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PROCEEDINGS OF THE SYMPOSIUM ON SPARK PLASMA SYNTHESIS AND SINTERING

Spark plasma sintering of UHTC powders obtained by self-propagating high-temperature synthesis

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Abstract Fully dense ZrB_2–SiC and HfB_2–SiC ultra-high-temperature ceramics (UHTCs) composites are fabricated by first synthesizing via self-propagating high-temperature synthesis (SHS) the composite powders from B_4C, Si, and Zr or Hf reactants, and subsequently consolidating the product by spark plasma sintering (SPS) without the addition of any sintering aid. It was found that the SHS technique leads to the complete conversion of reactants to the desired products and the SPS allows for the full consolidation (>99.5% relative density) under the optimal operating conditions of 1800 °C/20 min/20 MPa and 1800 °C/30 min/20 MPa, for the cases of ZrB_2–SiC and HfB_2–SiC, respectively. Based on the results reported in this work, it can be stated that the combination of SHS and SPS methods represents a particularly rapid and convenient preparation route (lower sintering temperature and processing time) for UHTCs as compared to the techniques available in the literature for the fabrication of analogous products.

Introduction

Because of their extremely high melting temperatures, i.e. >3000 °C, metal refractory borides such as zirconium diboride (ZrB_2) and hafnium diboride (HfB_2) are the most representative materials of the well known class of ultra-high temperature ceramics (UHTCs) [1, 2]. Besides their high-melting points, the growing interest in these materials is related to the peculiar combination of physical, thermal, and mechanical properties, such as high hardness, high electrical and thermal conductivity, chemical inertness, good thermal shock resistance, and high resistance to ablation in oxidizing environments. These features make UHTCs suitable for high-temperature applications in several fields where thermal, electrical, chemical, and wear resistance are required, such as cutting tools, metallurgy, microelectronics, and refractory industries in general [2]. More recently, these materials have found applications in aerospace industry as thermal protection systems (TPS) for space vehicles, specifically in leading edges and nose caps in hypersonic re-entry vehicles, rocket nozzle inserts and air-augmented propulsion system components [2–5].

A further improvement of the performance of ZrB_2- and HfB_2-based ceramic composites is obtained through the addition of secondary phases like SiC, whose presence makes the resulting UHTCs much more resistant to oxidation when the material is exposed to an oxidant environment at high temperatures [6–9].

Therefore, ZrB_2–SiC- and HfB_2–SiC-based composites have been investigated by several researchers and various methods for their preparation have been developed, mostly taking advantage of the hot pressing (HP) technique through which commercial ZrB_2 or HfB_2 and SiC powders are sintered [7–13]. Alternatively, the reaction synthesis

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and densification in one step was also carried out by reactive hot pressing (RHP), for instance starting from Zr, SiB_4, and graphite [14] or Zr, B_4C, and Si [15] for the synthesis of ZrB_2–SiC.

In this context, the main concern related to the use of the HP approach depends on its low heating rates which leads to relatively long processing times (typically on the order of hours). To facilitate sintering phenomena, certain ceramic phases, like Si_3N_4 [9], ZrN [7], HfN [16] have been used as sintering aids. However, also in these cases, the total sintering time still exceeds 1 h.

To overcome this problem, the relatively new sintering method known as spark plasma sintering (SPS), where the starting powders, either to be only consolidated or simultaneously reacted, are crossed by an electric pulsed current, was recently proposed for the fabrication of dense UHTCs [17–21]. It has been widely demonstrated, not only in the field of UHTCs, that processes conducted using SPS typically allow one to perform sintering at lower temperatures with respect to traditional HP, and shorter times but anyhow sufficient to achieve the complete densification of the material [22]. These features have also made possible to sinter nanometric powders by SPS with limited grain growth.

In the present study, we investigate a fabrication process, hereafter called SHS-SPS, for the preparation of a ZrB_2-25 vol.% SiC and HfB_2-26.5 vol.% SiC composites consisting of first obtaining the UHTC products in powder form via self-propagating high-temperature synthesis (SHS) and, subsequently, consolidating them by using the SPS apparatus. With regard to SHS, it is a well known combustion synthesis method based on the occurrence of strongly exothermic reactions that, once ignited, are able to propagate as a combustion wave through the entire reacting mixture, without requiring any other energy supply [23, 24].

The SHS-SPS approach was recently followed for the preparation of dense $4ZrB_2/4ZrC/1.5SiC$ composite [21]. It was experimentally observed that the optimal operating SPS conditions corresponding to the full consolidation (>99.5%) of this UHTC material, when starting from SHS powders, led to a still porous product (about 91% relative density) when using commercially available ZrB_2, ZrC, and SiC powders, mixed in the same proportions.

The influence of holding temperature and processing time related to the SPS apparatus is systematically investigated for both ZrB_2–SiC and HfB_2–SiC systems. The resulting optimal products are then characterized in terms of microstructure, hardness, fracture toughness, and oxidation resistance and the obtained results are compared with those reported in the literature relatively to analogous UHTCs prepared using other fabricating methods.

Experimental materials and methods

Characteristics and sources of reactants used for the preparation of bulk ZrB_2–SiC and HfB_2–SiC products are reported in Table 1. The starting mixtures to be processed by SHS were prepared by mixing reactants according to the following reactions:

$$2Zr + B_4C + Si \rightarrow 2ZrB_2 + SiC \tag{1}$$

$$2Hf + B_4C + Si \rightarrow 2HfB_2 + SiC \tag{2}$$

which correspond approximately to ZrB_2-25 vol% SiC and HfB_2-26.5 vol% SiC, respectively.

