Effect of the Heating Rate on the Formation Mechanism of Zirconium Diboride by Reactive Spark Plasma Sintering

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The synthesis of ZrB_2 from elemental reactants via reactive spark plasma sintering (SPS) process is markedly affected by the heating rate conditions adopted. Specifically, when the temperature during SPS is increased at 500 °C/min or faster, the synthesis reaction proceeds under the combustion regime. On the other hand, if heating rates equal or lower than 200 °C/min are considered, the process is governed by a gradual solid-state diffusion mechanism. Although the route involving the combustion synthesis event permits the obtainment of pure dense products at relatively milder conditions, the gradual evolution of the synthesis reaction is preferable. Indeed, the inconveniences encountered during the process (gas pressure increase, powder expulsion, product inhomogeneity, abrupt sample displacement, die/punches breakage) make its practical exploitation difficult. In contrast, safety conditions are preserved when sufficiently lowering the heating rates to suppress the combustion reaction. Correspondingly, 96 % dense monolithic products can be obtained at temperature levels of about 2,000 °C within 30 min total time.

1. Introduction

Transition metal diborides and carbides belong to the general class of Ultra-High Temperature Ceramics (UHTCs) and exhibit a combination of unique properties such as melting temperature above 3,000 °C, high hardness, electrical and thermal conductivities, good chemical and oxidation resistances, which make them suitable for various high-temperature structural applications (Rapp, 2006). These materials are particularly interesting in the aerospace industry, for the fabrication of components for hypersonic vehicles able to withstand severe flow conditions (Fahrenholtz et al., 2007). Additional applications include electrical devices (heaters), selective solar absorber, electrodes, high-temperature crucibles, cutting tools, etc. (Fahrenholtz et al., 2007).

Among the various UHTCs, the most representative and investigated system is ZrB_2, which is, in addition to the other interesting properties previously indicated, particularly suitable also because of its relatively low theoretical density, i.e. about 6.1 g/cm^3 (Guo, 2009).

In spite of its advantageous properties, the intrinsically high refractory character of ZrB_2 powders makes their complete consolidation a difficult target to achieve and this fact represents one of the main reasons which hindered the diffusion and application of this promising class of ceramics (Sonber and Suri, 2011).

In this context, it is crucial to develop and utilize more efficient consolidation technologies with respect to classical Hot Pressing (HP), where high sintering temperatures and prolonged processing times (on the order of hours) are generally needed. To this aim, the relatively novel Spark Plasma Sintering (SPS) is well known to provide a useful tool for processing difficult-to-sinter materials (Orrù et al., 2009). The same technology can be also used to make reaction synthesis and densification in one single processing step, by the so-called Reactive SPS (RSPS), starting from appropriate reactants (Nikzad et al., 2013).

Along these lines, various investigations aimed to the fabrication of dense monolithic ZrB_2 are recently accomplished taking advantage of the SPS method (Guo et al., 2008). Alternatively to the classical approach based on the densification of commercial powders (Zamora et al., 2012), few studies have been also addressed to investigate the reactive sintering of ZrB_2 by RSPS (Yuan et al., 2012). However, to the best of

our knowledge, no information regarding the reaction mechanism governing the reactive SPS process for the synthesis of ZrB_2 was provided to date.

In the present work, the synthesis and simultaneous consolidation by SPS of monolithic ZrB_2 from elemental powders is systematically studied. Specifically, the attention will be mainly focused on the study of the effect of the heating rate on process dynamics, kinetic mechanism, as well as product characteristics (density and microstructure).

2. Experimental

The initial mixture, consisting of Zr (particle size < 44 μm, > 98.5 % purity, Alfa-Aesar) and B (amorphous, 95 – 97 % purity, Aldrich) powders combined according to the following reaction stoichiometry:

$$Zr + (2+x) B \quad \rightarrow \quad ZrB_2 \tag{1}$$

was processed by reactive SPS. An excess of B (x = 0.1) with respect to ZrB_2 was required to compensate boron partial loss occurring during the synthesis reaction due to the presence of oxide impurities (B_2O_3 and ZrO_2) in the original reactants. Specifically, ZrO_2 can be reduced by the excess of B, i.e.:

$$3ZrO_2 + 4B \quad \rightarrow \quad 3Zr + 2B_2O_3 \tag{2}$$

while B_2O_3 is a volatile specie.

