EFFICIENT TECHNOLOGIES FOR THE FABRICATION OF DENSE ZrB_2- AND HfB_2-BASED ULTRA HIGH TEMPERATURE CERAMICS

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ABSTRACT

The Self-propagating High-temperature Synthesis (SHS) technique and the Spark Plasma Sintering (SPS) technology are combined in this work for the fabrication of fully dense MB_2-SiC and MB_2-MC-SiC (M=Zr, Hf) Ultra High Temperature Ceramics (UHTCs). Specifically, Zr or Hf, B_4C, Si, and, for the cases of the ternary systems, graphite powders are first reacted by SHS to successfully form the desired compounds. The resulting powders are then subjected to consolidation by SPS. In particular, by setting a dwell temperature level equal to 1800 °C, a mechanical pressure P=20 MPa, and a non-isothermal heating time t_h= 10 min, products with relative densities ≥ 98.5% are obtained for all systems investigated within 30 min of total processing time. The characteristics of the resulting dense UHTCs, i.e. hardness, fracture toughness, and oxidation resistance, are similar to, and in some cases superior than, those related to analogous products synthesized by alternative, less rapid, methods.

1. INTRODUCTION

Zr- and Hf- borides and carbides are considered the most representative members of the class of materials better known as Ultra High Temperature Ceramics (UHTCs) that are of practical importance due to the combination of several properties, such as extremely high melting temperatures, i.e. >3200 K, high hardness, high electrical and thermal conductivity, chemical stability, good thermal shock resistance and high resistance to ablation in oxidizing environments [1]. These characteristics make UHTCs suitable in different fields where thermal, electrical, chemical, and wear resistance are required, like cutting tools, metallurgy, microelectronics and refractory industries in general. More recently, these materials have been recognized particularly attractive in aerospace industry for the fabrication of components that are exposed to high-flow environments like leading edges and nose caps in hypersonic re-entry vehicles [1]. In this context, it is also well established the beneficial effect of SiC, used as additive, in terms of oxidation resistance at high temperatures [2].

The most general approach aimed to obtain dense UHTCs is based on the use of conventional Hot Pressing (HP) techniques, where the energy needed for the sintering process is provided by an external heating source [3]. The critical point is represented by the fact that HP requires not only high sintering temperatures and mechanical loads, but especially prolonged processing times, generally on the order of hours, to achieve acceptable relative density levels.

On the other hand, Spark Plasma Sintering (SPS), a relatively novel technology where the starting powders to be only consolidated or also simultaneously reacted are crossed by an electric pulsed current (cf. Fig. 1), offers a possible convenient tool to overcome the problems mentioned above [4]. In fact, various dense advanced materials with rather uniform and fine microstructure are obtained relatively faster and at lower temperature levels by SPS, with respect to HP [4].

In the present study, the SPS technology is coupled with the Self-propagating High-temperature (SHS) technique, that 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 [5]. Specifically, the proposed processing route consists of first obtaining the desired UHTCs, i.e. ZrB_2-25 vol% SiC, HfB_2-26.5 vol% SiC, ZrB_2-40 vol% ZrC-12 vol% SiC, and HfB_2-40.6 vol% HfC-11.2 vol% SiC, via SHS starting from Zr or Hf, B_4C, Si, and graphite. The obtained products in powder form are then subsequently consolidated by using the SPS apparatus. The influence of the total sintering time and dwell temperature during SPS is systematically investigated for all systems. The resulting optimal products are then characterized in terms of

microstructure, oxidation resistance, hardness, fracture toughness, and the obtained results are compared with those reported in the literature relatively to analogous composites prepared using other fabricating routes.