Powder mixing was performed in a SPEX 8000 (SPEX CertiPrep, USA) shaker mill for 30 min. Details on the experimental set-up used in this work for SHS and SPS are described elsewhere [24, 25]. About 8–9 g of the starting mixture were uniaxially pressed to form cylindrical pellets with a diameter of 16 mm, height of 30 mm, and a green density of ~50% of the theoretical value. The combustion front was generated at one sample end by using an electrically heated tungsten coil, which was immediately turned off as soon as the synthesis reaction was initiated. Then, the reactive process self-propagates until it reaches the opposite end of the pellet. The temperature during reaction evolution was measured using thermocouples (W-Re, 127 μm diameter, Omega Engineering Inc., USA). To convert the obtained SHS product to powder form, about 4 g of it were milled by means of the shaker mill apparatus mentioned above, using a stainless steel vial with two steel balls (13 mm diameter, 8 g weight) for 20 min. Particle size distribution of the obtained powders was determined using a laser light scattering analyzer (CILAS 1180, France).

An SPS 515 apparatus (Sumitomo Coal Mining Co. Ltd, Japan) was used in the temperature controlled mode for powder densification. This machine combines a 50 kN uniaxial press with a DC pulsed current generator (10 V, 1500 A, 300 Hz) to simultaneously provide a pulsed electric current through the sample and the graphite die containing it, together with a mechanical load through the die plungers. The effect of the dwell temperature, T_D, and the total sintering time, t_T, was investigated by performing all SPS experiments at a constant value of the mechanical

Table 1 Characteristics of the starting powders used in the present investigation

Powders	Vendor	Particle size (μm)	Purity (%)
Zr	Alfa-Aesar (00418)	<44	>98.5
Hf	Alfa-Aesar (10201)	<44	>99.6
B_4C	Alfa-Aesar (40504)	1–7	>99.4
Si	Aldrich (21,561-9)	<44	>99

pressure, i.e. $P = 20$ MPa, and heating time, i.e. $t_H = 10$ min, which represents the time required to reach the T_D value when starting from ambient temperature.

A certain amount (3–5 g) of the SHS powders was first cold-compacted inside the die (outside diameter, 35 mm; inside diameter, 15 mm; height, 40 mm). To protect the die and facilitate sample release after synthesis, a 99.8% pure graphite foil (0.13 mm thick, Alfa Aesar, Karlsruhe, Germany) was inserted between the internal surfaces of the die and the top and the bottom surface of the sample and the graphite plungers (14.7 mm diameter, 20 mm height). Both the die and the plungers were composed of AT101 graphite and provided by Atal s.r.l., Italy. In addition, with the aim of minimizing heat losses by thermal radiation, the die was covered with a layer of graphite felt (Atal s.r.l., Italy). The die was then placed inside the reaction chamber of the SPS apparatus and the system was evacuated down to 10 Pa. This step was followed by the application of 20 MPa mechanical pressure through the plungers.

A specific temperature program was set for a given time before starting each SPS run. Temperature, applied average current and voltage, mechanical load, and the vertical displacement of the lower electrode were recorded in real time during the process. In particular, temperatures were measured by a C-type thermocouple (Omega Engineering Inc., USA), which was inserted inside a small hole in one side of the graphite die. The measured displacement can be regarded as the degree of powdered compact densification. However, thermal expansion of the sample as well as that of both electrodes, graphite blocks, spacers, and plungers, are also responsible for the variation of this parameter. The contribution of the die/plungers ensemble is evaluated [25] by performing "blank tests", which consist in the application of same SPS conditions (temperature cycle, mechanical load, time, etc.) when the powder compact is not present. Thus, by subtracting the output from the "blank test" to the displacement measured during a typical SPS experiment, we obtain the sample shrinkage (δ), which will be considered in the following discussion. In any case, the real degree of consolidation was determined by measuring the density of the sample at the end of the process. For sake of reproducibility, each experiment was repeated at least twice. After the synthesis process, the sample was allowed to cool and then removed from the die.

The relative densities of dense products were determined by the Archimedes' method. The theoretical density of the ZrB_2–SiC and HfB_2–SiC composites, i.e. 5.37 and 9.17 g/cm^3, respectively, were calculated through a rule of mixture [26], by considering the density values of ZrB_2, HfB_2, and SiC as 6.1, 11.18, and 3.2 g/cm^3, respectively. Phase identification was performed by a Philips PW 1830 X-rays diffractometer using a Ni filtered Cu K_α radiation ($\lambda = 1.5405$ Å). The microstructure and local phase composition of end products were examined by scanning electron microscopy (SEM) (mod. S4000, Hitachi, Japan) and energy dispersive X-rays spectroscopy (EDS) (Kevex Sigma 32 Probe, Noran Instruments, USA), respectively.

Indentation method using a Zwick 3212 Hardness tester machine (Zwick & Co. GmbH, Germany) was used to determine Vickers hardness and fracture toughness (K_{IC}) of the obtained products. The applied loads used for both measurements were 1 kg (ZrB_2–SiC) and 10 kg (HfB_2–SiC) while the dwell time was 18 s.

The oxidation resistance of the UHTC products was determined by performing thermogravimetric analysis (TGA) using a TA SDA 2969 simultaneous DTA-TGA instrument. Specifically, two types of experiments were carried out. One of them was conducted under non-isothermal conditions, during which the specimen is heated slowly (2 °C/min) from room temperature to 1450 °C in air, while measuring the mass gain as a function of temperature. In the second test, after a rapid heating at 20 °C/min, TGA experiments were conducted isothermally at 1450 °C for about 4 h, during which the temporal variation of the mass sample was monitored.