About 3.2 g of the obtained mixture were reacted and consolidated in the form of cylindrical disks (about 15 mm diameter, 3 mm thickness) by Spark Plasma Sintering (SPS 515S model, Sumitomo Coal Mining Co Ltd) under vacuum conditions (about 20 Pa).

Details of the SPS apparatus and procedure are reported elsewhere for the sake of brevity (Musa et al., 2013). Briefly, during SPS runs, the current intensity was increased from zero at a constant rate up to a maximum level ($\bar{I}$) in a prescribed time interval t_H. Then, the $\bar{I}$ value was maintained for a certain duration t_D. The temperature profile follows the applied current, so that higher heating rates can be obtained by decreasing the t_H parameter. In particular, the latter one has been varied in the range 3 – 15 min. The mechanical pressure was applied from the beginning of each SPS experiment and was changed in the range 20 – 50 MPa. The reaction mechanism during RSPS was investigated by analyzing the samples obtained when the current application was interrupted at various time intervals $t_i \le t_f$, where $t_f = t_H + t_D$.

Relative density of polished SPSed ZrB_2 specimen was evaluated by the Archimedes' method and considering the theoretical value of 6.1 g/cm^3. All sintered materials were also characterized by phase composition (X-ray diffraction using a Philips PW 1830 X-rays diffractometer equipped with a Ni filtered Cu Kα radiation) and microstructure (Hitachi mod. S4000 SEM instrument equipped with a Kevex Sigma 32 Probe).

3. Results and discussion

The reactive SPS process for the preparation of bulk ZrB_2 was first investigated by setting t_H = 3 min. The related sample displacement (δ), gas pressure and temperature time profiles are shown in Figure 1(a) for the case when $\bar{I}$ = 1,200 A, P = 20 MPa and t_D = 20 min. Above the detection limit (approximately 600 °C) of the digital pyrometer, the measured temperature was observed to increase quite regularly, at an approximately constant heating rate of 500 °C/min, up to about 1,600 °C. Afterwards, the slope of the temperature profile decreases progressively to achieve the plateau value in the range 1,850 – 1,900 °C at the end of the SPS experiment.

As far as the sample displacement profile is concerned, Figure 1(a) shows that only modest changes were detected up to about 1.5 min from the beginning of the current application. In contrast, an abrupt variation in the δ parameter (about 5.3 mm) occurred in the narrow time interval $t_1 – t_2$. This event was recorded when the temperature of the die reached about 650 – 700 °C. Another important aspect in this regard is also represented by the corresponding sudden increase in the gas pressure (inset of Figure 1(a)) evidenced by the gas sensor installed inside the SPS chamber.

After the sharp sample shrinkage, the displacement curve first decreases down to about 4 mm and next gradually increases in a monotonic manner up to the end of the process.

The sudden displacement mentioned above can be ascribed to the occurrence of a combustion synthesis reaction. This statement was confirmed when examining the composition of the processing powders during the evolution of the reactive process (Figure 1(b)). Indeed, only original zirconium was evidenced by XRD at t = t_1, whereas boron was not detected by this analysis due to its amorphous nature. On the other hand, only the ZrB_2 compound, with no traces of neither elemental reactants nor other undesired phases, was found immediately after the sudden displacement change (t = t_2). Thus, it is possible to state that, under the heating rate conditions examined in the present case (t_H = 3min), the synthesis reaction (1) evolved under combustion

regime to convert completely the original powder into the desired product. This event is made possible by the strong exothermic character of the reaction for the formation of ZrB_2 from its elemental reactants, i.e. $-\Delta H_r^0$ = 322.586 kJ mol^{-1} (Barin, 1989). Hence, if the conditions for activating reaction (1) are achieved, a large amount of heat, in addition to that provided by the electric current (Joule effect), is rapidly liberated during the RSPS process. This fact is also responsible for the displacement decrease after its abrupt change, since thermal expansion of the sample undergoing sintering overcomes powders densification during this stage.

