Production Of Fully Dense Zrb_2-Sic Uhtc Materials

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Two different synthesis/sintering routes are proposed in this work for the preparation of fully dense $2ZrB_2$-SiC UHTC (Ultra High Temperature Ceramic) composite. Both processes start from commercial powders of Zr, B_4C and Si, and take advantage of the Spark Plasma Sintering (SPS) apparatus. In the first one, it is possible to gradually synthesize and fully consolidate in a single step the UHTC material. This result is achieved under the optimal operating conditions of 20 min total time (t_T) and with a maximum temperature (T_D) of 1900 ^oC.
The second proposed method consists in first synthesizing the composite powders by SHS (Self-propagating High-temperature Synthesis) and subsequently consolidate them by SPS. In this case, the optimal operating conditions able to guarantee the obtainment of a fully dense material are T_D=1600 °C and t_T=30 min or T_D=1800 °C and t_T=20 min.
On the basis of the results reported in this work, it can be stated that the two proposed methods represent particularly rapid and convenient preparation routes as compared to the techniques available in the literature for the preparation of analogous materials.

1. Introduction

The so-called Ultra High Temperature Ceramics (UHTC) are ceramic-based materials characterized by extremely high melting points, i.e. higher than 3000 ^oC, which make them suitable as Thermal Protection Systems (TPS). In this contest, particular interest is focused on metal refractory borides such as zirconium diboride (ZrB_2) and hafnium diboride (HfB_2), which are considered potential candidate materials as TPS for space vehicles (Savino et al., 2005). Moreover, it is also well established that the addition of silicon carbide (SiC) to these materials strongly improves their oxidation resistance at high temperature as well as room temperature strength (Fahrenholtz et al., 2004).
Therefore, ZrB_2-SiC- and HfB_2-SiC-based composites have been investigated by several researchers and various techniques for their preparation have been developed. Most of the methods proposed in the literature (Licheri et al., 2007 and references therein) for the obtainment of ZrB_2-SiC-based products in bulk form make use of the Hot Pressing (HP) technique, through which commercial ZrB_2 and SiC powders are sintered. On the other hand, the reaction synthesis and densification in one step of the ZrB_2-SiC composite was also accomplished by reactive hot pressing (RHP), starting from Zr, SiB_4 and graphite (Opeka et al., 1999) or Zr, B_4C and Si (Zhang et al., 2000). Regardless of the two possible options, i.e. sintering or synthesis and densification in a single step, the main concern regarding the use of traditional hot pressing approach is related to its low heating rates which leads to relatively long processing times (typically of the order of hours).

A new sintering method, the Spark Plasma Sintering (SPS), where the starting powders, either to be only consolidated or simultaneously reacted, are crossed by an electric current, was recently developed. Mechanisms and phenomena on which SPS is based are not completely clarified yet. However, pulse current passing through processing powders is supposed to generate a plasma discharge within the voids among the particles (Omori, 2000). Typically, processes conducted using SPS allow to perform sintering at lower temperatures with respect to traditional hot pressing, and shorter times but anyhow sufficient to reach the complete densification of the material.
In the present study, we report two recently patented (Licheri et al., 2006) processing routes for the fabrication of ZrB_2-SiC (ZrB_2/SiC molar ratio 2:1, corresponding approximately to ZrB_2-25 vol. %SiC) UHTC products in bulk form starting from powders of Zr, B_4C and Si. Specifically, one of the two processes, hereafter called Reactive Spark Plasma Sintering (RSPS), is based on the product synthesis and densification performed in a single step by employing the SPS apparatus. Alternatively, the second fabrication process (SHS-SPS) consists in first obtaining the UHTC product in powder form by self-propagating high temperature synthesis (SHS) and, subsequently, consolidating it by using the SPS apparatus. Regarding the SHS technique, 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 (Varma et al., 1998).
In the present work, the influence of holding temperature and processing time related to the SPS apparatus on the RSPS or SHS-SPS fabrication routes is systematically investigated. The obtained optimal products are then characterized in terms of microstructure, hardness, fracture toughness and oxidation resistance. The results are compared with those reported in the literature relatively to analogous ZrB_2-SiC products prepared using other fabricating methods.