Results and discussion

Synthesis of UHTCs by SHS

Consistently to the high enthalpy of reactions (1) and (2), i.e. $-\Delta H_r^o = 647.266$ kJ and 674.042 kJ [27], respectively, the syntheses of the resulting $2ZrB_2$–SiC and $2HfB_2$–SiC composites displayed a self-propagating behavior. Specifically, the maximum combustion temperatures measured during the SHS of ZrB_2–SiC and HfB_2–SiC products were equal to about 2200 °C and 2150 °C, respectively, while average front velocities, as determined from temperature profiles, were equal to 11 mm/s and 7 mm/s, respectively.

The corresponding diffraction patterns of the obtained UHTCs along with those of the starting mixtures are reported in Figs. 1 and 2. All the major peaks corresponding to the desired ZrB_2 or HfB_2 and SiC phases were detected. Moreover, no other secondary phases, including the impurities present in reactants (cf. Fig. 1a), were found in the final product. This finding is likely a consequence of the typical self-cleaning character of the SHS process [23]. Thus, it is possible to state that SHS proceeds in both cases to completion with the formation of the desired composite constituents according to reactions (1) and (2).

Following the procedure described in the section "Experimental materials and methods" before proceeding to the powder consolidation stage by SPS, the obtained SHS products were ball milled for 20 min. Size distribution of the resulting powders along with a SEM back-scattered

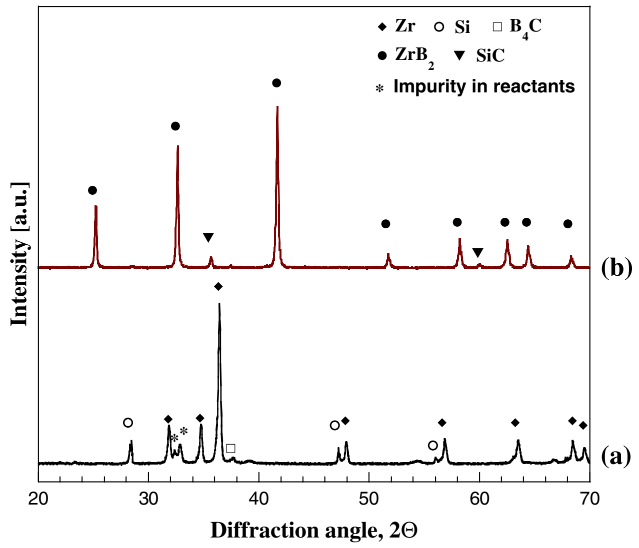

Fig. 1 Comparison of XRD patterns of starting reactants (**a**) and the ZrB_2–SiC product (**b**) obtained by self-propagating high-temperature synthesis according to reaction (1)

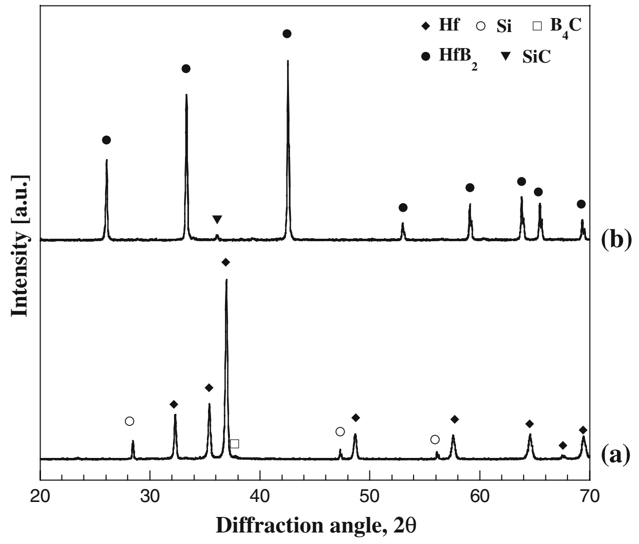

Fig. 2 XRD patterns of starting reactants (**a**) and the HfB_2–SiC product (**b**) obtained by self-propagating high-temperature synthesis according to reaction (2)

