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Original Article

Oxidation mechanisms under water vapour conditions of ZrB_2-SiC and HfB_2-SiC based materials up to 2400 °C

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ABSTRACT

This study aims at observing and understanding the oxidation mechanisms of ZrB_2-20 vol%SiC (ZS), HfB_2-20 vol%SiC (HS) and HfB_2-20 vol%SiC- 3 vol%Y_2O_3 (HSY) materials up to 2400 °C under water vapour conditions. After SPS sintering, fully densified samples were oxidized at several temperatures with 30 vol% H_2O/70 vol% Ar during 20 s. Weight variations as well as post-test microstructural and XRD analyses allowed understanding the influence of the composition on the oxidation behavior and the evolution of each oxide sublayer. Below 1550 °C, oxidation is limited, and thin oxide layers are observed. At 1900 and 2200 °C, ZS and HS show mechanical damage (cracks, spallation), while HSY keeps its structural integrity and interlayer adherence. The addition of Y_2O_3 reduces the damages due to thermal stresses in the material due to the stabilization of the cubic phase of HfO_2, and the formation of a $Y_2Si_2O_7$ interphase that mitigates thermal expansion mismatch between the SiC-depleted layer and the HfO_2 layer.

1. Introduction

Ultra-High Temperature Ceramics (UHTCs) are good candidates for several extreme applications: thermal protection materials on hypersonic aerospace vehicle or re-usable atmospheric re-entry vehicles, specific components for propulsion, furnace elements, refractory crucibles … This family of ceramic compounds is made of borides, carbides and nitrides such as ZrB_2, HfB_2, ZrC, HfC, TaC or HfN which are characterized by high melting point, high hardness, chemical inertness and relatively good oxidation resistance in severe environments.

Since the 2000 s studies to develop, in particular, hypersonic flight vehicles have led to a resurgence of interest for these materials. Indeed, hypersonic vehicles with sharp aerosurfaces (engine cowl inlets, wing leading edges and nosecaps) have projected needs for 2000–2400 °C materials which must operate in air and be re-usable. These conditions exceed the operating conditions for current structural materials for use in high-temperature oxidizing environments such as SiC or Si_3N_4-based materials, oxide ceramics and C/C composites with thermal protection, which exhibit good oxidation resistance only up to ~1600 °C. Therefore, the development of structural materials for use in oxidizing and rapid heating environments at higher temperature is of great engineering importance. Moreover, UHTC materials have also high thermal conductivities, which gives them good thermal shock resistance and makes them ideal to many high temperature thermal applications. For a leading edge for example, a high thermal conductivity reduces thermal stress within the material, by lowering the magnitude of the thermal gradient inside the part. Furthermore, it allows energy to be conducted away from the tip of the piece and re-radiated out of the surfaces of the component with lower heat fluxes. Diboride-based UHTCs also exhibit high electrical conductivity which is appreciable for manufacturing complex shape components for example (by using Electrical Discharge Machining).

Many studies have proved the potential of diboride materials with 20 vol.% SiC as additives at very high temperature [1–7]. Then several authors have studied other additives to assess their influence on the oxidation resistance of the UHTC. For example, addition of $TaSi_2$ in ZrB_2-SiC compositions led to an improvement of the resistance to oxidation up to 1600 °C, but was detrimental at higher temperatures [8,9]. Addition of Y_2O_3 in ZrB_2-SiC compositions was found to be detrimental above 1500 °C [10]. At temperatures higher than 2000 °C, authors have noted some mechanical degradations like spallation [11], non-adherence [12], or softening [13] of the oxide layer, even though sintering of the surface oxide layer might provide further protection towards oxidation at very high temperatures [14].

This paper is dedicated to the study of the oxidation mechanisms of HfB_2-SiC and ZrB_2-SiC based materials up to 2400 °C under water vapour conditions. After oxidation test using a home-made facility (BLOX4 [9]), post-test analyses (SEM, XRD) allow us to assess the influence of the composition, the temperature and the duration of the oxidation test on the oxidation behavior.

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Table 1
Sintering conditions, open porosity and oxidation conditions of the studied UHTC materials.

Composition	Reference	Sintering conditions	Open porosity%	Densification rate ρ/ρ_{th} %	Oxidation conditions
ZrB_2 + 20 vol% SiC	ZS-1200	2100 °C, 5 min	0.04%	> 99	1200 °C-20s
ZrB_2 + 20 vol% SiC	ZS-1550	2100 °C, 5 min	0.27%	> 99	1550 °C-20s
ZrB_2 + 20 vol% SiC	ZS-1900	2100 °C, 5 min	0.09%	> 99	1900 °C-20s
ZrB_2 + 20 vol% SiC	ZS-2200	2100 °C, 5 min	0.27%	> 99	2200 °C-20s
HfB_2 + 20 vol% SiC	HS-1200	2000 °C, 5 min	0.13%	> 99	1200 °C-20s
HfB_2 + 20 vol% SiC	HS-1550	2000 °C, 5 min	0.57%	97.2	1550 °C-20s
HfB_2 + 20 vol% SiC	HS-1900	2000 °C, 5 min	0.15%	> 99	1900 °C-20s
HfB_2 + 20 vol% SiC	HS-2200	2000 °C, 5 min	0.57%	97.2	2200 °C-20s
HfB_2 + 20 vol% SiC	HS-2400	2000 °C, 5 min	10.81%	89	2400 °C-20s
HfB_2 + 20 vol% SiC + 3vol% Y_2O_3	HSY-1200	1880 °C, 5 min	0.18%	98.6	1200 °C-20s
HfB_2 + 20 vol% SiC + 3vol% Y_2O_3	HSY-1550	1880 °C, 5 min	0.13%	98.4	1550 °C-20s
HfB_2 + 20 vol% SiC + 3vol% Y_2O_3	HSY-1900	1880 °C, 5 min	0.03%	98.9	1900 °C-20s
HfB_2 + 20 vol% SiC + 3vol% Y_2O_3	HSY-2200	1880 °C, 5 min	0.13%	98.3	2200 °C-20s

2. Materials and characterizations

2.1. Materials

The following materials were selected for the oxidation tests:

- ZrB_2 + 20 vol% SiC, labelled ZS.
- HfB_2 + 20 vol% SiC, labelled HS.
- HfB_2 + 20 vol% SiC + 3vol% Y_2O_3, labelled HSY.

