ULTRA-HIGH TEMPERATURE DIBORIDE CERAMICS FOR RLV'S HOT STRUCTURES

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In the frame of the Unmanned Space Vehicle (USV) technological program [1], the Sharp Hot Structures (SHS) Project is ongoing with the aim to evaluate the applicability of non-conventional ultra-high temperature ceramic materials to the manufacturing of slender-shaped hot structures, destined to the next generation of re-entry spaceplanes [2].

The main objective of this project is to provide on-ground qualified advanced technology products identified in critical parts of re-entry vehicles such as nose cap and wing leading edges to be then tested and validated on ground (using CIRA Scirocco Plasma Wind Tunnel Facility) and in flight conditions (using the USV Flying Test Bed X in a sub-orbital re-entry mission).

This paper describes the aforementioned project, and in particular focus on the research work performed on modified diboride compounds, conducted by CIRA in cooperation with the Italian National Research Council Institute for Ceramics (CNR-ISTEC). Zirconium and Hafnium diborides/Silicon carbide composites were extensively studied: those compounds are actually addressed as the sole materials that can be conveniently employed at temperatures above 2200K [3].

Material Choice Rationale

Future concepts for space launchers foresee sharp aerodynamic profiles as conventional aircrafts [4]. This kind of architecture offers several advantages with respect to current blunt shapes: maneuverability improvement, decrease of electromagnetic interferences and communication black-out and drag reduction during the ascent phase. As a drawback, aerodynamic heat flux increases dramatically (reaching 650-800 KW/m2). State of art hot structures materials cannot withstand the thermal requirements of future slender-shaped RLVs.

Aerospace research is moving towards ceramic systems based on hafnium, zirconium and titanium borides, in account of their high configuration stability (ablation resistance) in the presence of high velocity dissociated air, high thermal shock and thermal fatigue resistance [5].

Those material are characterized by very high melting point and, if blended with a proper reinforcing phase, they exhibit excellent oxidation resistance, thanks to the growth of a protective oxide layer on the surface of the component in oxidizing atmosphere, that hinders further oxidation of the bulk.

In the SHS project, conventional C/SiC materials produced by polymer infiltration and pyrolisis have been coupled to novel diboride materials in order to create a multi-material structure able to withstand the severe condition associated with slender-shaped hot structures and non-conventional reentry mission profiles. The product of the research is an innovative nose cap to be tested on the sub-orbital re-entry mission of the USV-X Flying Testbed currently scheduled in 2010.

This paper will report on the trade-off and on the process optimisation phases for the massive diboride employed in the manufacturing of the nose cap hot structure conical tip. The conical tip represents actually the part of the nose cap that is subjected to the most severe condition during the re-entry mission profile.

In the last section of this paper, a description of the nose cap demonstrator under development will also be provided, and the first arc-jet tunnel test performed at CIRA Scirocco [6] on an intermediate nose cap concept will be presented.

Metal Diborides selection and composition optimization

The final purpose of this research work is the identification of an optimum diboride material for the realization of a massive nose tip prototype, and the fabrication of the prototype itself.

The selected material had to be characterized by a high melting point (> 2000 °C), good mechanical properties, and a high resistance to oxidation. Further, since our final purpose is the fabrication of a nose tip prototype, the material had to be machinable with current ceramic shaping techniques, i.e. diamond machining (DM) or electrical discharge machining (EDM).

With this in mind our research work was split into two trade-off analyses whose final result is the determination of a composition, in terms of starting powder weight percentage, which gives the best material to be used for the fabrication of a nose tip prototype.

In the preliminary trade-off five different ceramic composites based on Zr abd Hf diborides were chosen and their microstructure and oxidation resistance were characterized. At the end, the best two performing materials were selected. These materials, which were representative of two different classes of ceramic composites, i.e. ZrB_2-SiC, and ZrB_2-$MoSi_2$, were used as inputs for a second trade-off analysis.

The purpose of the second trade-off was to optimize the material composition/process in order to achieve better material performances. At this purpose, five different compositions have been considered and the resulting materials have been characterized. The best performing material among this five has been selected for the realization of a nose tip prototype.

Preliminary Diboride trade-off

The results of this first trade-off analysis showed that samples with a high percentage of carbide compounds as reinforcing phase suffer from vast microstructural deterioration and low oxidation resistance.

Conversely, the presence of Silicon-containing compounds provided concrete benefits and significantly improved the resistance to oxidation. The formation of an external silica-based glassy layer was really effective in limiting the inward diffusion of oxygen into the inner bulk, thus enhancing the resistance to oxidation. The efficacy of such glassy coating in real or simulated re-entry conditions should be validated as well. Furthermore these two types of materials have a quite good conductivity and can be shaped by electrical discharge machining technique. Hence, the properties of these materials match very closely the requirements specified for the selection.

