

Influence of Mechanical and Electric Current Activation on the Mechanism of Formation and the Properties of Bulk B_4C - TiB_2 Composites Obtained by Reactive Sintering

Leila Nikzad^{a,b}, Roberto Orrù^{*a}, Roberta Licheri^a, Giacomo Cao^a

^aDipartimento di Ingegneria Meccanica, Chimica e dei Materiali, Unità di Ricerca del Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM) - Università degli Studi di Cagliari, Piazza D'Armi, 09123 Cagliari, Italy

^bDivision of Nanotechnology and Advanced Materials, Materials and Energy Research Center, Tehran, Iran, P.O. Box 14155-4777
 roberto.orrù@dimcm.unica.it

The preparation of dense nanostructured B_4C - TiB_2 is investigated through the combination of mechanical (Ball Milling) and electric current (Spark Plasma Sintering or SPS) activation of Ti, B and graphite powders. The full conversion of 8h milled reactants is obtained at much lower temperature (about 1200 °C), as compared to simply blended mixtures (>1600 °C). The formation of TiB_2 generally precedes that of B_4C . In addition, regardless of the milling treatment, an increase of the heating rate during SPS is found to produce a transition of the mechanism governing the formation of TiB_2 and B_4C , i.e. from gradual solid-solid to rapid combustion-type behavior. However, when unmilled powders are used, unreacted and intermediate species are still present in the product resulting after the combustion synthesis reaction takes place during sintering. In contrast, ball milled powders reacted completely under combustion regime, even when relatively milder heating rate conditions are adopted. SPS product density increases from about 82 % to 94 % of the theoretical value ($I = 1100$ A), as a consequence of the mechanical treatment. Correspondingly, a material with homogeneous phase distribution and grain size down to 100-200 nm is obtained. A further improvement of product density (> 96.5 %) is produced, at the expenses of a certain grain growth, when the applied current intensity is augmented to 1200 A.

1. Introduction

Due to their peculiar properties, noticeable research efforts have been made in recent years for the identification of suitable techniques for the fabrication of dense nanostructured materials, in which the grain size has to be, at most, few hundreds of nanometers (Koch, 2002). Specifically, when considering highly refractory ceramic products (borides, carbides, etc.), while the obtainment of nanosized powders is a relatively easy goal to achieve, the conventional Hot Pressing (HP) method typically requires very high temperatures and pressures, as well as prolonged processing times to overcome the intrinsic low sintering ability of these powders (Koch, 2002). This aspect holds also true when performing reactive sintering, where the reaction synthesis and densification is accomplished in a single step starting from appropriate reaction promoters. In addition, under the needed processing conditions, a significant grain growth occurs and the resulting bulk products generally exhibit coarse microstructure, regardless of the starting powders characteristics. Therefore, it is quite challenging to identify appropriate experimental protocols involving consolidation techniques which are able to preserve the nanostructure.

In this regard, one of the possible strategies recently proposed takes advantage of a relatively novel sintering technology, the Spark Plasma Sintering (SPS), where the starting powders, either to be only consolidated or simultaneously reacted, are crossed by an electric pulsed current (Orrù et al., 2009). The more favourable sintering conditions (lower temperature levels, higher heating rates and shorter dwell times) obtained by SPS, with respect to HP, avoid excessive grain growth and typically lead to materials

with relatively finer microstructure. In this context, a valid contribution towards this goal could be also provided through the mechanical treatment by ball milling (BM) of the powders to be sintered. Indeed, it is well known that BM is able to produce, by means of the so-called mechanical activation, grains refinement at the nanoscale and interface formation between particles, thus enhancing powders reactivity (Suryanarayana, 2001; Takacs et al., 2001; Locci et al., 2006; Licheri et al., 2010; Todde et al., 2011). Chemical and structural changes induced by BM are strictly related to the intensity of the mechanical treatment, which is typically regulated through the appropriate choice of the milling time and the ball to powder weight ratio (charge ratio) (Suryanarayana, 2001).

Along these lines, the simultaneous synthesis and densification by SPS of B_4C/TiB_2 composite (molar ratio equal to 1:1) starting from ball milled Ti, B and graphite reactants is investigated in the present study. In this regard, it should be noted that B_4C -based ceramics are very attractive materials in various innovative and traditional industrial fields, due to the combination of their outstanding hardness, high melting point, light weight, wear resistance, chemical stability, neutron absorption properties, etc. (Thevenot, 1990). In addition, the presence of TiB_2 is found to improve sintering ability and intrinsic brittleness characteristics.

