Fabrication and Characterization of SiC fiber reinforced HfB₂ Ceramics for Space Propulsion Components

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Cylindrical disks composed of HfB₂-26 vol%SiC are successfully fabricated by combining the Self-propagating High temperature Synthesis (SHS) and Spark Plasma Sintering (SPS) processes. Specifically, HfB₂ powders synthesized by SHS are mixed with SiC fibers and the resulting mixture is consolidated by SPS. The presence of SiC fibers was retained in the nearly full dense materials sintered at 1800 °C. The measured values of Vickers hardness, fracture toughness, flexural strength and elastic modulus at room temperature are 21.6±0.8 GPa, 6.2±0.5 MPa m\textsuperscript{0.5}, 429±45 MPa and 312±17 GPa, respectively. The obtained products are found to well resist to ablation, with weight losses below 0.25% when exposed to the most aggressive heat flux conditions (1250 W/cm\textsuperscript{2}). A nozzle component of the desired shape and size is finally obtained for space propulsion applications after electrical discharge machining the SPS material.

Keywords: Aerospace; UHTCs; Reinforcement; Self-propagating High-temperature Synthesis; Spark Plasma Sintering.

1. Introduction

Ultra High Temperature Ceramics (UHTCs) are monophasic or composite materials based on transition metal diborides (ZrB\textsubscript{2}, HfB\textsubscript{2}, TaB\textsubscript{2}, TiB\textsubscript{2}, NbB\textsubscript{2}, etc) and carbides (ZrC, HfC, TaC, TiC, NbC, etc.) compounds which are well recognized to exhibit a combination of attractive thermophysical and mechanical properties such as melting temperatures above 3000 °C, high hardness, good electrical and thermal conductivity, chemical inertness, etc. [1]. These and other peculiar characteristics (solar selectivity, low neutron absorption, etc.) makes UHTCs very suitable for applications where materials able to withstand to harsh environmental conditions are needed, for instance in the aerospace industry [1-5].

Unfortunately, the strong covalent character of the atomic bonding characterizing these ceramics as well as oxygen impurities usually present on their particles surface make the achievement of high densification level during their fabrication as bulk components a hard target. Furthermore, the resulting materials generally show low fracture toughness and not adequate high temperature oxidation properties, unless additional phases are introduced into the ceramic matrix.

The utilization of the Spark Plasma Sintering (SPS) technology was demonstrated convenient to overcome the first of these crucial issues [6]. Indeed, the use of SPS allows to lower the sintering temperatures and, above all, to markedly shorten the processing time, generally on the order of hours when powder consolidation is carried out with conventional pressureless sintering or HP techniques [4,7,8]. This feature represents a significant advantage when the difficult-to-sinter UHTC powders considered in this work have to be processed. This statement is testified by the several ultra refractory ceramics produced in massive form by SPS, particularly in the last decade or so [9-40]. Powders consolidation could be also facilitated by the introduction of appropriate Si-containing additives such as SiC, Si₃N₄, MoSi₂, etc. [14,15,41], which also improves the modest oxidation resistance at high temperature of monophasic UHTCs. However, the amount of these secondary phases should not exceed certain levels, otherwise the original attractive characteristics of these materials could be negatively affected.

As mentioned previously, the diffusion and practical utilization of UHTCs is also strongly inhibited by their low fracture toughness properties. For instance, \(K_c\) values for additive-free transition metal diborides usually fall in the range of 2.1-4.2 MPa m\textsuperscript{0.5} [4,21,30]. The preferable solution to improve this property in ceramics typically consists in the introduction of suitable reinforcing phases into the ceramic matrix. The purpose is to activate one or more toughening mechanisms such as crack deflection, crack pinning, crack bridging, etc., in the resulting composite system. The presence of SiC particles into the matrix determines an increase in fracture toughness, although the reported \(K_c\) are still generally less than 5.0 MPa m\textsuperscript{0.5} [4,8,10,42,43]. Several other studies have been recently reported in the literature addressed to the use of different types of reinforcement phases, such as SiC whiskers [21,44-46], SiC fibers [47,48], carbon fibers [49-51], carbon nanotubes (CNTs) [52-55], or graphene [56,57], on various UHTC systems.