In accordance to the experimental results, from the point of view of the oxidation resistance a diboride matrix composite including only silicon based compounds as a second phase was considered as one of the most promising composition. Both HfB_2 and ZrB_2 based composites behaves well but the latter have been preferred due to their lower specific weight.

Second trade off analysis

The second step of our study was a fine adjustment of the initial amount of reinforcing phase and of the other additives (e.g. sintering aids), in the ZrB_2 based composite materials selected from the first trade-off, with the aim to optimise its microstructure and thermo-mechanical properties.

At the end of the trade-off, a ZrB2 including only SiC as a second phase, together with a sintering aid, was selected. Fig.1 shows a SEM micrograph from a polished section of the chosen material. The bright particulars are secondary ZrO_2

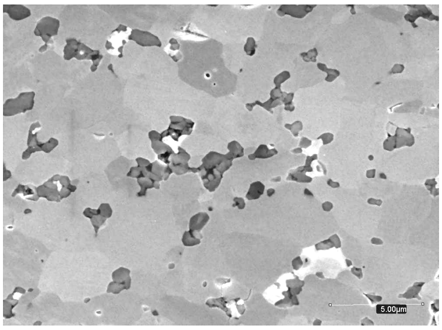

Fig. 1

SEM micrograph from a polished section of the selected ZrB2 compound

Massive Diboride Characterization

The material selected from the second trade-off for the realization of the nose tip prototype, has been completely characterized before final manufacturing of the tip. In particular room temperature and high-temperature thermo-mechanical analyses have been performed, microstructure of the as sintered material and of aged/oxidized samples have been characterized, oxidation, thermal shock and erosion resistance have been measured. Furthermore, emissivity and catalicity of the material have been studied and will be reported in a subsequent paper.

The result of our deep characterization campaign can be summarized as follows.

On the basis of the rule of mixture, the material has a relative density higher than 99%. The SEM examination of representative polished sections confirmed a residual porosity lower than 1%. The analysis of fracture surfaces showed an uniform microstructure. The fracture propagated through intragranular paths rather than intergranular. The examination of polished sections (obtained through conventional metallographic procedures) assessed the uniformity of the microstructure, in particular the good dispersion of the SiC particulate, mean size of the ZrB_2 grains of about 2 µm, and the presence of ZrO_2 as secondary phase.

A list of the main mechanical properties of the as sintered material is shown in table 1.

Property	Value
E (GPa)	480 ± 4
σ (MPa)	887 ± 125
N	0.13
CTE (10^{-6} m/°C)	7.11
Hv1.0 (GPa)	17.7 ± 0.4
K_{IC} (MPa $m^{1/2}$)	4.07 ± 0.03

Table 1.

Mechanical properties of the selected diboride material.

Thermal shock resistance was measured following the European Standard prEn 820-3. According to the indications of the prEN 820-3, the critical thermal shock for this material, i.e. the temperature at which the flexural strength of the material is one third of the non-oxidized material, was 400 °C. The thermal shock resistance was evaluated using the “water quenching” method (ENV 820-3) as a guide. A total number of 23 bars were tested.

The erosion tests were executed following the “sand blaster” technique, and using a Falex Air Jet eroder. The specimen were weighed before the test, and at regular intervals. The typical parameter, ΔE, which evaluates the resistance to erosion of a material, is defined by the ratio between the mass loss and the abrasive flow that stoke the surface. The man value of ΔE is about $62 \cdot 10^{-6}$, and is ery similar to Al_2O_3 composites toughened with SiC (whiskers) cutting tools.

As expected, the selected material showed a good oxidation resistance. In figure 2 the typical multi-layered configuration of the oxidized regions is shown. A silica layer (label-1) covers the external faces of the specimen. Underneath this layer, an oxidized region (label-2) extends for tenths of microns up to unreacted bulk (label-3). This silica layer, which is formed after exposure of the sampe at 1200 °C works very likely as a protective coating, avoiding further oxidation of the inner part of the material.

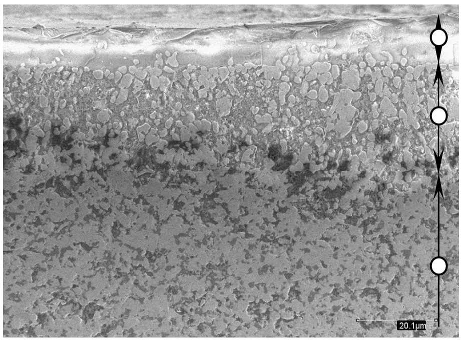

Fig. 2

Multi-layered configuration of the oxidized regions

Nose Cap structural concept and auxiliary material/process systems selected

Figure 1 depicts a schematic of the nose cap demonstrator under development, dubbed Nose cap 1. The nose is composed by: a) a bulk graphite core; b) a truncated conical C/SiC frame manufactured by polymer infiltration and Pyrolisis process c) a ZrB2-SiC coating applied on the C/SiC frame by plasma spray deposition technique; d) a ZrB2-SiC massive conical tip produced by sintering technique. Each of the identified (material)/(manufacturing process) systems was subjected to a complete characterization test campaign, in order to provide the thermo-mechanical design with the required database of properties.