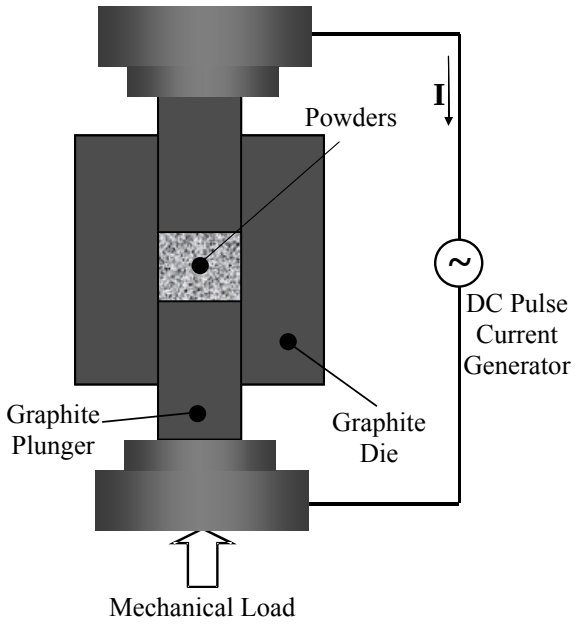

Fig. 1. Schematic representation of the Spark Plasma Sintering (SPS) system.

2. EXPERIMENTAL MATERIALS AND METHODS

The four different UHTC composites were prepared by SHS starting from reactants whose characteristics are reported elsewhere [6-7]. The initial mixtures were obtained by mixing reactants according to the following reactions:

$$2M + B_4C + Si \rightarrow 2MB_2 + SiC \quad (1)$$

$$8M + 2B_4C + 1.5Si + 3.5C \rightarrow \rightarrow 4MB_2 + 4MC + 1.5SiC \quad (2)$$

which correspond approximately to ZrB_2-25 vol% SiC, HfB_2-26.5 vol% SiC, ZrB_2-40 vol% ZrC-12 vol% SiC, and HfB_2-40.6 vol% HfC-11.2 vol% SiC, respectively. For the sake of simplicity, these systems will be indicated by ZS, HS, ZZS, and HHS, respectively, in what follows. Details on the experimental set-up used in this work for SHS and SPS are described elsewhere [5-7]. The consolidation stage by SPS is preceded by a ball milling step required to convert the obtained SHS porous products in powder form, following the procedure described in previous papers [6-7]. Here can be also found all the information related to the experimental procedure adopted for products characterization.

3. RESULTS AND DISCUSSION

According to the high enthalpy of reactions (1)-(2), i.e. 647.266 (ZS), 674.042 (HS), 2044.51 (ZZS) and 2315.634 kJ (HHS) [8], the synthesis of all four composites considered in this work exhibited a self-propagating character. Specifically, the maximum combustion temperatures and reaction front velocities were in the ranges of 2150-2250 °C and 7-11 mm/s, respectively.

SHS proceeded in all cases to completion with the formation of the desired composite constituents according to reactions (1)-(2). As examples, Figs. 2(a)-2(b) show the diffraction patterns of the obtained ZZS and HHS products along with those of the corresponding starting mixtures. All the major peaks related to the phases constituent the desired composites are present. Moreover, no other secondary phases including the impurities present in starting reactants when synthesizing the ZrB_2-based composites were found in the final product. This finding is likely a consequence of the typical self-cleaning character of the SHS process.

The obtained porous products were ball milled to lead powders with particles size < 70 μm and d_{50} in the range 2.51-7.23 μm, depending upon the system investigated.

SEM investigations conducted on all powders samples revealed that each SHS powder particle is a mixture of different phases consisting of MC, MB_2 (M=Zr or Hf), and SiC grains, each of them being typically less than 5 μm in size.

The sintering behavior of all composite powders synthesized by SHS was investigated using the SPS apparatus with the final goal of identifying the optimal operating conditions for obtaining fully dense UHTC products.

The dependence of products density on the SPS time (t_T) was studied in the range 0-30 min being the dwell temperature, T_D=1800 °C, the heating time t_H, which represents the time period set to reach the T_D value when starting from ambient temperature, equal to 10 min, and the mechanical pressure P=20 MPa. The obtained results are shown in Figs. 3(a)-3(b) for the ZZS, and HHS systems, respectively.