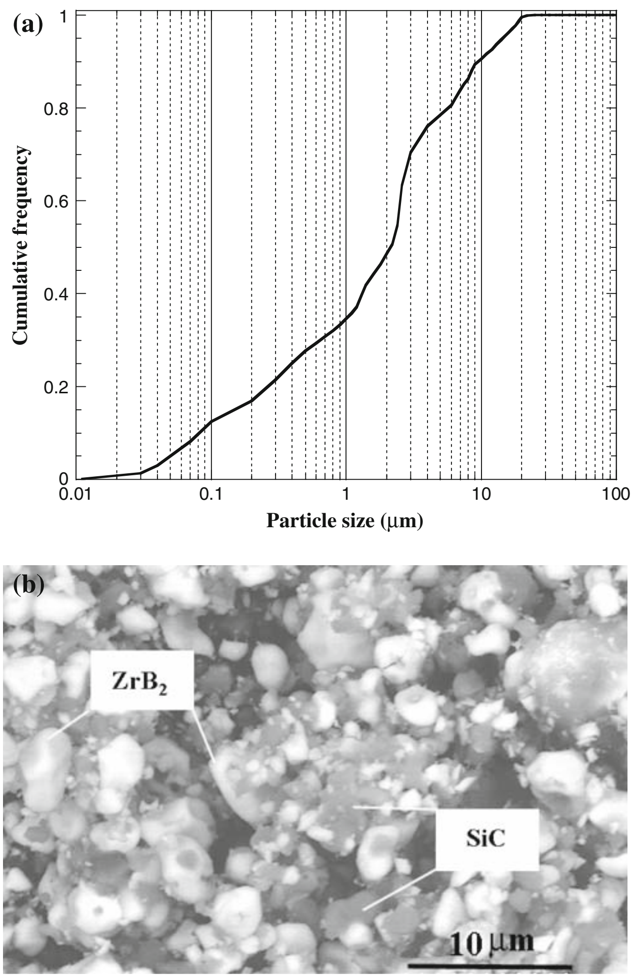

Fig. 3 Size distribution (cumulative curve) measured by laser light scattering (**a**) and SEM back-scattered micrograph (**b**) of SHS ZrB_2–SiC powders ball milled for 20 min that are to be densified by SPS

micrograph are shown in Fig. 3a and b for the case of the ZrB_2–SiC product. Fig. 3a shows that particles size less than 20 μm and with $d_{50} = 2.51 \pm 0.02$ μm are obtained. From the SEM back-scattered image reported in Fig. 3b, it is observed that, according to the results reported in Fig. 3a, each individual SHS powder particle is less than 20 μm in size. In addition, it may be seen that the synthesized powder mixture generally consists of ZrB_2 and SiC grains, each of them being typically less than 4 μm in size. A similar situation was encountered after milling the $2HfB_2$–SiC composite obtained by SHS. Specifically, in this case size distribution of the resulting powders reveals that particle size is less than 30 μm and $d_{50} = 3.0 \pm 0.2$ μm. Moreover, SEM investigation evidenced that each individual particle consisted of several HfB_2 and SiC grains, each of them being typically less than 4–5 μm in size.

Densification by SPS

Because the final goal of this work is to obtain dense UHTC materials, the composite powders synthesized by SHS were consolidated in the SPS apparatus. The sample shrinkage (δ), expressed as a percentage relative to its final value, and temperature time profiles recorded during the consolidation process of ZrB_2–SiC powders under the conditions of $T_D = 1800$ °C, $t_H = 10$ min, $t_T = 20$ min, and $P = 20$ MPa, are reported in Fig. 4a, while the corresponding average current and voltage behavior is shown in Fig. 4b.

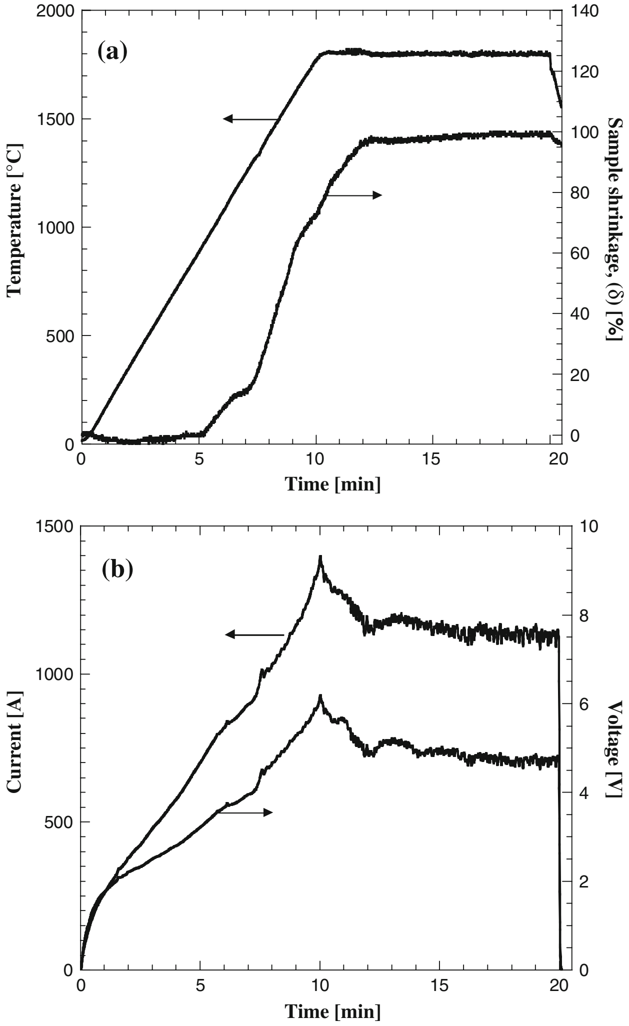

Fig. 4 Temporal profiles of SPS outputs during the preparation of dense UHTC products starting from $2ZrB_2$–SiC powders obtained by SHS: (**a**) temperature and sample shrinkage, (**b**) average current intensity and voltage ($T_D = 1800$ °C, $t_H = 10$ min, $t_T = 20$ min, $P = 20$ MPa)

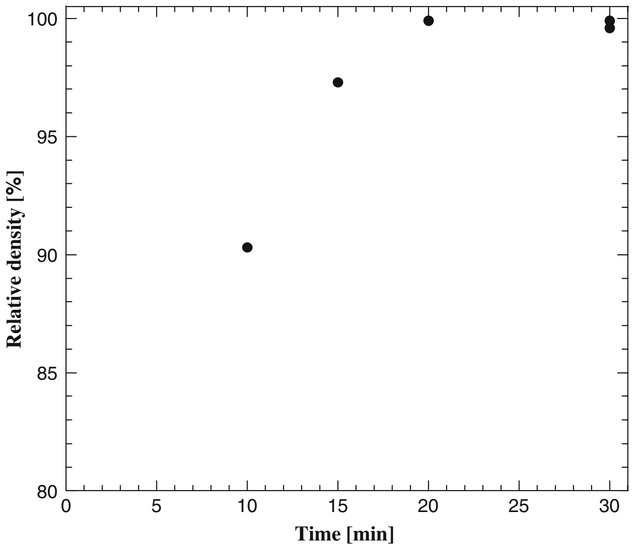

Fig. 5 Effect of SPS time on relative density of sintered ZrB_2–SiC powders synthesized by SHS ($T_D = 1800$ °C, $t_H = 10$ min, $P = 20$ MPa)