The effect of the milling treatment, the heating rate conditions and the applied current level on the reactive SPS (RSPS) process dynamics, reactants conversion, reaction mechanism, relative density, and product microstructure, are examined systematically in the this work.

2. Experimental materials and methods

Commercial Ti ($< 125 \mu m$, 99.5 purity, Merck), B (amorphous, $< 9 \mu m$, 95-97 % purity, Aldrich), and graphite ($< 20 \mu m$, Aldrich) powders were co-milled in a stoichiometric ratio according to the following reaction:



BM experiments, consisting of reiterated cycles of 1 h of milling followed by 1 h cooling, were conducted under Ar atmosphere in a shaker mill, using stainless steel vials and balls. In particular, powders milled for 8 h with a charge ratio, CR equal to 8 were prepared for RSPS experiments.

The 515S model SPS apparatus (Sumitomo Coal Mining Co. Ltd, Japan) was used to simultaneously react and consolidate the milled powders. This equipment combines a 50 kN uniaxial press with a 15 V, 1500 A DC power supply to provide a pulsed current through the powders and the die containing them. For comparison, simply blended (unmilled) reactants were also processed by SPS. About 2.5 g of powder mixture was placed inside a cylindrical graphite die with outside diameter of 30 mm, inside diameter of 15 mm, and 30 mm high. RSPS experiments were conducted in vacuum conditions (20 Pa) using the sintering apparatus under current controlled mode, by increasing, at a constant rate in a prescribed time interval (t_H), the average electric current from zero to a maximum value in the range of 1100-1200 A. The chosen current level (I) was then maintained for additional 5 min (t_D). The influence of the heating rate was investigated by changing the t_H value in the range 1-5 min, while the mechanical pressure was held constant to 20 MPa. The study of the mechanism of formation of the B_4C - TiB_2 ceramic during RSPS was conducted by analyzing the samples obtained when the current application was interrupted at various time intervals $t_i \leq t_f$, where $t_f = t_H + t_D$. Further details on SPS experiments can be found elsewhere (Licheri et al., 2010). All sintered materials were characterized by density measurement, phase composition and microstructure analysis. The theoretical density of the composite product (3.33 g/cm^3) was evaluated on the basis of B_4C (2.5 g/cm^3) and TiB_2 (4.5 g/cm^3) densities, using a suitable rule of mixture.

The average grain size of powdered samples was estimated by means of the Williamson and Hall method (Williamson and Hall, 1953) from the line broadening of XRD peaks.

3. Results and Discussion

The sample displacement (δ) and temperature time profiles measured during SPS ($I=1100 \text{ A}$, $P=20 \text{ MPa}$, $t_D=5 \text{ min}$) of unmilled powders when $t_H=5, 3$ and 1 min are shown in Figures 1(a)-1(c), respectively. The related compositional changes may be seen in Figures 2(a)-2(c).

Let's examine first the case when $t_H=5 \text{ min}$ (cf. Figure 1(a) and 2(a)). Although no variation of δ occurred up to $t_f=225 \text{ s}$ ($T=1070 \text{ }^\circ\text{C}$), the formation of TiB_2 and TiB phase (in traces) is already evidenced by XRD. Due to the relatively low temperature levels achieved, the presence of molten phases can be excluded, so that a solid-solid mechanism likely takes place. In particular, the chemical interaction of Ti and B is expected to lead first to the formation of Ti monoboride, i.e.:



that is subsequently converted to TiB_2 , according to the following reaction path:



A small and gradual increase of sample displacement is observed during the RSPS progress up to $t_2=250$ s, when the measured temperature is about 1220 °C. Correspondingly, the XRD analysis evidences a marked increase of TiB_2 peaks intensity, confirms the presence of TiB in the product, and indicates the formation B_4C . The appearance of the latter phase, which is accompanied by the graphite peak decreasing, could be then explained on the basis of the reaction:



The obtained results are consistent with previous literature studies, where the synthesis by SPS of B_4C from amorphous B and carbon black was reported to occur at about 1200°C (Anselmi-Tamburini et al., 2005). Figure 2(a) also indicates that significant amounts of reactants and intermediate species are still present at t_2 . These phases tend to disappear progressively and only traces of TiB are found when the temperature level approaches about 1600 °C at t_3 . Therefore, the latter condition can be regarded as the minimum T value required for the completion of the synthesis reaction when $t_H=5$ min.