Moreover, in order to test the adhesion between the C/SiC frame and the ZrB2 coating in operating conditions, an intermediate step between the laboratory scale characterization and the on ground testing of the above described nose cap 1 demonstrator was conducted, by producing a “Nose cap 0” demonstrator constituted of a graphite bluk, a C/SiC frame, and a ZrB2 coating. This prototype 0 was tested in the Scirocco plasma wind tunnel; test results are reported in the last paragraph of this paper.

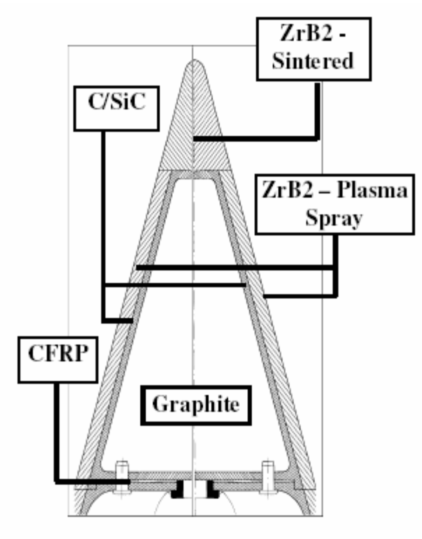

Fig. 3

Schematic of the nose cap scaled demonstrator

Massive Diboride Conical Tip Manufacturing

The material selected in the second trade-off and then entirely characterized has been used for the fabrication of the massive nose tip prototype.

The final nose tip, designed by CIRA, has been realized by hot pressing of about 5.5 Kg of raw powders, which, after the usual milling and drying stages, were transferrd in a hollow graphyte mould, and sintered using the parameters for the processing of the IST_01 material. The hot pressed material obtained in this way has a relative density higher than 98.5 %.

The billet obtained afer the sintering process was shaped by electrical discharge machining. (EDM), by Gianni Andalò S.r.l., Imola. The final ceramic prorotype is shown in figure 5.

This prorotype will tested in the Scirocco Plasma Wind Tunnel at CIRA.

Nose cap 0 arc jet testing

The SHS nose cap prototype 0, an intermediate step between the laboratory scale characterization and the final proptotype 1 validation, was designed in order to verify the coupling beween the C/SiC frame and the prayed ZrB2-SiC, and to set up a PWT test protocol in the Scirocco Tunnel [7]. This powerful plant (70 MW) produces a very uniform and large test jet (up to 2 m diameter). The process air is thermally energised into the segmented constricted Arc Heater reaching temperature values between 2000 and 10000 K. This energy is transformed in kinetic by the air passage through a convergent-divergent Conical Nozzle and an hypersonic test jet is generated with velocity ranging between 2000 to 6000 m/s and Mach number between 6 to 12 depending on the exit nozzle size.

The test requirement is the achieving on the SHS model ("SHS nose 0": stagnation radius of 6.5 mm measured on the real test article) of a stagnation pressure of about 10 mbar and a stagnation heat flux of about 900 kW/m2. These data have been transformed in the equivalent ones to be obtained on the calibration probe that is used in Scirocco to verify that the requested flow conditions are reached. This probe is a cooled copper semi-sphere with a radius of 50 mm, considered fully catalytic, able to measure the stagnation pressure and the thermal load by means of a Gardon gauge heat flux sensor. With the CFD support the flow requested conditions, specifically on the probe, have been calculated: 1) Stagnation Heat Flux of 300 kW/m2; 2) Stagnation Pressure of 10 mbar.

These flow conditions in Scirocco wind tunnel implies a plasma total enthalpy of about 5 MJ/Kg, i.e. lower than 10 MJ/kg. This value is the minimum that the Arc Heater is able to produce, otherwise the electrical discharge cannot be sustained. The test total enthalpy value of 5 MJ/kg will be obtained by injection of the process air in part into the arc heater and in part downstream in a mixing chamber between the arc-heater and the nozzle inlet [8].

In Figure 4 pictures of the SHS test model before the test mounted on the TA support CPA2 and during the test are shown.

