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Thermo-chemical surface instabilities of SiC-ZrB_2 ceramics in high enthalpy dissociated supersonic airflows

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ABSTRACT

The response of three different SiC-ZrB_2 ceramics obtained by hot-pressing was studied at typical conditions of thermal protection systems of a re-entry spacecraft. Button-like lab-scale demonstrators were manufactured and tested in high enthalpy dissociated supersonic airflows using an arc-jet ground facility. Under severe aero-heating of up to 21 MJ/kg of specific total enthalpy and 3.5 MW/m^2 of (cold-wall) heat flux the SiC-ZrB_2 UHTC buttons endured rather well, though thermo-chemical surface instabilities started taking place for side wall surface temperatures of some buttons above 2050 K. The experimental determinations of the surface temperature, correlated to the microstructure changes occurred during testing, allowed to interpret the observed phenomena. Potentials and limits of the oxidation-resistant SiC-ZrB_2 system to withstand such extreme conditions were outlined.

1. Introduction

Improved technologies and (re-usable) materials capable of operating under extreme conditions of temperature, heat flux and chemical attack are necessary to develop new generations of hypersonic flight vehicles and rocket engines. In this perspective, ultra-high temperature ceramics (UHTCs) are actively studied, pushed by the demand of materials/devices indispensable to operate in harsh environments typical of aerospace applications: the thermal protection structure (TPS) for hypersonic serves as the example that in recent years has fostered an extensive research effort [1–3].

Of the UHTC class of materials, ultra-refractory transition metal diborides such as ZrB_2 and HfB_2 are currently investigated as potential base materials owing to their unique combination of properties including melting points above 3500 K, high temperature strength of up to 700 MPa combined to unrivalled capability to manage and conduct heat when the service temperatures exceed 2200 K [4]. Monolithic diborides alone, though fully dense and strong, are however vulnerable to oxidation attack so that their oxidation rate is rapid and unacceptable for re-usable applications in extreme environments.

The state-of-the-art UHTCs are SiC-MeB_2 composites (Me = Zr, Hf), with SiC in the form of particle, short fiber, whisker and polymer-derived ceramic in amount from 10 to 50 vol% [5]. The addition of SiC to MeB_2-based ceramics not only improves their mechanical properties but also the oxidation resistance by altering the characteristics of the glassy component of the in-situ growing mixed oxide layer [6]. Silica-prevailing fractions in the boro-silicate glassy phase increase its viscosity and therefore reduce the permeability of oxygen through the glass, very fluid for temperature ranges above 1900 K. More viscous glasses with increased liquid temperatures may have the added benefit of suppressing the volatilization of the glassy phase.

As oxidation of the SiC-containing MeB_2 ceramics is anyhow inevitable, research efforts have been focused on improving their oxidation/ablation resistance adding different compounds to promote densification of the MeO_2 scale and slow down the volatilization of the protective boro-silicate glass. In addition to improving the high temperature properties, it may also possible to increase the dissipation of heat by maximizing the surface emittance of poorly catalytic hot structure surfaces [7].

Talmy et al. [8] found that the oxidation resistance of hot-pressed ZrB_2 + 25 vol% SiC composites could be improved by addition of diborides of Cr, Ti, Ta, Nb and V. These additions result in the nucleation and growth of the respective oxides in the glass. The improved oxidation resistance comes from the fact that borate and silicate glasses containing oxides of the Group IV–VI transi-

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tion metals are immiscible and therefore lead to phase separation. Such systems contain compositions with very high viscosity and liquids temperatures. In the same way, addition of 5-20 vol% WC to ZrB_2–SiC ceramics increased the oxidation resistance of ZrB_2 ceramics by changing the morphology of the zirconia scale formed during oxidation [9].

Now, most experiments to verify the suitability of materials for TPS application in harsh conditions were often conducted in furnace environments in which temperature, pressure, gas composition and its flow speed are more easily controllable because thermo-chemical equilibrium prevails. However, the thermal protections intended for the hot structures (leading edge, nosecone, control surfaces as flaps or ailerons) of a hypersonic flight vehicle encounter partly and even fully dissociated airflows in chemical non-equilibrium with the hot structure's surfaces [10]. This leads to different (radiative equilibrium) surface temperature for materials of different intrinsic compositions *under the same testing conditions*. It follows that a proper qualification of the developed materials should be conducted in representative simulated flight conditions. According to Parthasarathy et al. [10], key parameters most suited to represent the hypersonic flight conditions with respect to the materials survivability are the heat flux, the total or stagnation pressure, the dynamic pressure, the flow velocity near the solid body surface behind the bow-shock and its composition. The degree of dissociation of the gaseous elements and their catalytic recombination efficiency at the body's surface are also of major importance. In fact, in case of plasma flows energized via an arc-heater, the dissociated gases, which actually carry the enthalpy, may recombine (or not) at the material's surface. It implies that the (hot-wall) heat flux may vary significantly depending on the catalytic recombination efficiency of the material's surface.