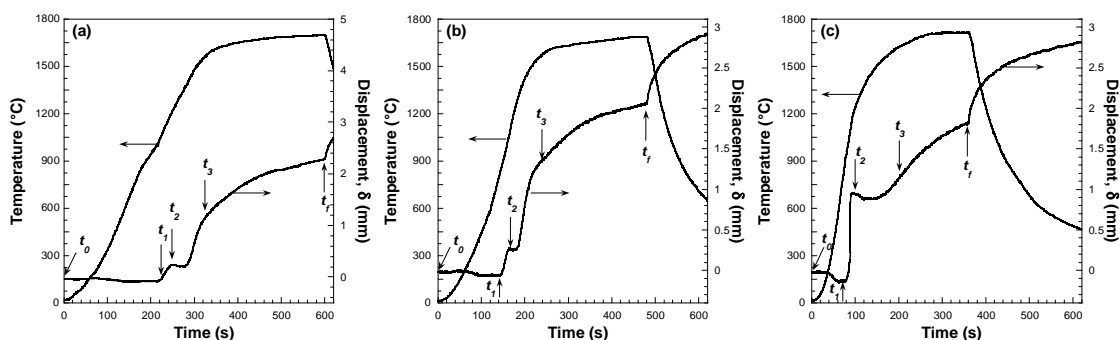


Figure 1: Temperature and sample displacement time profiles during SPS when using unmilled reactants: (a) $t_H=5$ min, (b) $t_H=3$ min and (c) $t_H=1$ min

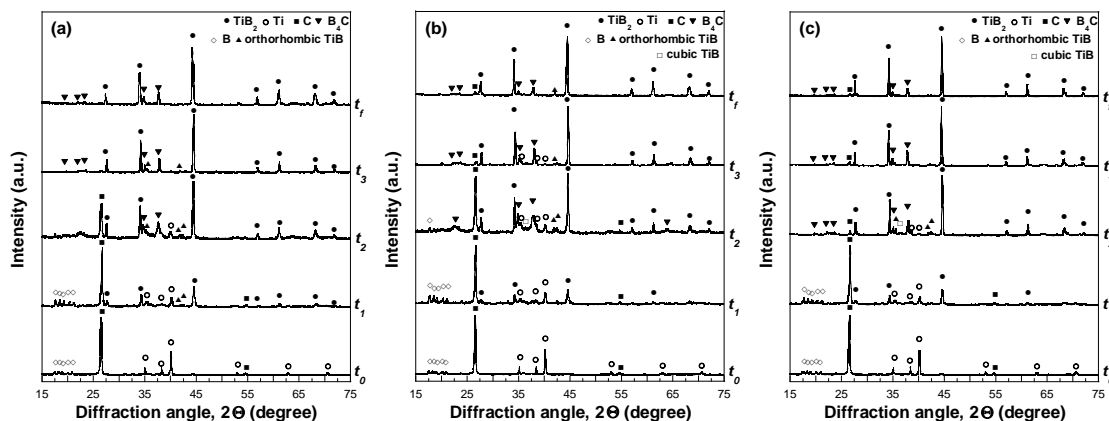


Figure 2: XRD patterns of SPS products obtained starting from unmilled reactants: (a) $t_H=5$ min, (b) $t_H=3$ min and (c) $t_H=1$ min

The influence of the heating rate on the kinetics of the reactive process and product composition can be seen from the results shown in Figures 1(b)-1(c) and 2(b)-2(c), where the SPS outputs (T and δ) and the related XRD patterns are reported for the cases of $t_H=3$ and 1 min, respectively. Similarly to the situation described above, the synthesis of TiB_2 - B_4C composite when $t_H=3$ min (Figures 1(b)-2(b)) follows a gradual solid-solid mechanism and is completed only when $T>1600$ °C. In contrast, the unmilled system behaves quite differently when the heating rate is further increased ($t_H=1$ min) during RSPS (cf. Figures 1(c)-2(c)). First of all, a marked and sharp sample shrinkage of about 1 mm is seen within the narrow time interval t_1 -

t_2 . Moreover, the rapid formation of TiB_2 , the presence of B_4C and a significant reduction of the graphite signal are correspondingly evidenced by XRD. Therefore, when t_H was set equal to 1 min, both composite constituents are formed during the occurrence of the abrupt compact displacement, to indicate that reactions (2)-(4) take place in a very short time interval. According to similar experimental findings reported in the literature (Orrù et al., 2009), the sharp sample displacement represents a manifestation of the occurrence of rapid combustion synthesis reactions. Such assumption is also supported by the decrease of δ observed for a certain time period after t_2 (Figure 1(c)), due to the heat released by the exothermic event, with consequent thermal expansion of the sample undergoing sintering.