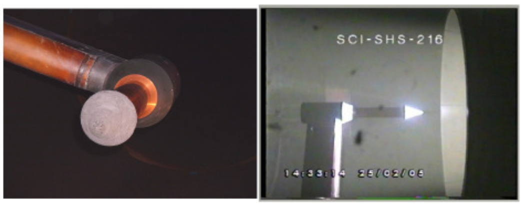

Fig. 4.
SHS Nose_0 before and during the test

The SHS Nose 0 test campaign has been successfully conducted. The SHS nose has been tested three times consecutively by increasing the plasma exposure of the model from 20 seconds to 50 seconds. The measured experimental main parameters and quantities are reported in Table 1.

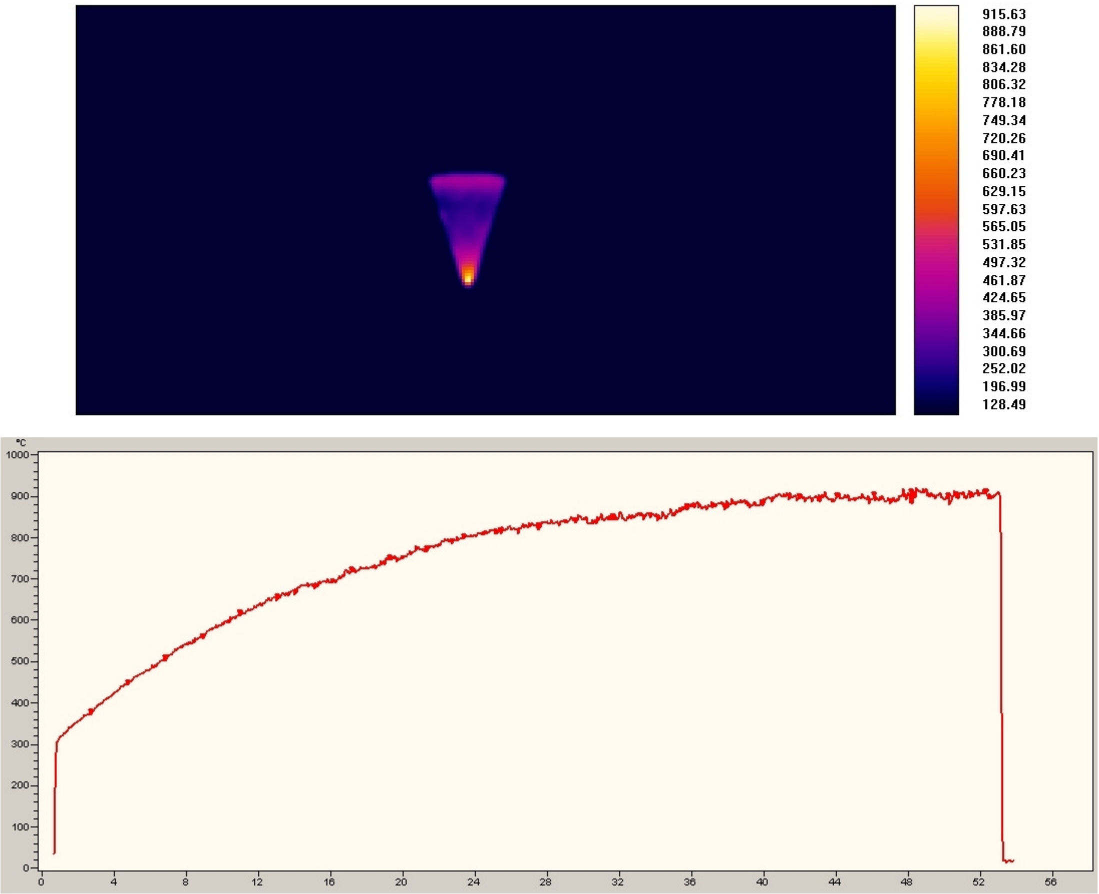

Fig. 5

Scirocco PWT Performance Map.

Parameter	Numerical Values
Arc heater current (A)	1700±100
Arc heater voltage (V)	8000±150
Total mass flow rate (kg/s)	1.22±0,02
Arc Heater total enthalpy (MJ/kg)	6,4±0,5
Arc heater total pressure (bar)	4,3±0,1
Probe stagnation pressure (mbar)	12,3±1,1
Probe stagnation heat flux (kW/m2)	360±90

Table 1

Arc-Jet Experimental Conditions

In Figure 5 the temperature map from the IR thermography is shown in the case of the longest run at the end of the plasma exposure. In the same figure it is also reported the temperature profile of the hottest point visible from the side view by means of the IR thermographic investigations. This point do not corresponds to the stagnation point but, approximately, to the conjunction point between the spherical stagnation part and the cone shape.

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