2. Experimental materials and methods

The starting mixture to be processed either by RSPS or SHS for the preparation of bulk ZrB_2-SiC products were obtained by mixing reactants according to the following reaction:

$$2Zr + B_4C + Si \rightarrow 2ZrB_2 + SiC \quad (1)$$

Characteristics and sources of reactants as well as details on the experimental procedure and set-up used in this work for SHS and SPS are described elsewhere for the sake of brevity (Cincotti et al., 2003; Locci et al., 2006; Licheri et al., 2007). Briefly, an SPS 515 apparatus (Sumitomo Coal Mining Co. Ltd, Japan) was used for consolidation of the obtained powders under temperature controlled mode. The SPS 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. During SPS, temperature, applied current, voltage, mechanical load and sample shrinkage (δ) were obtained in real time.

3. Results and discussion

3.1 Synthesis and simultaneous densification by RSPS

The formation of the UHTC composite during the SPS process was studied by investigating the influence of the processing time (t_T) on the composition of the

obtained RSPS products when the dwell temperature, T_D, was set equal to 1900 ^oC, the heating time, t_H, was 10 min, and P=20 MPa. As indicated by the compositional changes of the RSPS product observed as the reaction time increases (cf. Figure 1), the synthesis reaction of ZrB_2 and SiC starting from the Zr, B_4C and Si proceeds gradually. Specifically, the first evidence of product formation (ZrB_2) is found at 4 min (cf. Figure 1(c)), while all starting reactants are almost completely converted within 6 min (cf. Figure 1(g)) and a product containing only the desired carbide and boride phases is obtained at 8 min (Figure 1(h)). In addition, the maximum transformation rate is observed in the temporal range 4.5-5.5 min (cf. Figures 1(d)-1(f)).

Since the synthesis reaction is almost completed in less than 6 min, i.e. when the maximum temperature measured in the die was below 1200 °C, it is likely that the formation of the desired composite by the RSPS process is governed by a solid-state diffusion mechanism, because under these thermal conditions all starting reactants and final products are solid.

The evolution of densification phenomena during the synthesis of ZrB_2-SiC by RSPS can be deduced from Figure 2, where the end-products density is plotted as a function of the time intervals during which the current is applied.

It is seen that samples obtained when the time interval is less than 8 min show very high degree of porosity as a consequence of the incomplete sintering process, although the complete conversion is reached (cf. Figure 1). On the other hand, as the processing time is increased from 8 to 15 min, the relative density of the product increased markedly from 60 to about 98.5% of the theoretical value (5.37 g/cm^3). Moreover, a further increase of the synthesis time to 20 min or higher leads to fully dense products (relative density > 99.5% of the theoretical value).

These findings are important as they provide evidence that the conversion of starting reactants to the desired product contributes only modestly to the densification. In fact, higher densities are achieved only after the completion of the reaction through the sintering of the product. This is another, albeit indirect, evidence for the occurrence of the synthesis reaction between solid state phases.

The effect of dwell temperature, T_D, on the synthesis of ZrB_2-SiC by means of the RSPS process was subsequently studied by simultaneously applying a constant mechanical pressure (P=20 MPa) and setting different T_D values, i.e. 1400, 1600, 1800, 1850 and 1900 °C. The heating time, t_H, and the dwell time, t_D, were 10 and 20 min, respectively, in order to maintain a total synthesis time, t_T, equal to 30 min.

Although the complete conversion to the desired product is achieved in all cases, the situation is quite different from the densification point of view. In fact, as shown in Figure 3 where the effect of the dwell temperature on the density of the final product is reported, it is seen that the relative density of the RSPS product increased markedly, from 69% to values higher that 99.5% of the theoretical density, when T_D was augmented from 1400 to 1900 ^oC.

On the basis of the results reported above, it can be concluded that the optimal operating conditions able to guarantee the obtainment by RSPS of a fully converted and dense ZrB_2-SiC product are T_D=1900 °C, t_H=10 min, t_T=20 min, P=20 MPa.