From the sample shrinkage profile (cf. Fig. 4a), no significant changes are manifested during the first 5 min of the SPS process. However, as the experiment proceeds, δ increases gradually, although with different rates, to reach its final value (2 mm) within 12 min. Regarding the electrical behavior of the system (cf. Fig. 4b), it is observed that, as soon as the SPS experiment was started, to obtain the selected thermal profile, the proportional-integral-differential (PID) controller gradually augments the current with a consequent voltage increase. As the dwell temperature is reached, both current and voltage rapidly decrease down to the corresponding stationary values, i.e. about 1150 A and 5 V, respectively. Sample shrinkage, temperature, current and voltage time profiles recorded during the SPS process of HfB_2–SiC powders obtained by SHS were qualitatively very similar to those obtained for the ZrB_2–SiC system and shown in Fig. 4a, b. This fact holds also true when setting different T_D and t_T values. Thus, analogous considerations can be made.

The effect of the SPS time in the range 10–30 min on product's relative density when the conditions are $T_D = 1800$ °C, $t_H = 10$ min, and $P = 20$ MPa, is reported in Fig. 5 for the ZrB_2–SiC system. It is found that a still porous product (90.3% of the theoretical value) was obtained at the end of the heating stage (10 min). However, the specimen was significantly consolidated as the sintering time was prolonged to 15 min (97.3%) and, finally, a fully dense material (density higher than 99.5%) was obtained when $t_T = 20$ min.

For the same system, the effect of dwell temperature, T_D, on sample densification was investigated by SPS in the range 1400–1800 °C, by maintaining constant mechanical pressure ($P = 20$ MPa) and heating time ($t_H = 10$ min). The obtained results are reported in Fig. 6 when the total processing time, t_T, was set to 20 and 30 min. As expected, when the dwell temperature is increased, residual porosity in the SPS product is gradually eliminated. Moreover, it can be concluded that, within the range of experimental conditions investigated, to guarantee the preparation of a fully dense material (relative density >99.5% of the theoretical value) the optimal operating conditions are $T_D = 1600$ °C, $t_T = 30$ min or $T_D = 1800$ °C, $t_T = 20$ min.

The dependence of product's relative density on the SPS time during the consolidation of HfB_2–SiC when $T_D =$ 1800 °C, $t_H = 10$ min, and $P = 20$ MPa, is shown in Fig. 7. It is seen that the bulk product obtained when $t_T = 20$ min was not fully densified (about 96% relative density), in contrast to the case of the consolidation of ZrB_2–SiC

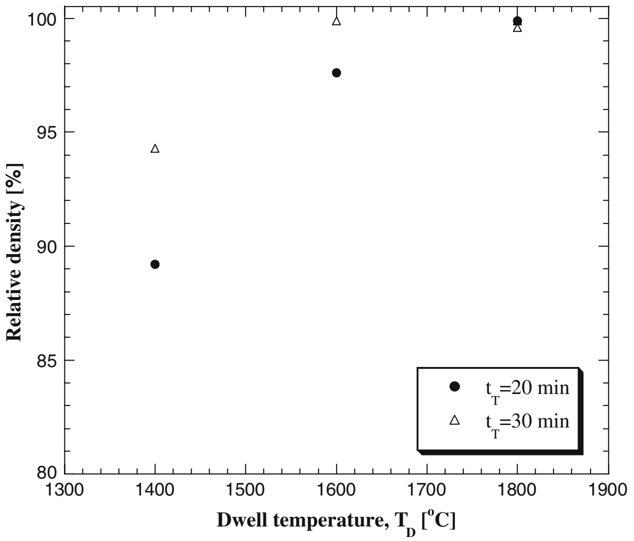

Fig. 6 Effect of dwell temperature on relative density of sintered ZrB_2–SiC powders synthesized by SHS (t_H = 10 min, P = 20 MPa)

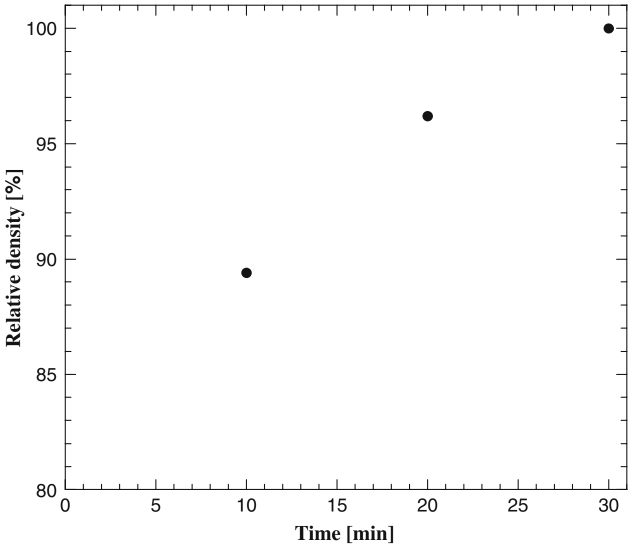

Fig. 7 Effect of SPS time on relative density of sintered HfB_2–SiC powders synthesized by SHS (T_D = 1800 °C, t_H = 10 min, P = 20 MPa)

powders (cf. Fig. 5). However, the complete densification was achieved when the total SPS time was prolonged to 30 min. The relatively higher dwell time required to fully consolidate HfB_2–SiC powders can be explained on the basis of the higher refractory character of HfB_2 as compared to ZrB_2, i.e. 3245 °C and 3380 °C melting points [2], respectively, as well as to the slightly finer powders processed for the case of ZrB_2–SiC.