The obtained results generally indicate an improvement of the fracture toughness of the ceramics when adding these phases. However, their beneficial effect could be strongly inhibited if they lose their original nature during the sintering stage. For instance, Zhang et al. [45] found that SiC whiskers were not stable in...
the ZrB₂ matrix above 1900 °C and degenerated into particles. Accordingly, in a more recent study [21], the presence of whiskers was preserved in 96% dense materials obtained by SPS at about 1700 °C, whereas their original nature was lost for sintering temperatures exceeding 1830 °C.

To avoid such drawbacks, the temperature during the consolidation step should be properly controlled and maintained as lower as possible. In this regard, the use of the SPS technology certainly contribute to reach this goal. Of course, a further important role in this context is played by the characteristics of initial powders which generate the ceramics matrix. Indeed, their densification behaviour depends not only by their nominal composition, but it is also influenced by other features such as particles size, surface area, surface defects, etc., which are, in turn, affected by their preparation method. In this regard, it was found that the consolidation of ultra refractory products such as ZrB₂ [58], TiB₂ [59], ZrB₂-ZrC-SiC [13] is made easier when using powders prepared by Self-propagating High temperature Synthesis (SHS), a well known combustion synthesis technique [60], instead of other commercially available and prepared by alternative methods. Such peculiarity was ascribed by Mishra et al. [58] to the high defect concentration in SHS powders generated by the severe heating and cooling rate conditions (on the order of 10⁵ and 10⁴K/min, respectively) encountered during the evolution of the synthesis reaction. Furthermore, when this process is exploited for the in-situ synthesis of ceramic composites, for instance ZrB₂-ZrC-SiC, the different phases display very fine sized grains and strong bonds at the interfaces [13]. Consequently, diffusion distances are reduced and sintering phenomena promoted.

Based on the previously discussed advantages of SHS and SPS techniques, their combination has been exploited for the fabrication of a wide variety of UHTC materials in bulk form [9-11,13,15-17,21,22,29-31,34-38,40]. In particular, one of this study [21] involves the preparation by SHS of the UHTC powders, their subsequent combination with reinforcing whiskers, and the consolidation of the resulting mixture by SPS.

Along these lines, the latter approach is adopted in this work for the fabrication of a nozzle for space propulsion applications composed of HfB₂ and chopped SiC fibers as matrix and reinforcing phase, respectively. Specifically, such rocket engine component should be able to resist at high temperature under the aggressive environments represented by the exhausted gases generated by the used propellants. The choice of the material composition is based on the analysis of previous results reported in the literature on analogous systems as well as by comparing their resistance at high temperature under different gas flows. The preparation of the final prototype is preceded by an intense characterization activity aimed to evaluate the most relevant thermomechanical and thermophysical properties for the selected system.

2. Experimental materials and methods

The preparation of transition metal diboride powders (MeB₂ with Me= Hf, Zr, Ta) to be subsequently combined with reinforcing SiC fibers was carried out by self-propagating high temperature synthesis, according to the following reaction stoichiometry:

$$\text{Me} + (2+x) \rightarrow \text{MeB}_2$$  \hspace{1cm} (1)

In addition, standard, not reinforced, binary composites were synthesized by SPS as follows:

$$2\text{Me} + \text{B}_4\text{C} + \text{Si} \rightarrow 2\text{MeB}_2 + \text{SiC}$$  \hspace{1cm} (2)

Reactants, whose characteristics are reported in Table 1, were first placed inside a plastic bottle and then mixed in a SPEX 8000 (SPEX CertiPrep, USA) milling device using zirconia balls. The slight excess of boron in reaction (1), i.e. x=0.1-0.2, with respect to that strictly required for the synthesis of the diboride compound, is because a certain amount of this reactant is lost during reaction occurrence. Indeed, as explained elsewhere [21], the presence of oxide impurities or adsorbed moisture in the original reactants produces the formation of volatile B₂O₃ and, in turn, a lack of boron which needs to be compensated.