Analogous behavior is obtained for the ZS and HS

composites. It is seen that in all cases a fully dense material can be obtained at this temperature within 30 min. Figs. 3(a)-3(b) show that the ZrB_2-based composites densified relatively faster as compared to the HfB_2 systems. This is consistent to the higher refractory character of the Hf-borides and carbides., i.e. melting temperature of 3523 and 4103 K, respectively, relative to the Zr-based products, i.e. melting temperature of 3323 (ZrB_2) and 3805 (ZrC) [8]. Specifically, the maximum relative density levels achieved for each system are 99.6, >99.9, 98.7, and 98.5%, for the cases of ZS, HS, ZZS, and HHS, respectively.

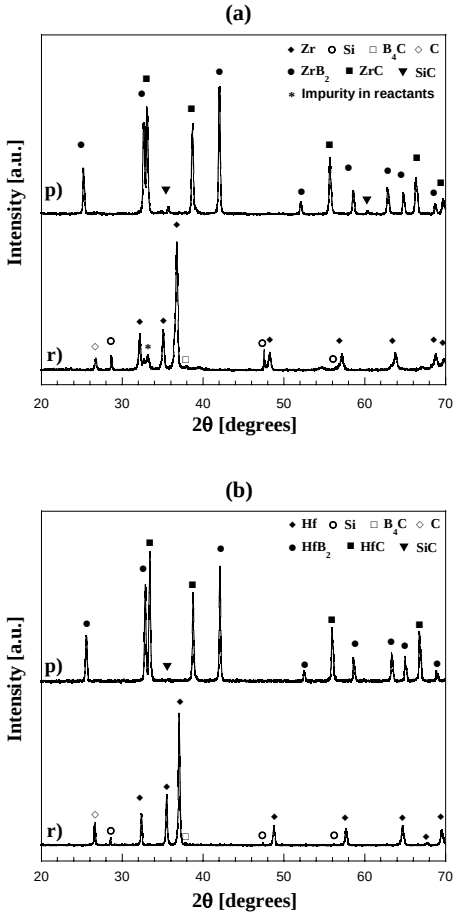

Fig. 2. Comparison of XRD patterns of r) starting reactants and p) products obtained by self-propagating high-temperature synthesis according to reaction (2): (a) ZZS, and (b) HHS.

Two SEM micrographs of the ZZS and HHS dense composites obtained in this work after consolidation by SPS under the conditions T_D=1800 °C, P=20 MPa, t_H=10 min, and t_T in the range 10-30 min depending on the system considered, are shown in Figs. 4(a)-4(b).

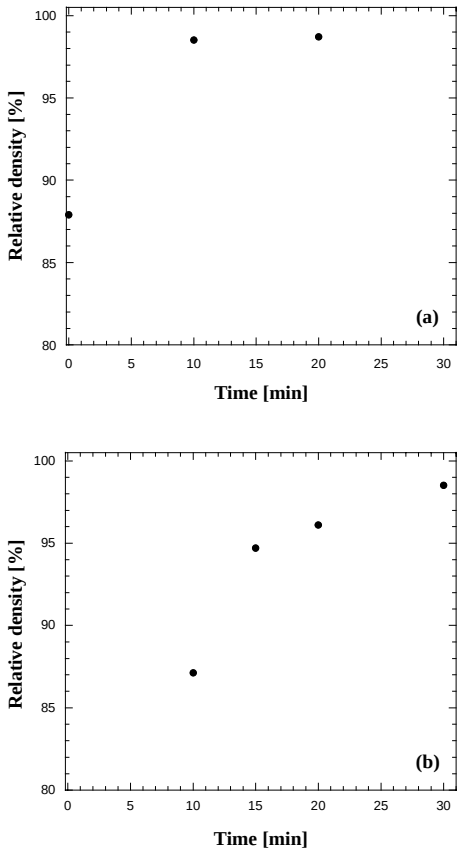

Fig. 3. Effect of SPS time on relative density of sintered ZZS (a), and HHS (b) powders synthesized by SHS (T_D=1800 °C, t_H=10 min, P=20 MPa).