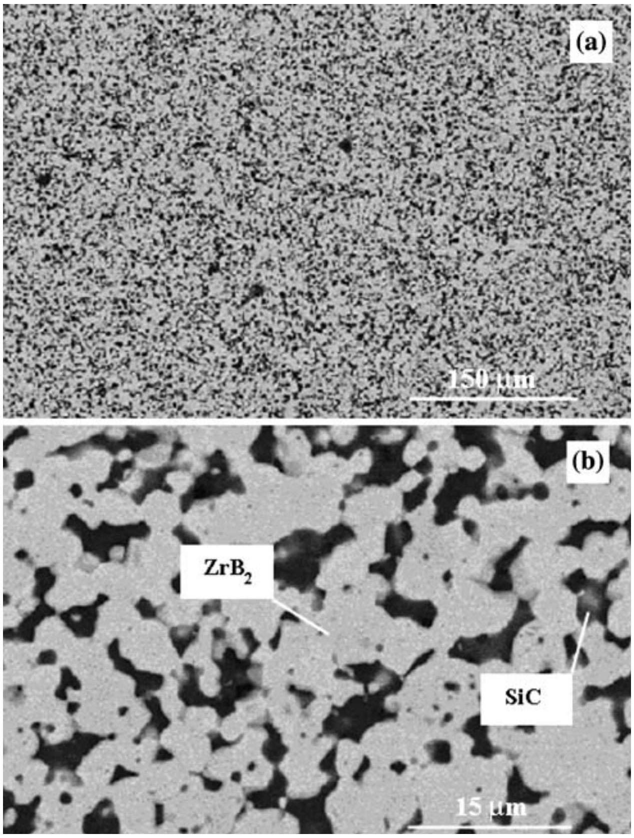

Fig. 8 SEM back-scattered micrographs of ZrB_2-SiC SPS product (T_D = 1800 °C, t_H = 10 min, t_T = 20 min, P = 20 MPa) at different magnification (**a**) 200× and (**b**) 2000×

Products characterization

Two back-scattered SEM micrographs at different magnification of the ZrB_2–SiC compact obtained after consolidation by SPS under the conditions T_D = 1800 °C, P = 20 MPa, t_H = 10 min, and t_T = 20 min are shown in Fig. 8a and b. Analogously, Fig. 9a and b shows two SEM images related to the HfB_2–SiC dense sample obtained under the identified optimal SPS operating conditions for this system, i.e. T_D = 1800 °C, P = 20 MPa, t_H = 10 min, and t_T = 30 min. In both cases, the carbide (dark region) and boride (light zone) phases appear well distributed throughout the sample.

With regard to the mechanical properties determined for the ZrB_2–SiC product, it was found that the Vickers hardness using 1 kg load was about 16.7 ± 0.4 GPa, whereas the fracture toughness (K_{IC}) was 5.0 ± 0.3 MPa $m^{1/2}$. Relatively higher values, i.e. the Vickers hardness and K_{IC} were about 19.2 ± 0.6 GPa and 7.0 ± 0.7 MPa $m^{1/2}$, respectively, were obtained when characterizing the fully dense HfB_2–SiC SPS material using 10 kg load. These values are comparable to, and in some cases better than, those reported in the literature for similar systems [16, 19, 28]. As an example, the HfB_2-20 vol.% SiC material fabricated by Gasch et al. [28] using the HP technique was characterized by Vickers hardness = 19–21 GPa and K_{IC} = 4.1–4.2 MPa $m^{1/2}$.

The oxidation resistance of both the UHTC composites produced has been measured using TGA by monitoring the

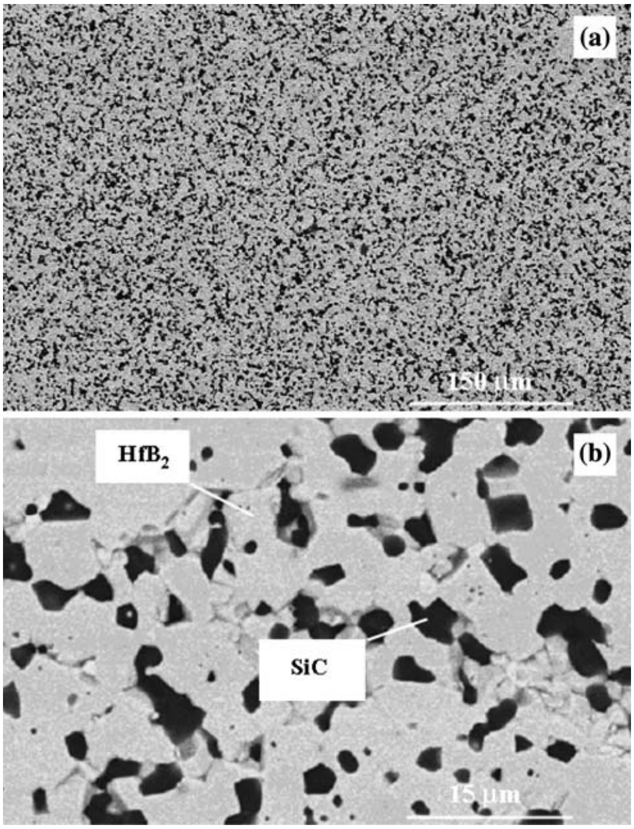

Fig. 9 SEM back-scattered micrographs of HfB_2–SiC SPS product ($T_D = 1800$ °C, $t_H = 10$ min, $t_T = 30$ min, $P = 20$ MPa) at different magnification (**a**) 200× and (**b**) 2000×