In spite of the marked change of the sample displacement during the reactive process, the relative density of the end-product was relatively modest, i.e. about 87 %. This feature could be ascribed to the relatively low mechanical pressure (20 MPa) applied for the entire duration of the sintering process. To improve the densification level, the applied mechanical pressure was then increased. In particular, according to recent findings reported in the literature on different monolithic UHTCs (Musa et al., 2011), a two steps mechanical load cycle, where the pressure was increased from 20 to 50 MPa immediately after the combustion synthesis takes place, was adopted. A material with density slightly higher than 95 % was correspondingly produced.
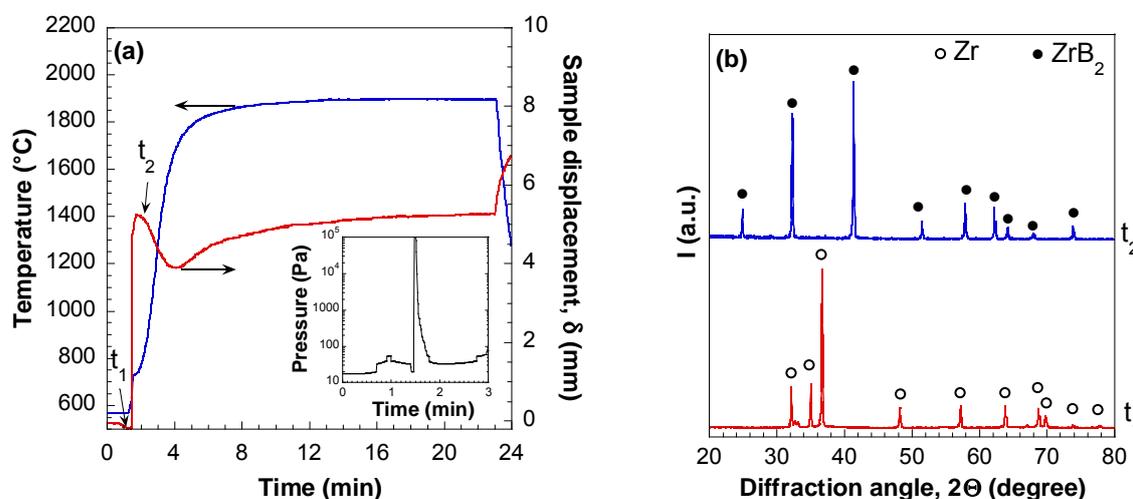

Figure 1: SPS output time profiles (a) and XRD patterns (b) of products obtained before and after the sharp sample displacement for the case of t_H = 3 min.

Unfortunately, it is important to note that the rapid sample shrinkage and the corresponding gas release observed during the combustion synthesis reaction are responsible for some negative consequences. Indeed, the sudden gas pressure increase was found to produce up to 30 wt. % powders losses. Although the expulsed material did not contain any unreacted powders, so that the prescribed reaction stoichiometry was preserved, it certainly represents a drawback for the fabrication of bulk ZrB_2 materials. This consideration holds also true when considering the characteristics of the resulting bulk products which displayed inhomogeneities in their microstructure.

As expected, the combustion regime was also established if the heating rate is further increased, i.e. when operating with t_H < 3 min. Correspondingly, the negative features described previously became even worst (dies/plungers breakage). In this regard, we caution the reader to operate under such conditions for the sake of safety.

Thus, in order to make the exploitation of the RSPS process for the obtainment of dense ZrB_2 possible, less critical conditions should be identified. Along these lines, the possible beneficial effects deriving when the heating rate value is decreased, i.e. t_H > 3 min, have been investigated.

In particular, the results obtained when the simultaneous synthesis and densification of ZrB_2 was conducted at t_H = 10 min will be reported and discussed in what follows. The related sample displacement, gas pressure and temperature time profiles are shown in Figure 2(a) when $\bar{I}$ = 1,300 A, P = 20 MPa and t_D = 20 min. Under the latter conditions, it is seen that the temperature of the die surface increases at a constant rate of approximately 200 °C/min up to 1,950 °C. Thus, the thermal equilibrium is shortly achieved at slightly higher temperature levels (2,000 °C).

In contrast to the behavior observed when setting t_H = 3 min, no sudden changes in the pressure profile is evidenced if t_H = 10 min (inset of Figure 2(a)). Indeed, the development of gases takes place gradually, so that they can be more easily expulsed from the powders container.

As far as the sample displacement curve is concerned, only negligible changes of this parameter were observed during the first 9.5 min from the current application, i.e. for temperature levels below 1,900 °C. On the other hand, as the temperature is further raised to its maximum level, δ increases with significantly higher rates to reach a value of about 2.4 mm in 2 min. During the progress of the RSPS process, such parameter varies modestly, thus reaching its maximum level of 2.9 mm at the end of the SPS experiment.