It is seen that three different phases, distributed quite uniformly all over the sample, are easily distinguishable. As indicated in the Figures, the brighter, medium bright and darker zones correspond to ZrC (or HfC), ZrB_2 (or HfB_2), and SiC, respectively. The grain phase of each phase is less than 5 μm, i.e. slightly larger that the average grain size observed in the SHS powders. This is an indication of the fact that grain growth is not significant during SPS.

The mechanical properties of the SPSed UHTCs are summarized in Table 1 along with the corresponding relative densities. The best result in terms of both Vickers hardness and fracture toughness (K_{IC}) is obtained for the case of the HS system. Anyway, all values are comparable to, and in some cases better than, those reported in the literature for similar systems [7 and references therein].

For instance, the ZrB_2-20 vol% SiC and ZrB_2-6.4 vol%

ZrC-20 vol% SiC materials fabricated by Wu et al. [9] using the Reactive Hot Pressing method displayed Vickers hardness of 13.6-16.7 GPa and K_{IC} of 4.5-5.1 MPa $m^{1/2}$, respectively.

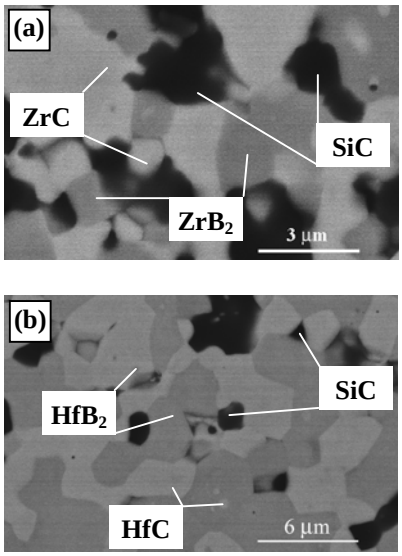

Fig. 4. SEM back-scattered micrographs of dense SPSed ZZS (a), and HHS (b) products.

Table 1. Properties of dense SPSed UHTC composites

System	Relative density [%]	Hardness [GPa] (Applied load)	K_{IC} [MPa $m^{1/2}$]
ZS	99.6	16.7 ± 0.4 (1 kg)	5.0 ± 0.3
HS	>99.9	19.2 ± 0.6 (10 kg)	7.0 ± 0.7
ZZS	98.7	16.9 ± 0.2 (10 kg)	5.9 ± 0.5
HHS	98.5	18.3 ± 1.1 (10 kg)	6.2 ± 0.7

The oxidation resistance of the composites produced in this work by the SPS method have been measured using TGA by monitoring the mass change of the sample subjected to an oxidizing environment (air) at high temperature. In particular, the results obtained during dynamic measurements (2 °C/min) and isothermal tests (1450 °C) are reported in Figs. 5(a)-5(b) for the cases of HS and HHS systems under 100 cm^3/min air flow. It is apparent that the binary system exhibits a remarkably higher resistance to oxidation.

Similar results are obtained when considering the ZS and ZZS samples. Moreover, they are comparable to those reported by other authors for UHTCs with analogous composition and prepared by alternative processing methods [10].