mass change of the sample subjected to an oxidizing environment (air) at high temperature. Specifically, two types of measurements have been performed and the obtained oxidation tests results related to ZrB_2–SiC specimens are reported in Fig. 10a and b. During the non-isothermal test (cf. Fig. 10a), the specimen was heated at relatively low heating rate (2 °C/min) from room temperature up to 1450 °C. Conversely, the second one (cf. Fig. 10b) was conducted isothermally at 1450 °C, for about 4 h, after a rapid heating stage (20 °C/min).

The oxidation behavior exhibited by the ultra-refractory composites obtained in this work is similar to that observed by other authors when characterizing UHTC materials with analogous composition and fabricated with other methods [7, 14]. In particular, such behavior is consistent with the well known formation of a protective layer of borosilicate glass on the surface of the oxidized material. Specifically (cf. Fig. 10a), the onset of the oxidation reaction, which corresponds to the point where the sample starts to gain weight, was recorded at about 740 °C. Afterwards, the weight first increases up to a maximum level at $T = 1028$ °C, then decreases reaching a minimum value at 1194 °C and, finally, increases again until the final temperature is achieved.

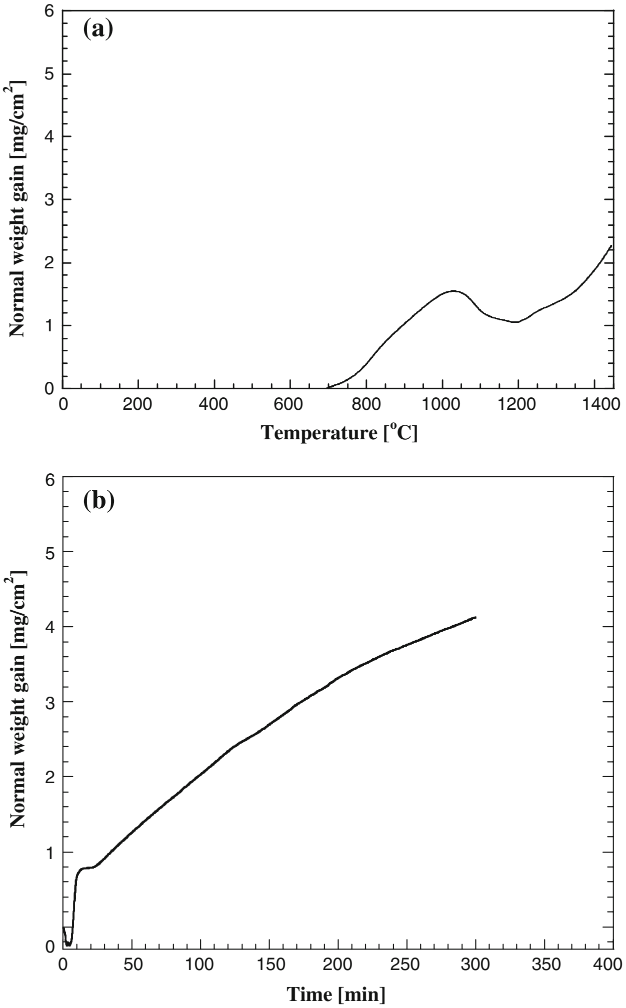

Fig. 10 Specific weight change during TGA oxidation in air of the sintered ZrB_2–SiC sample ($T_D = 1800$ °C, $t_H = 10$ min, $t_T = 20$ min, $P = 20$ MPa) obtained starting from powders synthesized by SHS as a function of (**a**) temperature (non-isothermal run with the heating rate equal to 2 °C/min) and (**b**) time (isothermal run at 1450 °C)

In general, it can be stated that the UHTC composites first synthesized by SHS and subsequently sintered by SPS under the optimal operation conditions reported above, exhibits relatively low and thermally stable oxidation rate up to 1450 °C.

Summary and concluding remarks

With the final goal of fabricating fully dense ZrB_2–SiC and HfB_2–SiC composites (with a ZrB_2/SiC and HfB_2/SiC molar ratio of 2), a method consisting in two steps was adopted. Specifically, taking advantage of the highly exothermic reactions (1) and (2), the starting reactants, i.e. Zr or Hf, B_4C, and silicon, were firstly reacted by SHS to form the ZrB_2–SiC and HfB_2–SiC composites, respectively.

Thus, the obtained powders were subsequently consolidated without the addition of any sintering aid using an SPS apparatus. It was determined that, the optimal operating conditions corresponding to the obtainment of a fully dense material (relative density >99.5% of the theoretical value) are (T_D = 1600 °C, t_T = 30 min or T_D = 1800 °C, t_T = 20 min) and (T_D = 1800 °C, t_T = 30 min) for the case of ZrB_2–SiC or HfB_2–SiC, respectively, with the applied pressure and the heating time equal to 20 MPa and 10 min, respectively.