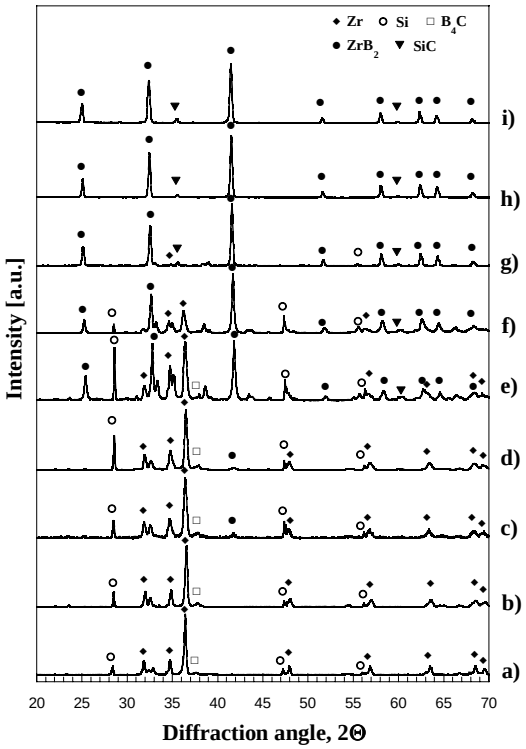

Figure 1. XRD patterns of RSPS products obtained for different values of the time interval during which the pulsed electric current is applied (T_D=1900 °C, t_H=10 min, P=20 MPa): a) Reactants; b) t_T=3 min; c) t_T=4 min; d) t_T=4.5 min; e) t_T=5 min; f) t_T=5.5 min; g) t_T=6 min; h) t_T=8 min; i) t_T=10 min.

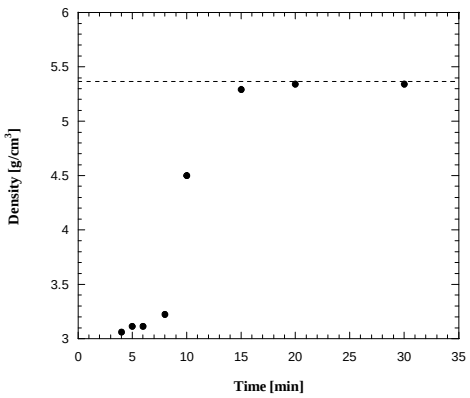

Figure 2. Densities of end-products obtained by RSPS as a function of the SPS holding time t_T (T_D=1900 °C, t_H=10 min, P=20 MPa). The dotted line indicates the theoretical density of ZrB_2-SiC (ZrB_2/SiC molar ratio equal to 2)

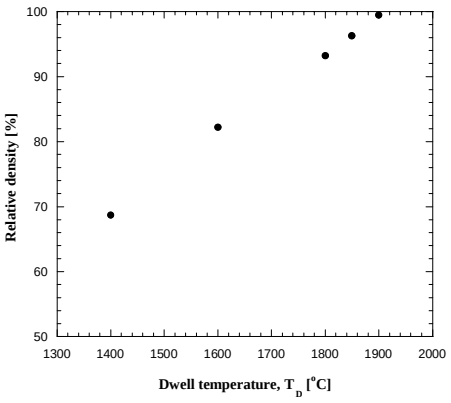

Figure 3. Relative densities of end-products obtained by RSPS as a function of the dwell temperature (t_H=10 min, t_T=30 min, P=20 MPa.).

3.2 Synthesis by SHS and densification by SPS

According to the high enthalpy of reaction (1), i.e. $-\Delta H_r^o$ = 647.266 kJ (Barin, 1993), the synthesis of the resulting $2ZrB_2$-SiC composite displayed a self-propagating behaviour. The maximum temperature value was about 2200°C and front velocity, as calculated from temperature profiles, was equal to 11±1 mm/s. The diffraction pattern of the obtained UHTC SHS product along with that of the starting mixture are reported in Figure 4. Phase analysis of diffraction patterns showed that reaction proceeds to completion with the formation of the desired boride and carbide products.

Since the final objective of this work is to obtain dense UHTC materials, the composite powders synthesized by SHS were processed in the SPS apparatus.

The dependence of products relative density on the SPS time was investigated when T_D=1800 °C, t_H=10 min, P=20 MPa (Licheri et al., 2007). It was found that a still porous product (90.3% of the theoretical value) is obtained at the end of the heating stage (10 min). However, the specimen was significantly densified as the sintering time was prolonged to 15 min (97.3 %) and, finally, a fully dense material (higher than 99.5 %) was produced when t_T=20 min.