To obtain the various ceramic materials, cylindrical pellets of 10 mm diameter and 20-30 mm height, prepared by uniaxially pressing the reactants mixture, were then reacted by SHS. Details on the related experimental set-up can be found elsewhere [61]. Before the consolidation stage, the combustion synthesized products were reduced in powder form after a short (20-30 min) ball milling treatment. The composite mixture for fabricating the reinforced ceramic was prepared by blending the diboride powder with SiC fibers in molar ratio 2:1, respectively, for the sake of comparison with product resulting from reaction (2). It should be noted that the original fibers (Figure 1) were suitably house chopped before combining them with UHTC powders. An ultrasonic treatment (SONICA S3 ETH, Soltex, Italy) of the fibers in ethanol was carried out before their homogenization for 24 h with the UHTC diboride powder using an Orbital Shaker Device (VDRL 711/CT, ASAL Srl, Italy). To prevent segregation phenomena for sedimentation, the obtained slurry was finally dried in a rotary evaporator (Rotavapor R-210S, Buchi, Italy).

Depending on the product characterization to be carried out as well as the fabrication of the final prototype, the following four types of dense specimens have been produced by SPS in this work:

- a) cylindrical disks of about 15 mm diameter and 3 mm high, for standard characterization (density measurements, SEM), thermogravimetric analysis (TGA), hardness, thermal diffusivity, thermal conductivity, specific heat, and coefficient of thermal expansion (CTE);
- b) cylinders of approximately 15 mm diameter and 22 mm high, for ablation tests;
- c) cylindrical pellets of 10 mm diameter and 20-30 mm height, prepared by uniaxially pressing the reactants mixture, were then reacted by SHS. Details on the related experimental set-up can be found elsewhere [61]. Before the consolidation stage, the combustion synthesized products were reduced in powder form after a short (20-30 min) ball milling treatment. The composite mixture for fabricating the reinforced ceramic was prepared by blending the diboride powder with SiC fibers in molar ratio 2:1, respectively, for the sake of comparison with product resulting from reaction (2). It should be noted that the original fibers (Figure 1) were suitably house chopped before combining them with UHTC powders. An ultrasonic treatment (SONICA S3 ETH, Soltex, Italy) of the fibers in ethanol was carried out before their homogenization for 24 h with the UHTC diboride powder using an Orbital Shaker Device (VDRL 711/CT, ASAL Srl, Italy). To prevent segregation phenomena for sedimentation, the obtained slurry was finally dried in a rotary evaporator (Rotavapor R-210S, Buchi, Italy). Depending on the product characterization to be carried out as well as the fabrication of the final prototype, the following four types of dense specimens have been produced by SPS in this work:

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Vendor</th>
<th>Size</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>Alfa-Aesar</td>
<td>&lt; 44 µm</td>
<td>&gt; 99.6</td>
</tr>
<tr>
<td>Zr</td>
<td>Alfa-Aesar</td>
<td>&lt; 44 µm</td>
<td>&gt; 98.5</td>
</tr>
<tr>
<td>Ta</td>
<td>Alfa-Aesar</td>
<td>&lt; 44 µm</td>
<td>&gt; 99.9</td>
</tr>
<tr>
<td>Amorphous B</td>
<td>Aldrich</td>
<td>&lt; 9 µm</td>
<td>95-97</td>
</tr>
<tr>
<td>B₄C</td>
<td>Alfa-Aesar</td>
<td>1-7 µm</td>
<td>&gt; 99.4</td>
</tr>
<tr>
<td>Si</td>
<td>Aldrich</td>
<td>&lt; 44 µm</td>
<td>&gt; 99</td>
</tr>
</tbody>
</table>

...
c) samples of about 40 mm diameter and 5 mm high, to be cut and machined for obtaining the specimens required for fracture toughness measurements;

d) cylinder of approximately 35 mm diameter and 25 mm high, for producing the desired nozzle.

Samples (a) and (b) were obtained using a lab scale SPS equipment (515 model, Fuji Electronic Industrial Co. Ltd., Kanagawa, Japan) under vacuum (20 Pa) conditions. The electric current limitation of 1500 A makes this sintering machine unable to produce the larger diameter specimens (c) and (d). Therefore, a more performing SPS-like equipment (HPD 25-1 model, FCT Systeme GmbH, Rauenstein, Germany), able to provide electric current intensities up to 8000 A, was utilized to this purpose.