The effect of the heating rate decrease on the mechanism of formation of ZrB_2 can be inferred after examining the compositional changes of the processing powders during the RSPS process. To this aim, the XRD spectra of the samples corresponding to the different time intervals t_i indicated in Figure 2(a) are reported in Figure 2(b). The incipient formation of ZrB_2 was evidenced by XRD at t = t_1, when the temperature was slightly above the detection limit of the pyrometer. Subsequently, as the applied current was gradually increased, starting reactants were progressively converted to the diboride phase. Thus, as the temperature approached 1,400 °C (t = t_3), the complete reactants conversion is almost achieved. Indeed, only minor amounts of Zr, which are eliminated during the progress of the RSPS process, were correspondingly detected by XRD. It should be noted that the sample displacement did not vary up to this stage. Based on the relatively low temperature levels (≤ 1,400 °C) needed to complete the synthesis of ZrB_2 and minor sample shrinkage correspondingly observed, it is possible to state that the RSPS process conducted at heating rates equal to 200 °C/min is governed by a solid-state diffusion mechanism.
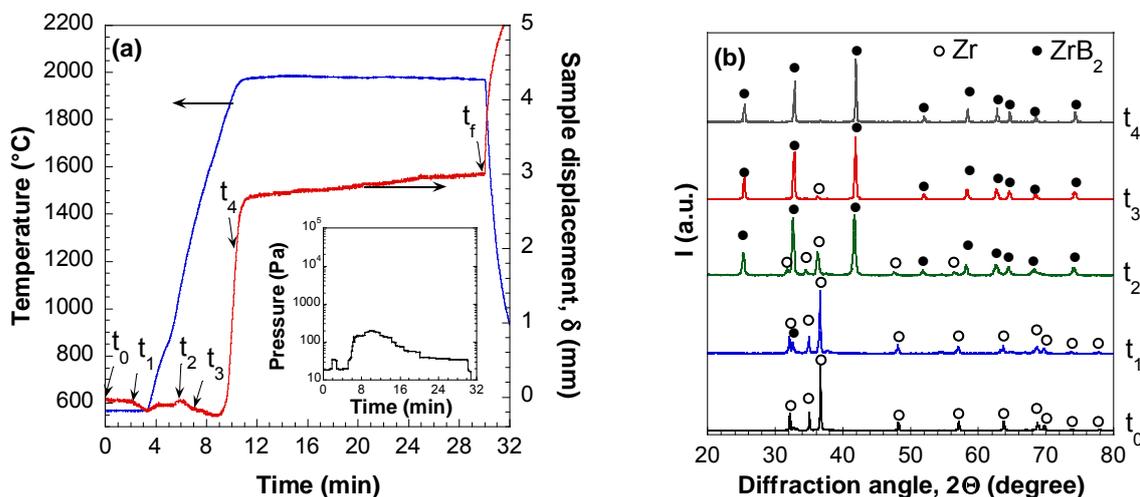

Figure 2: SPS output time profiles (a) and XRD patterns (b) of products obtained for different values of the time interval during which the pulsed electric current is applied for the case of t_H = 10 min.

To further support the latter statement, the specimens undergoing reactive SPS were analyzed by electron microscopy. In particular, a SEM micrograph relative to a sample processed at 200 °C/min, and obtained when the application of the electric current was interrupted before the complete reactants conversion (t = t_2 in Figure 2(a) – 2(b)), is shown in Figure 3(a).

It is seen that a ZrB_2 layer is formed around each Zr particle. As the synthesis reaction proceeds, B diffuses deeper and deeper through the formed ZrB_2 and the unreacted core shrinks in size. A single phase product is finally obtained at the end of the RSPS process (t = t_f in Figure 2(a)). The Archimedes 'method provided a density value of about 96 %. A SEM micrograph of the fracture surface of the end-product is shown in Figure 3(b). The reported microstructure confirmed the good level of consolidation achieved, with a residual amount of closed pores few microns sized.

