been found to aid the sintering of ZrB_2 and to increase its oxidation resistance due to the formation of a viscous borosilicate glass with low vapour pressure [10–13]

C/C and C/SiC composites currently used in aerospace applications are characterized by good thermo-mechanical properties, low thermal expansion, low density and good thermal shock resistance. However, in C/C composites the carbon fibres undergo oxidation already at 500 °C, while in C/SiC or SiC/SiC composites the protective layer of liquid SiO_2, originating from the oxidation of SiC matrix at 1100 °C, becomes chemically active above 1650 °C, leading to high removal rates [14–16].

Several approaches have been materials and overcome their respective weaknesses. One method involves the reinforcing of C/C composites with UHTC particles by dispersing the latter in the phenolic resin and then infiltrating the carbon fabrics which in turn leads to increased ablation and oxidation resistance [4,14,15]

Another approach involves the coating of C/C composites with a layer of UHTC phase in order to retain the mechanical properties provided by the carbon substrate and exploit the ablation and oxidation resistance provided by the coating. Common issues are coating spallation deriving from the CTE mismatch between the two materials. In this regard, Corral et al. have been able to achieve a good interface between the carbon substrate and the UHTC coating and demonstrated the increased oxidation resistance at $T > 1600$ °C [16–19].

However, all the aforementioned approaches introduce only a little percentage of the UHTC phase in the final material. Some works have been done on UHTCs reinforced with carbon spheres or short fibres [20–23], but there are very few works concerning the performance of continuous fibre reinforced composites with a UHTC-rich matrix under oxidizing atmospheres. Sciti and Zoli have successfully obtained carbon fibre reinforced UHTCs via slurry infiltration and hot pressing [24,25]. The main problem in the manufacturing of these composites is usually associated to the difficult infiltration of the fibre preforms [24] and the sintering process [25] that can severely damage the fibres. Preliminary studies on these materials have shown their promising mechanical properties and oxidation resistance at 1500 °C [26,24]. Recent studies on the kinetics of oxidation of a carbon fibre reinforced ZrB_2 composite doped with 10 vol.% SiC have shown that the critical temperature for these composites is below 1000 °C, where the formation of a protective borosilicate scale is slow and not effective and the fibres get excessively

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damaged. However, at temperatures above 1200 °C a borosilicate glass forms at an appreciable rate and quickly protects the underlying fibres, preventing further oxidation of the material [13].

Previous studies on the effect of different oxygen partial pressures on the oxidation resistance of ZrB_2 ceramics doped with 20% and 30% SiC have shown that higher SiC contents are beneficial in oxygen-rich environments but the effect is reversed in oxygen-poor atmospheres due to the active oxidation of SiC to $SiO_{(g)}$ [27]. The latter issue has raised many concerns regarding the use of SiC in ceramic composites.

However, the majority of these works has been carried out on bulk ceramics with high SiC contents (> 20 vol.%) [28–31]. There is still a limited amount of literature on the oxidation resistance of low sic-bearing UHTC composites reinforced with fibres and how the fibre orientation influences oxidation depending on the final application. Moreover for fibre reinforced ceramics the amount of readily available SiC is actually halved, since ~50% of the composite is constituted by the fibre reinforcement.

In the present work carbon fibre reinforced ZrB_2-SiC composites were fabricated by slurry infiltration and hot pressing. SiC was added in amounts ranging from 5 to 20 vol.% of the ceramic matrix and the oxidation resistance was evaluated at 1500 and 1650 °C in air. The samples were exposed directly to the target temperature for short times in order to bypass the critical temperature of 1000 °C and trigger the oxidation of SiC to SiO_2 [13].

2. Experimental

2.1. Materials

Commercially available powders were used for the fabrication of ceramic composite materials: ZrB_2 (H.C. Starck, grade B, Germany, specific surface area 1.0 m^2/g, particle size range 0.5–6 μm, impurities (wt.%): 0.25 C, 2 O, 0.25 N, 0.1 Fe, 0.2 Hf), α-SiC (H.C. Starck, Grade UF-25, Germany, specific surface area 23–26 m^2/g, D50 0.45 μm Italian retailer: Metalchimica). Unidirectional high modulus carbon fibre fabrics (Granoch, Yarn XN80-6 K fibres; tensile modulus of 780 GPa and tensile strength 3.4 GPa, 10 μm fibre diameter. Supplier: G. Angeloni) were used as carbon preforms.