Densities of polished SPSed specimens were determined by geometric/gravimetric measurements and the Archimedes’ method. The theoretical density of the composite systems were calculated through a rule of mixture [62], by considering the density values of pure HfB$_2$, ZrB$_2$, TaB$_2$ and SiC as 11.18, 6.1, 12.6, and 3.2 g/cm$^3$, respectively. The resulting values for 2HfB$_2$-SiC, 2ZrB$_2$-SiC, and 2TaB$_2$-SiC are 9.04, 5.37, and 9.98 g/cm$^3$, respectively.

A Philips PW 1830 X-rays diffractometer with Cu K$_\alpha$ radiation ($\lambda$=1.5405 Å) and Ni filter was used for phase identification. Final products microstructure was examined by High-Resolution Scanning Electron Microscopy (HRSEM, mod. S4000, Hitachi, Tokyo, Japan), coupled with energy dispersive X-rays spectroscopy (EDS) (Thermo Fisher Scientific, Waltham, MA, USA).

TGA measurements were carried out using a NETZSCH STA 409PC Simultaneous DTA-TGA Instrument in air, nitrogen and carbon dioxide flows under isothermal or non-isothermal conditions. In particular, TGA tests in air and $N_2$ were performed up to 1450 °C whereas, due to some technical limitation of this device, the maximum temperature adopted for experiments under CO$_2$ flow was 800 °C. Tests were conducted using rectangular parallelepiped shaped specimens of approximately 3mm x 3mm x 2 mm size obtained by cutting the various highly dense monophasic and composite samples produced by SPS.

Vickers hardness of the reinforced HfB$_2$ product was determined according to the UNI EN 843-4 using a Hardness tester machine (AFFRI WIKI 200 JS 2, AFFRI Inc., Wood Dale, IL, USA). The applied load and the dwell time were 9.807 N was 15 s, respectively. The obtained value was the average of 5 different measurements.

The fracture toughness ($K_{IC}$) was determined at room temperature and 1500 °C using the Chevron-Notched-Beam (CNB) in flexure on machined bars 25 mm x 2.5 mm x 2 mm (length x width x thickness, respectively) according to the UNI EN 14425-3 using a MTS 858 Mini Bionix® device (MTS Systems Corporation, Eden Prairie, MN USA). This apparatus was also used for performing the four-point bending flexural test according to the UNI EN 843-1, from which the flexural stress ($\sigma$) and the modulus of elasticity (E) in bending are evaluated.

The coefficient of thermal expansion of the ceramic composite was measured in air on machined bars 14.21 mm x 2.5 mm x 2 mm sized under two different temperature ranges up to 1400 °C according to the UNI EN 14425-3. To this aim, an optical dilatometer (vertical) from Expert System Solutions S.r.l (Modena, Italy) was employed.

The standard ASTM E 285-80 method was used to evaluate the thermal insulation characteristics and the weight losses of the UHTC material. In particular, an oxyacetylene burner was utilized under different heat flux (450, 1050 and 1250 W/cm$^2$), ablation time (80-120 s) and oxygen/acetylene ratio (1.3-1.7) conditions.

As mentioned previously, cylindrical samples of about 15 mm diameter and 22 mm high were used. Temperatures during the test were measured by two k-type thermocouples inserted into the sample in two small holes previously drilled on the lateral specimens surface (Figure 2) by Electrical Discharge Machining (EDM).