As expected, the gradual solid-state diffusion regime is also observed when operating with t_H > 10 min. On the other hand, a peculiar situation was encountered, when the RSPS process was conducted with heating rates between 200 and 500 °C/min, i.e. 3 min < t_H < 10 min. Correspondingly, the two synthesis mechanisms discussed above were both randomly observed. To explain such dual behavior, the existence of a transition zone, where the two kinetic mechanisms are both possible, may be assumed. This outcome can be related to the heterogeneous nature of the starting powders mixture, so that the interfaces established between reactants might be locally different within the sample. The occurrence of a combustion reaction might be also

anticipated if the electric current or the applied pressure are not uniformly distributed across the sample. Therefore, if one or all the conditions above are met, hot spots or more reactive areas may be encountered inside the compact. Consequently, the synthesis reaction might be locally activated and the generated reaction front self-propagates through the sample even when heating rates lower than 500 °C/min are set. As stated above, in order to avoid the establishment of the combustion regime during the RSPS process, the electric current should be increased more gradually, i.e $t_H \geq 10$ min, for the system taken into account in the present work.
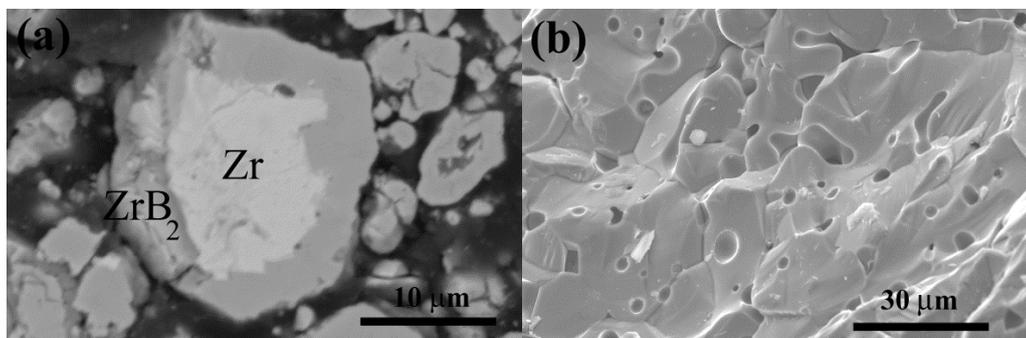

Figure 3: evolution of the microstructure of samples obtained by reactive SPS when t_H = 10 min ($\bar{I}$ = 1,300 A, P = 20 MPa, t_D = 20 min): (a) t = t_2 and (b) t = t_f in Figure 2(a).

4. Summary and concluding remarks

The reactive Spark Plasma Sintering process for the fabrication of ZrB_2 from elemental reactants can be conducted, depending upon the heating rate conditions, under two different regimes. Specifically, when the temperature was increased at 500 °C/min or faster, the synthesis process evolved under the combustion mode. On the other hand, a gradual solid-state diffusion mechanism governs the reactive process conducted with heating rates equal or lower than 200 °C/min.

When the first heating rate condition was considered, the combustion synthesis reaction was activated as soon as the temperature of the die was about 750 °C. Correspondingly, the initial reactants were rapidly and fully converted to ZrB_2. However, highly dense products could be obtained only after the dwell time at the maximum temperature (1,850 – 1,900 °C) or the applied mechanical pressure level were increased. Regarding the latter parameter, a significant improvement in sample consolidation (density higher than 95%) was obtained when the applied pressure was switched from 20 to 50 MPa immediately after the synthesis reaction.

Alternatively, when the heating rate was decreased down to 200 °C/min or lower values, the transformation of elemental reactants to ZrB_2 took place gradually. The presence of a solid-state diffusion mechanism is supported by the corresponding SPS process dynamics, specifically the negligible sample shrinkage, and the relatively low temperature levels (below 1,400 °C) required to complete the synthesis reaction. A pure dense product (relative density of about 96 %) was obtained when an electric current of 1,300 A was applied for 20 min along with a mechanical pressure of 20 MPa.

In spite of the advantages observed when the synthesis reaction evolves under the combustion regime, i.e. lower current (temperature) levels and shorter processing times are needed, its practical exploitation is hindered by several drawbacks. Indeed, when the strong exothermic reaction taking place within the die/plungers ensemble (confined environment) leads to a sudden gas pressure increase, caused by the volatile species instantaneously liberated during the combustion synthesis event. This fact not only determined the expulsion of significant amount of powders from the die, but also negatively affected the microstructure of SPSed products. Furthermore, the abrupt sample displacement taking place during the synthesis reaction should be avoided, or carefully controlled, for safety reasons, as it may lead to die/punches breakage. All these aspects certainly indicate that, in view of a possible process scale-up for the fabrication of ZrB_2 by reactive SPS, heating rates should not exceed certain critical values, so that the occurrence of combustion synthesis event can be suppressed.

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