As seen from the XRD results reported in Figure 2(c), residual Ti, graphite and TiB are still found in the sample after the combustion synthesis reaction. However, such secondary species are almost fully eliminated at $t=t_3$, when T is about 1600 °C, analogously to the results obtained at slower heating rates.

Density measurements indicate that powders densification is anticipated as t_H is decreased, although relatively highly porous specimens (only 82 % dense) are produced regardless the heating rate adopted. Therefore, the correspondingly different kinetic mechanism taking place seems to play a marginal role on product densification.

The RSPS process dynamics and end-products characteristics is now examined for the case when the 8h milled powders are processed by SPS at the different heating rates considered for unmilled reactants. The sample shrinkage temporal changes are plotted in Figures 3(a)-3(c) while the corresponding evolution of product composition are shown in Figures 4(a)-4(c) for the cases of $t_H=5$ min, 3 min and 1 min, respectively. It should be noted that the T profiles are not reported, since only modest differences are found as compared to those ones displayed in Figures 1(a)-1(c) relatively to unmilled powders. First of all it is seen that the milling treatment ($t=t_0$ in Figures 4(a)-4(c)) causes a marked XRD peaks broadening, as a consequence of grains size refinement and internal strain increase, and the formation of TiB and TiB_2 . The latter finding can be readily motivated by the increase of the interfacial area between reactants subjected to BM. In this regard, SEM investigations indicate that Ti grain sizes after the 8 h BM treatment fall in the nanometer range (50-150 nm).

The combined analysis of Figures 3(a) and 4(a) reveals that, although sample shrinkage becomes significant only when $t > t_2$, marked changes in product composition are obtained for shorter time intervals. In particular, when the T level of about 860 °C was achieved at t_1 , the contents of both TiB_2 and TiB start to increase at the expenses of Ti, according to reactions (2) and (3). TiB_2 becomes the dominant phase in the product 30 s later (t_2), while only minor amounts of TiB are detected, thus evidencing the prominent role played by reaction (3). At this stage, the application of the Williamson-Hall method provides a value of about 50 nm for the average grain size of TiB_2 . The preservation of the nanostructure is explained by the low temperatures required for such solid-state chemical transformations. The appearance of B_4C peaks in the XRD pattern is evidenced at $t_3=240$ s, when T was about 1200 °C, while sample displacement shows only a modest increase. A significant TiB_2 peaks narrowing is correspondingly observed, to denote a certain grains coarsening. In any case, the average grains size estimated using the Williamson-Hall formula still falls in the nanometric range (< 100 nm). This holds also true until the end of the experiment (t_f). On the basis of the obtained results, it is possible to state that the RSPS process conducted at $t_H=5$ min using 8 h milled powders is still governed by a solid-solid mechanism, as for the case of unmilled reactants. Nevertheless, full conversion is achieved at relatively lower temperatures, i.e. about 1200 °C instead of 1600 °C. This outcome can be readily justified by the role played by the BM process to reduce powders size and promote interfacial formation between reactants, both of which facilitate mass transport by diffusion and, therefore, the occurrence of synthesis and sintering processes.

A completely different situation is encountered when setting $t_H=3$ min (cf. Figure 3(b)), where the sharp, albeit small, sample displacement evidenced in the short time interval t_1-t_2 corresponds to the sudden and complete formation of TiB_2 and B_4C (cf. Figure 4(b)). This outcome clearly indicates that the synthesis process takes place under combustion regime. As seen in Figures 3(c)-4(c), such behaviour is confirmed when still increasing the heating rate ($t_H=1$ min). Although a qualitatively similar RSPS dynamics was also manifested when processing unmilled powders at $t_H=1$ min (cf. Figures 1(c)-2(c)), the corresponding reaction did not go to completion in that case. Furthermore, the results described above show that relatively low heating rates ($t_H=3$ min) are sufficient to activate the combustion synthesis process when using 8 h milled powders.