3. Results and discussion

3.1. Screening of UHTC candidates

The optimization of the synthesis and consolidation conditions for obtaining highly dense MeB$_2$ and MeB$_2$-SiC products (Me=Zr, Hf, Ta) by combining the SHS and SPS processes was carried out in previous studies [10,15,17,21,30]. Thus, the identified optimal reactants composition and the related SPS parameters have been adopted in this work for the obtainment of the bulk materials. In particular, based on the XRD spectra of Si-HS powders shown in Figure 3, the synthesis reactions (1) and (2) went to completion with the resulting
The selection of the most promising UHTC candidate to be considered for the fabrication of the nozzle component in this work was first made by considering the properties reported in the literature for the six systems above \([10,15,17,21,30]\). The obtained results for the diboride ceramics, to be possibly reinforced with the introduction of SiC fibers, are summarized in Table 2. It should be noted that all of these ceramics but one were produced by the SHS-SPS route also considered in this work. The exception is represented by HfB\(_2\), whose sintered sample obtained by SPS from combustion synthesized powders was highly porous (about 92% relative density) \([21]\). In contrast, the reactive SPS route, consisting in the synthesis of the diboride phase according to reaction (1) and its simultaneous densification, provided a highly dense sample (Table 2). Of course, the use of the reactive sintering route is not convenient for the fabrication of the fiber reinforced material, since the high temperature locally reached by the compact, as a consequence of the heat liberated due to the exothermicity of the synthesis reaction, would produce the degradation of the reinforcing phase.

Vickers hardness and fracture toughness data shown in Table 2 evidence that the sintered HfB\(_2\) material displays better mechanical characteristics with respect to the other counterparts. Similar considerations can be also made when the comparison is extended to the SiC-containing MeB\(_2\) products obtained by SHS-SPS \([10,15,17]\).

Another important indication for the final choice of the material to be used for the fabrication of the nozzle component is certainly provided by its resistance when exposed to specific gaseous environments at high temperatures. To this aim, various TGA experiments have been performed in the present study using gas flows consisting of air, nitrogen and carbon dioxide. The related curves, showing the mass change of the samples during dynamic (non-isothermal) or isothermal tests are reported in Figure 4. As expected, the test conducted in air confirms that the additive free diborides show very low oxidation resistance above 800 °C. Nonetheless, HfB\(_2\) seems to be relatively more stable as compared to the other two competitors. This outcome is also valid when analyzing the binary systems, which all benefit of the presence of SiC for improving their resistance. Similar findings could be deduced when examining the TGA curves corresponding to the isothermal tests conducted at 1450 °C under nitrogen. Also in this case, the HfB\(_2\)-based ceramics exhibit, particularly the binary one, a significantly lower mass increase with respect to the others. Finally, as far as the test carried out under CO\(_2\) is concerned, very comparable results are obtained for the three series of UHTCs.

The results described above allow us to conclude that HfB\(_2\) is the most promising base system, among those ones examined in this work, to be used in combination with SiC fiber for the fabrication of the nozzle prototype. Therefore, the material considered heretoafter for further characterization as well as for the preparation of the nozzle component will be obtained from a mixture composed of HfB\(_2\) powders synthesized by SHS with 26 vol.% of SiC fibers, as described in the Experimental section.

### Table 2. Characteristics of the MeB\(_2\) products (Me=Zr, Hf, Ta) obtained by combining the SHS and SPS technique.

<table>
<thead>
<tr>
<th>System</th>
<th>Density, (\rho) (%)</th>
<th>Mechanical properties</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB(_2)</td>
<td>98.3±0.3</td>
<td>HV=11.0±0.4 GPa, (KIC = 2.1±0.5) MPa·m(^{0.5})</td>
<td>[30]</td>
</tr>
<tr>
<td>HfB(_2)*</td>
<td>98.7±1.1</td>
<td>HV=18.1±0.9 GPa, (KIC = 3.5±0.5) MPa·m(^{0.5})</td>
<td>[21]</td>
</tr>
<tr>
<td>TaB(_2)</td>
<td>93.9±0.3</td>
<td>HV=17.5±0.4 GPa, (KIC = 3.2±0.6) MPa·m(^{0.5})</td>
<td>[30]</td>
</tr>
</tbody>
</table>

*This material was obtained by reactive SPS.