2.2. Process

Powder mixtures containing ZrB_2 and SiC ranging from 5 to 20 vol.% were prepared by wet ball-milling of the commercial powders and then dried with a rotary evaporator. The composites were prepared through slurry infiltration of unidirectional carbon fibre preforms and hand lay-up in a 0–90° configuration. Hot pressing was carried out at 1900 °C, under a uniaxial pressure of 40 MPa and an holding time of 10 min, on the basis of previous studies [25]. Four specimens containing SiC in amounts ranging between 5 and 20 vol.% were fabricated by adjusting the powder suspension rheology accordingly. Due to the intrinsic variance of the manual process, it was not possible to obtain the same exact fibre contents for all samples. Since the values remain within the 5% scattering, they were considered comparable for this study.

2.3. Microstructure analysis

The microstructure and elemental composition were analysed on polished and fractured surfaces by field emission scanning electron microscopy (FE-SEM, Carl Zeiss Sigma NTS Gmbh Öberkochen, Germany) and energy dispersive x-ray spectroscopy (EDS, INCA Energy 300, Oxford instruments, UK). Specimens for microscopy were prepared by cutting cross sections, mounting them in epoxy resin and polishing them down to a 0.25 μm finish with diamond abrasives, using semi-automatic polishing machine (Tegramin-25, Struers, Italy). The polished samples were then washed with ethanol and acetone in an ultrasonic bath, dried under IR light and cleaned with a plasma cleaner (Colibrì Plasma RF 50 KHz, Gambetti, Italy) at 40 W for 5 min. For the oxidized samples, a thin carbon coating was applied with a turbo-pumped sputter coater (Q150T, Quorum Technologies Ltd, UK) on the surface of the specimens to avoid electron scattering on the insulating oxides during SEM analysis.

The fibre volumetric amount was determined by taking into account the fibre areal weight (g/m^2) given by the supplier, number of layers and sample area. The matrix amount was then determined as the difference between the total pellet weight and the fibre weight. The theoretical density of the materials based on the initial composition was calculated using the rule of mixture. The mean grain size of ZrB_2 was evaluated via image analysis with the software Image-Pro Analyser 7.0, following the standard ISO 13383-1, method A2. X-Ray diffraction analysis was carried out on the samples oxidized at 1500 and 1650 °C using a Bruker D8 Advance apparatus (Bruker, Karlsruhe, Germany).

2.4. Oxidation tests

Regular bars with dimensions 2.5 × 2 × 12 mm (Width × Thickness × Length) were machined from the sintered pellet. The samples were cleaned with acetone in an ultrasonic bath and dried at 100 °C. The oxidation tests were carried out in a bottom-up loading furnace (FC18-0311281, Nannetti Antonio Sauro S.R.L., Italy) at 1500 and 1650 °C in air for 1 min. The furnace was heated to the target temperature with a rate of 5 °C/min. Then the specimens were introduced in the furnace using a porous alumina sample holder. After reaching thermal equilibrium (30 s), the sample was kept in the furnace for 1 min. At the end of the oxidation test, the specimens were quickly taken out and let to cool down naturally in air. For the test at 1650 °C, an additional minute was needed to reach thermal equilibrium.

3. Results and discussion

3.1. Microstructure of the sintered material

In Table 1 the physical properties of samples ZS5-20 are reported. UHTC composites are usually difficult to sinter due to the low diffusivity of ZrB_2 and the presence of large amounts of fibres that constrain the matrix shrinkage. A porosity of ~5 vol.% was obtained only for the sample with a SiC content of 20 vol.%, owing to SiC capability of aiding the sintering of ZrB_2 via liquid phase sintering [32,33]. There is also a slight decrease of the ZrB_2 grain size associated with the increase of SiC content, which is consistent with the results obtained by Fahrenholtz et al. [34].

In Fig. 1 the low magnification micrograph of sample ZS10 is shown as an example. The black dots and lines represent the carbon fibres stacked in a 0/90° configuration, while the light phase is the UHTC matrix.

Samples manufactured with this process may be characterized by non-infiltrated areas and cracks in the matrix-rich regions which originate from the constrained shrinkage of the ceramic matrix during sintering and the mismatch between the thermal expansion coefficients of the matrix and fibres ($6.5 \cdot 10^{-6}\,K^{-1}$, $2 \cdot 10^{-6}\,K^{-1}$, respectively [9]).

In our case it was possible to obtain the homogenous infiltration of the fibres in all samples. In Fig. 2 the high magnification micrographs of

Table 1
Physical properties of samples ZS5, ZS10, ZS15, ZS20.

	ZS 5	ZS 10	ZS 15	ZS 20
Density (g/cm3)	3.65	3.86	3.95	4.00
Porosity (vol. %)	12.9	9.8	7.5	5.4
Fibre (vol. %)	40	38	37	37
ZrB_2 grain size (μm)	~3.4	~2.8	~2.5	~2.0