Regarding the characteristics of the ultra-refractory materials prepared in the present work, i.e. hardness, fracture toughness, and oxidation resistance, the obtained results are similar to, and in some cases better than, those related to analogous UHTC products synthesized by competitive methods. In addition, the adopted process is characterized by shorter processing times and/or lower sintering temperature, when compared to the other fabrication methods proposed in the literature. For instance, when commercially available ZrB_2 and SiC powders were sintered by HP, it was reported [11, 12] that 450 min, along with T = 1900 °C and P = 32 MPa, was the total time required to obtain a near full dense ZrB_2/20–30 vol.% SiC. Analogously, the fabrication of dense HfB_2-20 vol.% SiC was carried out by HP when the conditions were T = 2200 °C, 1 h dwell time, and P = 25 MPa [28]. However, it is worth noting that the heating time, which was not specified in this work, still had to be added to the reported holding time (60 min), to calculate the total duration of the sintering process.

Therefore, it can be concluded that the adopted preparation route to obtain completely dense ZrB_2/25 vol% SiC and HfB_2/26.5 vol% SiC from B_4C, Si, and Zr, or Hf, is particularly rapid and convenient as compared to the competitive techniques available in the literature. Such demonstrated advantages can be firstly explained because the process considered in this work is based on the use of an in situ very rapid method, i.e. the SHS, able to synthesize in few seconds very fine grained UHTC products. This fact, along with the low cost of installations and simplicity of the SHS process, represents an important feature in view of possible large scale exploitation of UHTC powders characterized by improved sinterability. Moreover, it was determined that the use of the very efficient sintering technique, such as SPS, allows one to perform powder consolidation at lower temperatures (at least 100–200 °C less) with respect to traditional HP, and, above all, relatively shorter times, i.e. 20–30 min in the present study. These peculiar conditions are not only sufficient to reach the complete densification of the UHTC composites, but are also suitable for limiting grain growth during the sintering process, which is an important issue for those materials whose properties are negatively affected by increased grains size.

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References

1. Upadhya K, Yang JM, Hoffmann WP (1997) Am Ceram Soc Bull 58:51
2. Fahrenholtz WG, Hilmas GE, Talmy IG, Zaykoski JA (2007) J Am Ceram Soc 90:1347
3. "Thermal protection materials and systems branch" NASA web site (http://asm.arc.nasa.gov/materials.html) visited on October 2007
4. Levine SR, Opila EJ, Halbig MC, Kiser JD, Singh M, Salem JA (2003) J Eur Ceram Soc 22:2757
5. Savino R, De Stefano Fumo P, Paterna D, Serpico M (2005) Aerosp Sci Technol 9:151
6. Tripp WC, Davis HH, Graham HC (1973) Am Ceram Soc Bull 52:612
7. Monteverde F, Bellosi A (2003) J Electrochem Soc 150:552
8. Monteverde F, Bellosi A (2005) Solid State Sci 7:622
9. Monteverde F, Bellosi A (2005) J Eur Ceram Soc 25:1025
10. Monteverde F, Guicciardi S, Bellosi A (2003) Mat Sci Eng A 346:310
11. Fahrenholtz WG, Hilmas GE, Chamberlain AL, Zimmermann JW, Fahrenholtz B (2004) J Mater Sci 39:5951. doi:10.1023/B:JMSC.0000041691.41116.bf
12. Chamberlain AL, Fahrenholtz WG, Hilmas GE, Ellerby DT (2004) J Am Ceram Soc 87:1170
13. Marschall J, Erlich DC, Manning H, Duppler W, Ellerby D, Gasch M (2004) J Mater Sci 39:5959. doi:10.1023/B:JMSC.0000041692.72915.e8
14. Opeka MM, Talmy IG, Wuchina EJ, Zaykoski JA, Causey SJ (1999) J Eur Ceram Soc 19:2404
15. Zhang G-J, Deng Z-Y, Kondo N, Yang J-F, Ohji T (2000) J Am Ceram Soc 83:2330
16. Monteverde F, Bellosi A (2004) J Mater Res 19:3576
17. Medri V, Monteverde F, Balbo A, Bellosi A (2005) Adv Eng Mater 7:159
18. Anselmi-Tamburini U, Kodera Y, Gasch M, Unuvar C, Munir ZA, Ohyanagi M, Johnson SM (2006) J Mater Sci 41:3097. doi:10.1007/s10853-005-2457-y
19. Monteverde F, Melandri C, Guicciardi S (2006) Mater Chem Phys 100:513
20. Monteverde F (2007) J Alloys Comp 428:197
21. Licheri R, Orrù R, Musa C, Cao G (2008) Mater Lett 62:432
22. Munir ZA, Anselmi-Tamburini U, Ohyanagi M (2006) J Mater Sci 41:763. doi:10.1007/s10853-006-6555-2
23. Munir ZA, Anselmi-Tamburini U (1989) Mater Sci Rep 3:277
24. Cincotti A, Licheri R, Locci AM, Orrù R, Cao G (2003) J Chem Technol Biot 78:122
25. Locci AM, Orrù R, Cao G, Munir ZA (2006) J Am Ceram Soc 89:848
26. Matthews FL, Rawlings R (1994) Composite materials: engineering and science. Chapman & Hall, Great Britain
27. Barin I (1993) Thermochemical data of pure substances. VHC, Weinheim, Germany
28. Gasch M, Ellerby D, Irby E, Beckman S, Gusman M, Johnson S (2004) J Mater Sci 39:5925. doi:10.1023/B:JMSC.0000041689.90456.af