The effect of dwell temperature, T_D, on the densification of the SHS ZrB_2-SiC powders was investigated by SPS in the range 1400-1800 °C, by maintaining constant the mechanical pressure (P=20 MPa) and heating time (t_H=10 min), while the cases of total processing time, t_T, equal to 20 and 30 min were considered. The obtained results are reported in Figure 5. 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, in order to guarantee the preparation of a fully dense material (relative density higher than 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).

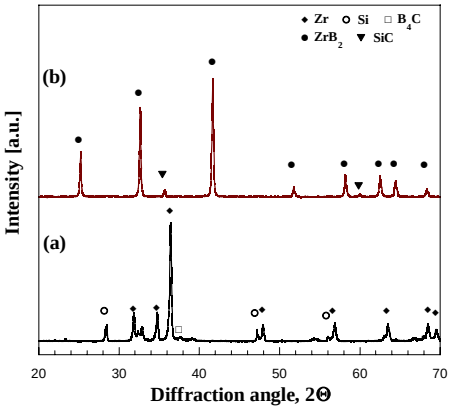

Figure 4. Comparison of XRD patterns of starting reactants (a) and the UHTC product (b) obtained by SHS according to reaction (1).

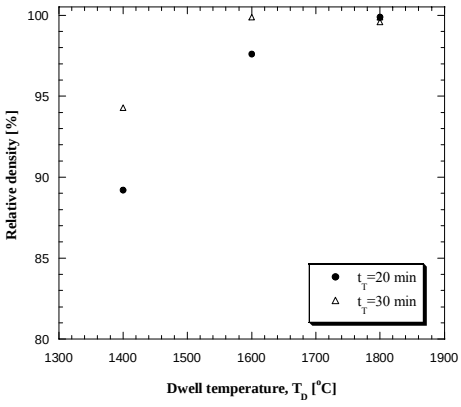

Figure 5. Effect of dwell temperature on relative density of sintered ZrB_2-SiC powders synthesized by SHS (t_H=10 min, P =20MPa.).

4. Concluding remarks

With the final goal of obtaining fully dense ZrB_2-SiC composite (ZrB_2/SiC molar ratio equal to 2) two different processing methods, i.e. the RSPS and SHS-SPS, are proposed and optimized in this work. Both processes start from commercial powders of Zr, B_4C and Si, and make use of the Spark Plasma Sintering (SPS) apparatus. Using the RSPS method, it was possible to synthesize and fully consolidate in a single step the desired UHTC material under the experimental conditions T_D=1900 ^oC, t_H=10 min, P=20 MPa. The other proposed method (SHS-SPS) consisted in two steps. The starting reactants were firstly reacted by SHS to form the ZrB_2-SiC composite. Subsequently, the SHS powders were completely densified by SPS under the optimal conditions T_D=1600 °C and t_T=30 min or T_D=1800 °C, t_T=20 min, and P=20 MPa.

The characteristics of the final products (hardness, fracture toughness, and oxidation resistance) are not reported here for the sake of brevity. However, the obtained results are similar to and, in some cases, better than the UHTC composites synthesized by competitive methods (Licheri et al., 2007 and references therein). In addition, both the RSPS and SHS-SPS processes are characterized by shorter processing times and lower sintering temperature, when compared to the others fabrication methods**.** In fact, the total time needed to obtain by RHP a dense ZrB_2-SiC product was 90 min (Opeka et al., 1999). Moreover, when considering pure sintering processes performed by HP, it was reported that 450 min, T=1900 ^oC, P=32 MPa were the conditions to obtain a near full dense ZrB_2/20-30 vol. % SiC (Fahrenholtz et al., 2004).

Therefore, it can be concluded that the two proposed reactive methods represent particularly rapid and convenient preparation routes to obtain completely dense UHTC products as compared to the other techniques reported in the literature. Such demonstrated advantages can be explained because both of them are based on the combination of *in-situ* methods for the synthesis of the ZrB_2-SiC composite, either directly carried out during the densification process or, preliminarily performed, by SHS, with the use of the very efficient SPS technique.

5. References

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