The milling treatment also provides a marked positive effect on powder densification. Indeed, specimens obtained at the end of the process (t_f) display, regardless of the heating rate conditions, relative densities of about 94 %, that are significantly higher with respect to the samples produced when processing simply blended powders (82 %) under the same SPS conditions ($I=1100$ A).

The microstructure of the obtained final products corresponding to the different t_H values considered are shown in Figures 5(a)-5(c). A very homogeneous and fine-grained microstructure is generally obtained, to indicate the beneficial influence of BM towards the obtainment of massive $\text{TiB}_2\text{-B}_4\text{C}$ composites with good phases distribution and small-sized grains. Such result is a consequence of the combined effect of reactants/products grain refinement, the interface formation between reagents and intermediate species, as well as the formation of nanostructured TiB and TiB_2 during milling. The beneficial contribution of product formation during BM for the fabrication of dense nanostructured ceramics by RSPS was also evidenced when processing other systems (Orrù et al., 2009). Indeed, the presence of these species provide large amounts of crystallization seeds, able to promote nucleation rate, instead of grains growth, during the RSPS process, thus leading to a fine grained microstructure.

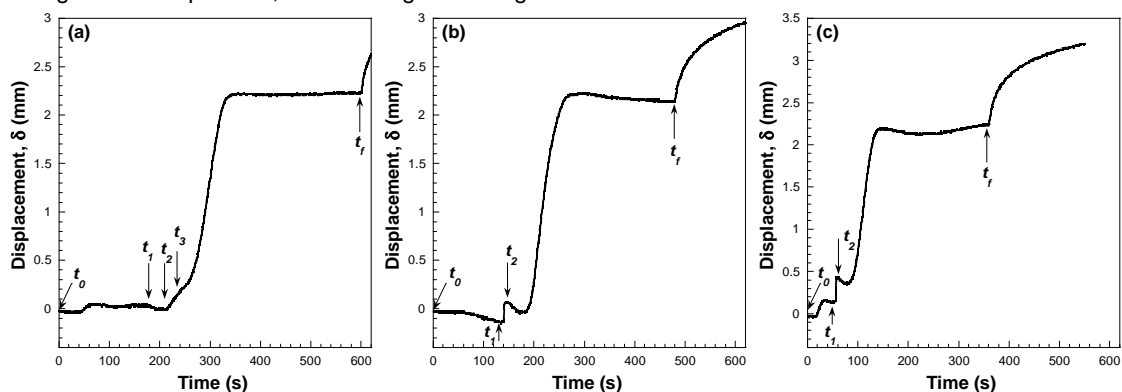


Figure 3: Sample displacement time profiles during SPS when using 8h milled reactants: (a) $t_H=5$ min, (b) $t_H=3$ min and (c) $t_H=1$ min

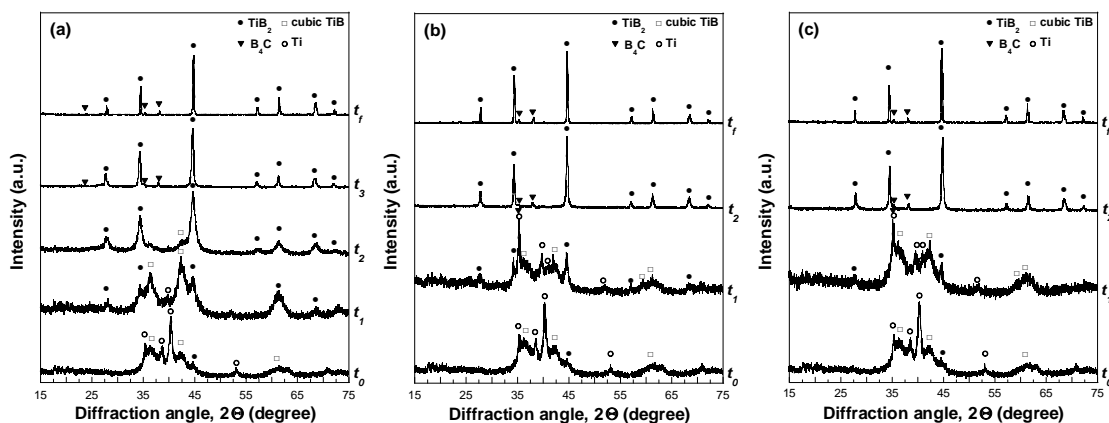


Figure 4: XRD patterns of SPS products obtained starting from 8h milled reactants: (a) $t_H=5$ min, (b) $t_H=3$ min and (c) $t_H=1$ min