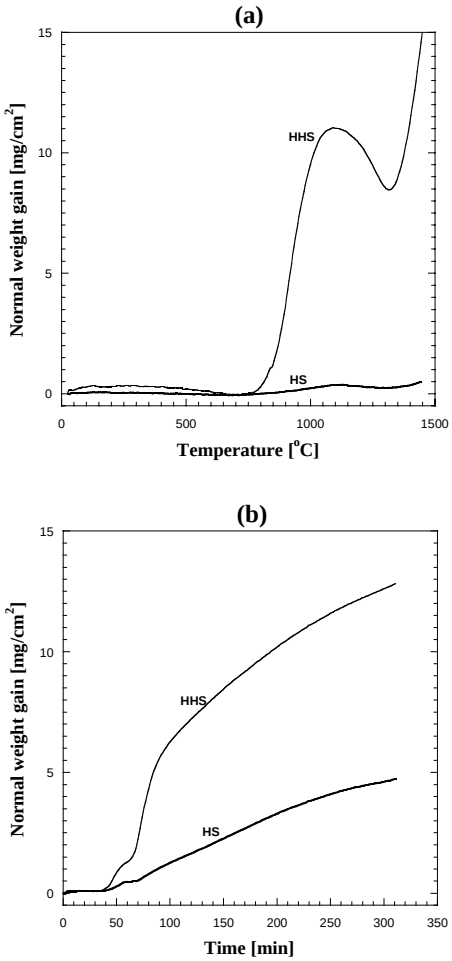

Fig. 5. Specific weight change during TGA oxidation in air of the sintered HS and HHS samples as a function of (a) temperature (non-isothermal run with the heating rate equal to 2 °C/min) and (b) time (isothermal run at 1450 °C).

Such oxidative behavior can be interpreted on the basis of several studies reported in the literature on this subject [10-12]. Briefly, the very volatile B_2O_3, obtained from the oxidation of MB_2 (M=Hf, Zr), i.e. $MB_2 + 2.5\ O_2 \rightarrow MO_2 + B_2O_3(l)$, combines with SiO_2 formed from SiC oxidation, i.e. $SiC + 1.5O_2 \rightarrow SiO_2 + CO$, to give a silica-rich borosilicate glass layer. The latter one reduces boria evaporation, other than acting as an oxygen diffusion barrier, thus providing improvement of oxidation resistance of the UHTC material. The fact that the ternary composites display relatively low resistance to oxidation,

can be related to the lower SiC content in the composite, in comparison with the case of binary systems, as well as to the presence of MC. In fact, although Hf and Zr carbides are potentially able to increase the resistance to ablation in the UHTCs, they oxidize rapidly to form MO_2 and carbon oxides. The formation of a porous product is then favoured, thus permitting the oxygen to diffuse through the bulk of the UHTC material.

4. CONCLUSIONS

In this work, a process consisting of two steps was adopted for the fabrication of fully dense MB_2-SiC and MB_2-MC-SiC (M=Zr and Hf) composites. The latter ones were first synthesized by SHS taking advantage of the highly exothermic character of the corresponding reactions of formation and the obtained powders were subsequently consolidated without the addition of any sintering aid using an SPS apparatus.

Based on the systematic study performed to evaluate the effect of the processing time on the densification process while maintaining the other parameters constant, i.e. T_D=1800 °C, P=20 MPa, and t_H=10 min, it was determined that near-fully dense products (≥98.5%) can be obtained for all systems investigated within 30 min of total processing time.

The characteristics of the resulting dense UHTCs, i.e. hardness, fracture toughness, and oxidation resistance, are similar to, and in some cases superior than, those related to analogous products synthesized by competitive methods. However, as a relevant difference, the adopted processing route is characterized by significantly shorter processing times and/or lower sintering temperature, when compared to the others fabrication methods proposed in the literature**.**

The fabricated MB_2-MC-SiC composites display relatively low resistance to oxidation while the binary systems exhibit low and thermally stable oxidation rate up to 1450 ^oC. This behaviour is likely a consequence of the oxidation of MC and the relatively lower SiC content in the ternary composites, being SiC responsible of the formation of a borosilicate glass able to protect the bulk material.

5. ACKNOWLEGMENTS

IM (Innovative Materials) S.r.l., Italy, is gratefully acknowledged for granting the use of SPS apparatus. The authors thank Eng. Leonardo Esposito (Centro Ceramico di Bologna, Italy) for performing hardness and fracture toughness measurements.

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