![Figure 4. TGA curves relative to tests conducted under different environments (air, N\(_2\), and CO\(_2\)) on spark plasma sintered monophasic and binary dense UHTCs.](image-url)
3.2. Preparation and characterization of HfB₂·SiCₓ samples

The HfB₂·SiCₓ mixture was processed by SPS at dwell temperatures (T_d) equal to 1700 and 1800 °C, holding time of 20 min and mechanical pressure of 60 MPa. The product obtained at the relatively lower temperature was still rather porous, with a relative density of about 91.6%. The densification was highly improved when the T_d value was increased to 1800 °C, so that a 99.6% dense ceramic was obtained. Four SEM micrographs showing the fracture surfaces of the materials obtained under both temperature conditions are reported in Figure 5. Two phases are readily distinguishable, the darker and lighter ones corresponding to silicon carbide and hafnium diboride, respectively. The incomplete and the nearly full densification levels achieved for the samples processed at 1700 and 1800 °C, respectively, are confirmed. These micrographs also evidenced that although a larger number of SiC fibers (indicated with the yellow arrows) can be detected in the material sintered at the relatively lower temperature, most of them are also very well visible in the completely dense product. The latter outcome clearly testifies that fibers degradation is significantly prevented also when operating at 1800 °C. Therefore, the latter condition was then chosen for the obtainment of the nearly full dense HfB₂·26 vol.%SiCₓ ceramic.

The latter material was widely characterized to evaluate its mechanical and thermophysical properties and the obtained results are reported in Tables 3-6. Specifically, the measured Vickers hardness (21.6±0.8 GPa) is higher than the values reported in Table 2 for the monophasic HfB₂ (18.1±0.9 GPa). The fracture toughness of the HfB₂·26 vol.%SiCₓ product determined at room temperature from Chevron-Notched specimens is K_IC ≈ 6.2±0.5 MPa m^(0.5). This value is significantly higher than those obtained in the literature for systems with similar nominal composition [4,8,21,42,43]. For instance, the reported K_IC values for HfB₂·20 vol.%SiCₓ, and HfB₂·30 vol.%SiCₓ at room temperature are 4.15 and 3.9 MPa m^(0.5), respectively [4]. Again, a fracture toughness of 4.6±0.3 MPa m^(0.5) was found for hot-pressed HfB₂·20 vol.%SiCₓ, and HfB₂·30 vol.%SiCₓ products obtained by Zhang et al. [42]. This property was slightly improved, up to 5.2±0.3 MPa m^(0.5), in presence of 5 vol.% AlN [42]. These considerations hold also true when considering the HfB₂·20 vol.%SiCₓ·20 vol.%TaSiₓ system investigated by Justin and Jankowiak [43], i.e. K_IC ≈ 4.6±0.2 MPa m^(0.5). Furthermore, the toughness value measured in this work was not only superior to that relative to additive free HfB₂ products (3.5±0.5 MPa m^(0.5)) but also to that of the ceramic composite containing 26 vol.% SiC whisker, i.e. 3.9±0.3 MPa m^(0.5), prepared following the same processing route [21]. Thus, based on the results obtained in this work, superior benefits could be obtained with the introduction of the SiC fibers in the HfB₂ matrix rather than equal amounts of whiskers.

The other properties obtained for the HfB₂·26 vol.%SiCₓ system are comparable, and in some cases enhanced, with respect to those relative to other UHTCs with similar composition [8,42]. For instance, the strength value at room temperature of 429±45 MPa found in this work was higher with respect to that measured for...
HfB$_2$-20 vol.%SiC by Zhang et al. [42], i.e. 353±35 MPa, and falls within the range of values, i.e. 356±91-453±46 MPa, reported by Gashch et al. [8] for different HfB$_2$-20 vol.%SiC-based materials. As far as the ablation test results is concerned, it is seen that temperature levels up to approximately 1100 °C were achieved by the sample as the conditions became progressively more severe (Figure 6). In addition, due to heat losses across the sample, temperature differences of about 100 °C were measured by the two thermocouples when it was subjected to relatively high heat fluxes (Figure 6d). Moreover, the data reported in Table 6 evidenced that the weight losses of the samples increases monotonically as the applied heat flux is progressively augmented. Nevertheless, regardless the adopted ablation conditions, extremely low mass losses are found during the various tests, i.e. about 0.22% at most.