Aero-thermodynamic wind tunnels were often used to reproduce heat fluxes and pressures corresponding to the flight conditions in order to test the ablation resistance of TPSs, as well as to investigate others aero-thermochemical issues. They are mainly fed by an electric arc-heater and work in a continuous fashion. The gas is energized by the arc-heater and then suddenly expands through a converging-diverging nozzle. Its composition abruptly changes and only ad-hoc diagnostics allow to determine it accurately [10–12]. Due to the fact that is very difficult to control all the dimensionless thermo-fluid dynamic numbers such as Mach, Reynolds, Knudsen numbers, the numerical modelling becomes a viable and largely recommended tool, not only to predict the thermo-chemical evolution of the gas but also to characterize the flow-field surrounding the test article inside the testing chamber. In addition, because the flow conditions generated in high-enthalpy plasma wind tunnels are very complex, the verification of the free-stream flow conditions must be a combined effort of experimental diagnostics and numerical tools through an interactive process, providing a step-by-step improved understanding of the facility performances [11].

Such vital implications set the basis of the present paper. In this regard, different authors recently reported the occurrence of rapid and spontaneous rises of the sample's surface temperature of SiC-MeB_2 bulk ceramics *under steady free-stream conditions*. It is clear that understanding and predicting any thermo-chemical instabilities along the materials surface is of fundamental importance because their occurrence in some hot parts of the flying vehicle might lead to the catastrophic failure of the entire mission together with the loss of its payloads. Marschall and co-workers, studying the performances of ZrB_2-30SiC materials in *sub-sonic* high enthalpy dissociated airflows, concluded that this sort of (spontaneous) temperature jump is associated to a transition in the surface chemistry involving the Si-containing compounds [12]. Ping et al. confirmed the occurrence of surface temperature instabilities (under steady free-stream conditions) of hot-pressed x·SiC-ZrB_2 ceramics, x = 10, 15 vol%, investigating them using high enthalpy and dissociated *sub-sonic* airflows of a high frequency plasma wind tunnel [13]. The occurrence of similar thermo-chemical surface instabilities was also observed and documented by Simonenko et al. during tests in high-enthalpy *sub-sonic* airflows of y · SiC—HfB_2 ceramics, y = 10, 15, 20 vol% [14].

Similar phenomena of spontaneous surface temperature rises were also observed in SiC-containing ceramic-matrix composites (CMCs). Hald H. studied C/C-SiC materials for re-usable space transport applications and attributed the occurrence of sudden temperature jumps to the passive-to-active transition of SiC [15]. In contrast, other authors converged to associate such spontaneous phenomena to an augmented exothermic heat release in the surface chemistry of the SiC coating of the CMCs [16–20]. In particular, Luo et al. tested C_F/SiC—HfC composites in a plasma wind tunnel [18]: under high enthalpy dissociated *sub-sonic* airflows, the abrupt temperature jump was attributed to a change in the catalytic surface efficiency from silica to hafnia.

The present work aimed at designing the initial composition of different ZrB_2-15vol% SiC mixtures in view to promote not only an overall ability to densify below 2173 K but also to obtain more stable (boro-silicate) glassy layer capable of maintaining steady surface temperatures under the effects of a high enthalpy dissociated supersonic airflow. Compared to the previous works [12–20], the gas velocity imposed during the experiments object of the present work is *supersonic*. Transient thermo-chemical surface instabilities of three different SiC-ZrB_2 ceramics were addressed thanks to in-situ infrared diagnostic techniques. Focused post-test analyses on the tested materials helped to correlate the microstructure changes of the exposed surfaces to the observed phenomena.

2. Materials, methods and models

2.1. Manufacturing and characterization of SiC-ZrB_2 ceramics

Three different SiC-ZrB_2 compositions (vol%), hereafter labelled as follows

$$\mathrm{ZSZ}: ZrB_2 + 15SiC + 3ZrH_2$$

$$\mathrm{ZSB}: ZrB_2 + 15SiC + 5B_4C$$

$$\mathrm{ZSW}: ZrB_2 + 15SiC + 2B_4C + 0.7WC$$

were processed batching commercially available non-oxide powders: ZrB_2 grade B, SiC grade BF12 and B_4C grade HS from H.C. Starck (Germany), and ZrH_2 grade C from Chemmetal (Germany). The powder mixtures were weighed and then wet-homogenized for 24 h in polyethylene bottles, using silicon carbide media and absolute ethyl alcohol. Only for the composition ZSW, the as-received ZrB_2 grade B powder was first comminuted using the planetary mill (mod. Pulverisette 6 FRITSCH, Germany). In this respect, the jar (made of WC-6%Co) was partly filled of as-received ZrB_2 powder and WC balls 0.6 mm in diameter.

A cumulative time of effective grinding up to 30 min was set, pausing the comminution each 5 min. The ZrB_2 powder, ground in this manner, was thus batched into the only ZSW composition. The overall enrichment of 0.7 vol% WC in the ZrB_2 powder was estimated weighing jar and balls before and after planetary grinding. The three ceramic slurries mixed so far were dried through a rotary evaporator and sieved (mesh opening 250 μm). The dried powder mixtures were hot-pressed in vacuum (10–100 Pa) mastering specific ramps for temperature and mechanical pressure (Table 1). The final sintered pieces were billets 45 mm in diameter and about 15 mm thick.

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