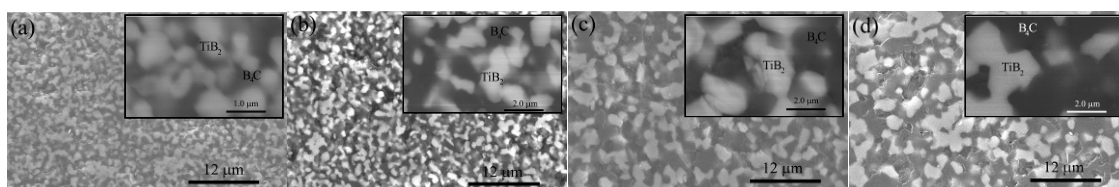


Figure 5: SEM micrographs of SPS products obtained starting from 8h ball milled reactants: (a) ($I=1100$ A, $t_H=5$ min) (b) ($I=1100$ A, $t_H=3$ min), and (c) ($I=1100$ A, $t_H=1$ min), (d) ($I=1200$ A, $t_H=5$ min)

Figure 5(a) shows that, for the case when $t_H=5$ min, grains of both ceramic phases are generally in the range 100-200 nm. When the heating rate is augmented, product microstructure becomes slightly coarser, with grains size that is found to increase up to about 2 μm at $t_H=1$ min (Figure 5(c)). Such behaviour can be associated to the combustion reaction mechanism involved. Indeed, the heat released during the occurrence of exothermic reactions produces powders local heating. Consequently, although the

measured temperature of the die is relatively low (cf. Figures 1(a)-3(a)), the actual thermal levels achieved by the powders undergoing reactive SPS are relatively higher and may lead to a certain grain growth. In contrast, the latter phenomenon is expected to be less important when the t_H parameter is increased, since the chemical transformations take place more gradually. Thus, relatively slow heating rates seem to be more favourable to preserve the nanostructure during the fabrication of dense B_4C-TiB_2 by RSPS.

In order to further improve sample density with respect to the value of about 94 % obtained at 1100 A, the applied electric current intensity is increased up to 1200 A, while maintaining unchanged the other SPS conditions. Products with relative density of 96.7 ($t_H=1$ min) and 97.8 % ($t_H=5$ min) are correspondingly obtained. In both cases, the maximum temperature recorded at the end of the sintering process was about 1820 °C, i.e. about 100 °C higher than that measured at 1100 A. The improved densification can be readily explained by the increased electrical power correspondingly supplied to the system undergoing sintering. The higher T achieved by Joule effect clearly promotes the occurrence of powders sintering, although other possible phenomena (electromigration, etc.) may be also activated or enhanced by the increase of the electric current intensity (Orrù et al., 2009). A SEM micrograph of the bulk product obtained at 1200 A when $t_H=1$ min is shown in Figure 5(d). It is seen that a sufficiently good homogeneity in phases distribution is maintained while the grains size of TiB_2 and B_4C tends to increase as compared to the lower current case (1100 A) displayed in Figure 5(a). The higher temperature reached when increasing the I value represents the most direct explanation for the observed grains coarsening.

4. Concluding remarks

The fabrication of dense fine grained B_4C-TiB_2 composite from elemental powders is studied in this work through the combined use of ball mill and Spark Plasma Sintering (SPS) facilities. The mechanism governing product formation is found to be markedly affected by the mechanical activation of reactants as well as the heating rate adopted during the SPS process. First of all, the full conversion of 8 h milled powders to the TiB_2-B_4C composite is achieved at much lower temperatures (about 1200 °C), as compared to unmilled reactants (>1600 °C). In addition, when the latter ones are processed at relatively low heating rate conditions, the desired product is formed through relatively slow solid-solid reactions. In contrast, when the same powders are more rapidly heated during SPS, a combustion synthesis process occurs but the resulting product also contains not negligible amounts of unreacted and intermediate phases. Sample density obtained by SPS when $I = 1100$ A increases from about 82 % to 94 % after 8 h BM treatment. In addition, a composite material with homogeneous phase distribution and fine-grained microstructure is produced when using mechanically activated powders. In this regard, the best result is obtained at relatively low heating rate conditions, when the average grain size of both ceramic phases is in the range 100-200 nm. Finally, an improvement of product density (>96.5 %), accompanied by a certain grain growth, is obtained when the applied current intensity is increased to 1200 A.

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