To fulfill such requirements and taking into account of the material removal for machining, grinding and polishing steps that have to necessarily follow the sintering stage, a cylindrical sample of 35 mm diameter and 25 mm high was produced by SPS. To this aim, the FCT Systeme machine, able to provide the current intensity to achieve the desired densification level for such large size specimens, was used. Thus, the required amount of HfB$_2$ product was first synthesized by SPS and the resulting powders mixed with the chopped SiC fibers, according to the procedure already followed when considering smaller samples. The resulting HfB$_2$-SiC$_x$ material showed relative density above 96.5% of the theoretical value. The sample was then subjected to EDM to obtain the nozzle with the prescribed shape and size. Two optical photographs of the produced component, to be validated under actual operating conditions, are shown in Figure 7.

3.3. Fabrication of the nozzle component

According to the constraints prescribed in view of its final utilization, the nozzle to be finally obtained should consist of a hollow component with a cylindrical shape with external diameter of approximately 32 mm and 22 mm height. The varying sectional area to be crossed by the flowing medium has to display the diverging/converging parts with diameters of about 22 and 17 mm on the opposite sides of the component, whereas that in correspondence of the throat nozzle has to be about 12 mm.

4. Summary and concluding remarks

The fabrication of a nozzle component composed of HfB$_2$-26 vol.%SiC$_x$ is addressed in this work taking advantage of the Self-propagating High temperature Synthesis and Spark Plasma Sintering technologies. The selection of HfB$_2$ as the ceramic matrix to be reinforced with SiC fibers was made after comparison of the properties of not reinforced MeB$_2$-based UHTCs (Me=Zr, Ta and Hf) produced with the same processing route. In addition, in view of the actual harsh conditions to which the nozzle have to withstand, several TGA tests using different gas flows (air, N$_2$ and CO$_2$) have been carried out. Both literature data and TGA results allowed us to identify the HfB$_2$ system as the most promising candidate, among those ones tackled in this work, for space propulsion applications.

Thus, HfB$_2$ powders were first successfully synthesized by SPS from elemental powders and, after being mixed with the required amount of chopped SiC fibers, subsequently spark plasma sintered. SEM analysis indicated that fibers were highly preserved when the sintering process was conducted at 1700 °C and the resulting product was about 92% dense. The nearly full consolidation (>99.5%) was obtained when the holding temperature was increased to 1800 °C. The presence of SiC fibers in the sintered product was also evidenced in the latter case by SEM.

The nozzle fabrication was preceded by a comprehensive characterization of this specific material aimed to the evaluation of the most relevant mechanical and thermophysical properties. The obtained results are comparable, and in some cases superior, with respect to those ones reported in the literature for UHTCs systems with similar composition. Very promising are the outcomes deriving from the ablation tests conducted under different heat flux conditions. Indeed, the composite material produced by SPS was found to resist significantly to the most severe condition taken into account, corresponding to heat flux, ablation time, and oxygen/acetylene ratio equal to 1250 W/cm$^2$, 100 s, and 1.7, respectively. This statement is clearly demonstrated by the extremely low weight change (about 0.22%) correspondingly measured.

The processing route above was finally adopted for producing large sized UHTC specimens from which, after suitable electrical discharge machining, a nozzle component was fabricated. Although the final validation of the obtained prototype will be defined only after examining its behaviour under actual operating
conditions, some concluding considerations can be made. Indeed, the results reported in this work testify the capability of the proposed processing route to produce completely dense ceramics where the original fibrous character of the reinforcing phase introduced into the HfB$_2$ matrix can be highly preserved. This was made possible by the relatively milder sintering conditions applied to consolidate the starting mixture. Beneficial effects in this regard are undoubtedly provided by the use of the SHS method for the synthesis of highly sinterable UHTC powders. In addition to this aspect, the utilization of the SPS technology, where the powder undergoing consolidation can be rapidly heated so that the processing time is significantly shortened, further contributes to prevent or limit fibers degeneration during sintering.

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- Prof. Luigi Torre and Dr. Maurizio Natali (Università degli Studi di Perugia, Italy) for performing the ablation tests;
- Andaló Gianni S.r.l. (Imola, Italy) for EDM of large sized samples.

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