Powders of ZrB_2 (H.C. Starck, grade A, d_{50} = 2.8 µm), HfB_2 (H.C. Starck, grade A, d_{50} = 7.6 µm), SiC (H.C. Starck, BF12, d_{50} = 0.6 µm) and Y_2O_3 (Ampere Industrie) were weighed to reach the target compositions. The powder mixtures were attrition-milled for 5 h in cyclohexane using zirconia or WC media, then dried in a rotary evaporator and sieved down to 50 µm mesh size. Sieved powders were sintered by Spark Plasma Sintering (SPS) (FCT System Gmbh, HD 125, Mateis, Lyon, France) between 1880 °C and 2100 °C (Table 1) with 7 MPa under Ar atmosphere. 2-mm-thick pellets are sintered using a 20 mm in diameter die coated with papyex. Prior to characterization tests, the graphite coating was removed.

2.2. Characterizations

The bulk density and open porosity of materials were measured by the Archimedes method. Then, the densification level was calculated as the ratio of the apparent density on the theoretical density of the powder mixture. Values are reported in Table 1.

Oxidation tests were carried out in the BLOX (Oxidation Laser Bench) facility at ONERA (Fig. 1). BLOX is a custom-made device used for oxidation tests at very high temperatures (up to 2500 °C) in controlled atmospheres (H_2O, Ar, N_2, H_2, air…) at pressures ranging from few millibars to 4 bar [9]. Heating of samples is ensured with a high-power CO_2 laser (2 kW), and surface temperature of the sample is measured with two bicolor pyrometers. Surface temperature can be monitored throughout the experiment with a dedicated software that acts on the laser power to reach the target temperature. A video camera allows the observation of the sample during testing.

All the tests were carried out at a total pressure of 1 bar, under an H_2O/Ar atmosphere (30/70 vol%, in Standard Liter). First, vacuum is made inside the chamber. Then, argon is introduced and water vapour is injected in the chamber through a peristaltic pump up to 1 bar, and the chamber itself is thermostated at 150 °C to keep water gaseous. Thus, the only oxidizing species in the atmosphere is water vapour. Pyrometers can measure surface temperatures from 1000 to 2500 °C. Once 1000 °C is reached (laser power ramp), a temperature ramp of 5 °C/s is imposed, allowing the sample to reach the target temperature (1200, 1550, 1900, 2200 or 2400 °C). After a dwell time of 20 s, the temperature is decreased at the same rate. Examples of temperature profiles and laser power profiles vs time are presented in Fig. 1. During

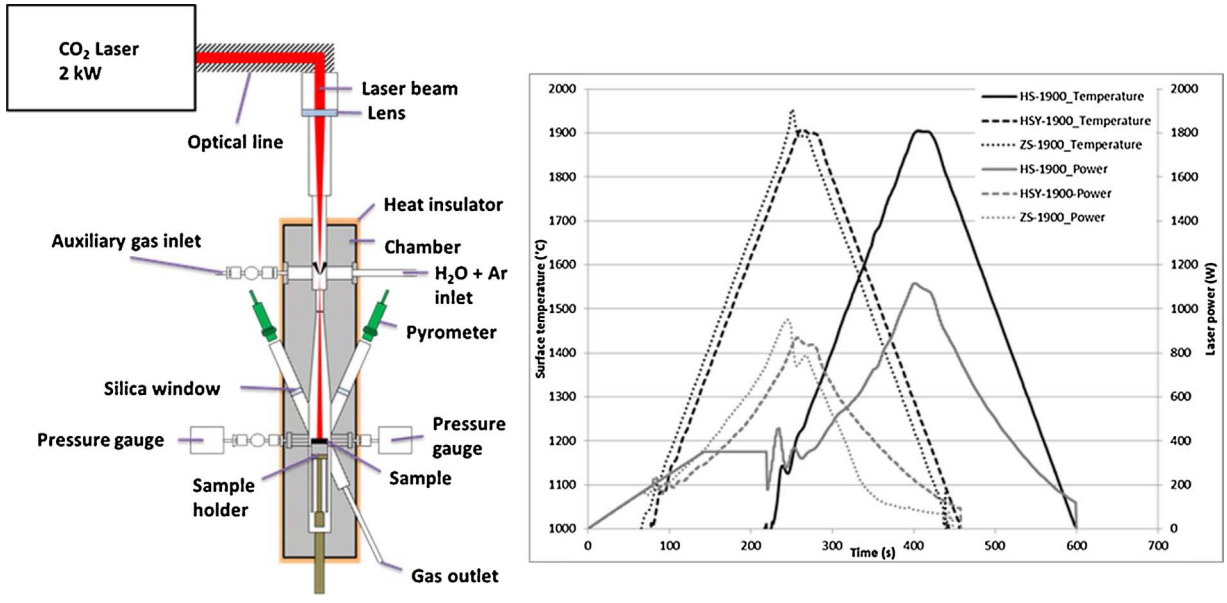

Fig. 1. (left) Schematic view of the BLOX apparatus, (right) Surface temperature and laser power vs time during oxidation of HS-1900, HSY-1900 and ZS-1900.