Simultaneous Spark Plasma Synthesis and Densification of TiC-TiB₂ Composites

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The simultaneous synthesis and densification of dense TiC-TiB₂ composite has been investigated starting from Ti, B₄C, and C as reactants, and using the spark plasma sintering (SPS) technique. The optimal conditions for complete conversion of the reactants to the composite were determined for different applied DC current levels. A kinetic investigation performed allows us to conclude that solid-state diffusion is the mechanism governing the synthesis process. It is seen that TiC is the first phase formed, while TiB₂ formation occurs afterward. Two intermediate boride phases, i.e. TiB and Ti₃B₄, are also formed but, as the SPS holding time was augmented, they were gradually and completely converted to TiB₂. Moreover, it is found that in order to reach relatively high dense products, an electric current needs to be applied for time intervals longer than those required for obtaining complete conversion. A pure dense product (relative density \sim 98%) was obtained when an electric pulsed current of 1100 A and a mechanical pressure of 20 MPa were applied for about 4 min.

I. Introduction

CERAMIC composites containing carbides and borides of transition metals possess such desirable properties as high melting temperatures, low densities, good thermal and chemical stability, high hardness, and excellent wear resistance.^{1,2} In particular, these composites have superior mechanical properties (e.g., wear resistance and fracture toughness) relative to their constituent ceramic components.^{3,4} This fact makes them attractive as structural materials, where good mechanical properties and high-temperature resistance are required. In addition, because of their high electrical conductivity, they can also be used as materials for "Hall–Heroult" electrolytic cells for the production of aluminum.²

Several methods have been utilized for the preparation of dense $TiC-TiB_2$ composites with varying proportions of carbide and boride constituents.

For example, 2TiB_2 -TiC composites were formed through a directional reaction between molten Ti and B₄C preforms in a furnace at 1600° - 1800° C.⁵ Also, 2TiB_2 -TiC dense composites

were synthesized by reactive sintering of powder mixtures of Ti and B₄C (3:1 molar ratio).⁶ Titanium carbide–titanium boride composites of different compositions were also produced by transient plastic-phase processing (TPPP) starting from Ti, B₄C, TiC_{0.5}, and TiB₂ powders.^{1,3,7}

The self-propagating high-temperature synthesis (SHS) coupled with explosive shock consolidation (ESC) was used to synthesize dense TiC-TiB₂ composites starting from Ti, C, and B₁₃C₂ powders.⁸ Similar processes were utilized by Song et al.,⁹ who used a combination of SHS and dynamic compaction starting from B₄C, C, and Ti, and by Zhang et al.,² who took advantage of pseudo-hot isostatic pressing (PHIP). TiC-2TiB₂ composites were also fabricated from blends of Ti-B₄C by using either thermal explosion (1000°C, 50-150 MPa) or reactive hot-pressing (1100°C, 150 MPa) methods.^{10–12} Dense TiB₂–15% TiC composites were obtained by high-pressure sintering (HPS) of TiC and TiB₂ powders as well as by high-pressure self-combustion synthesis (HPCS) starting from elemental reactants.⁴ Two different Ti-B-C composites were fabricated using reaction synthesis of Ti and B_4C in 3/1 and 4.8/1 molar ratios by hot pressing (35 MPa, 1800°C, 1 h).¹³ Dense nanometric TiB₂-TiC composites were recently generated by the field-activated pressure-assisted synthesis apparatus (FAPASA) using elemental Ti, C, and B powders that had been mechanically activated by highenergy ball milling.¹⁴ A Ti–B–C composite was also prepared by reaction hot pressing at 1800°C and 35 MPa starting from Ti/ B_4C powders premixed at a molar ratio of $4.8/1.^{15}$

In the present study, the simultaneous synthesis and consolidation of the titanium carbide–titanium diboride (TiC– $TiB_2 = 1:1$ molar ratio) composite using the spark plasma sintering (SPS) method was investigated from a Ti, B₄C, and C powder mixture. This technique, which is based on the simultaneous application of a pulsed DC current and a uniaxial mechanical load through the reacting sample, has been previously shown to be effective in the preparation of dense, bulk materials.^{16–19}

Specifically, the effect of boron carbide particles size on the conversion degree of reactants to the desired composite, the influence of the applied electric current level on the synthesis process dynamics, and the effect of the processing time on product densification were studied. Moreover, a kinetic investigation of the synthesis process where the initial powders are transformed to the final product is performed.

II. Experimental Materials and Methods

The characteristics of the starting powders used in the present investigation along with their sources are reported in Table I. Titanium, boron carbide (B_4C) , and amorphous carbon pow-

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Table I	Starting	Powders	Used	in the	Present	Investigation

Reactant	Vendor	Particle size	Purity (%)
Titanium (Ti)	Sigma-Aldrich (366994)	-325 mesh	99.98
Boron carbide (B_4C)	Alfa Aesar (40504)	1-7 μm	99.4
Boron carbide (B_4C)	Alfa Aesar (10922)	22-59 μm	99+
Carbon black (C)	Alfa Aesar (39724)	0.042 μm	99.9+

ders were dry mixed in the stoichiometric ratio corresponding to the following chemical reaction:

$$4\mathrm{Ti} + \mathrm{B}_{4}\mathrm{C} + \mathrm{C} \to 2\mathrm{Ti}\mathrm{C} + 2\mathrm{Ti}\mathrm{B}_{2} \tag{1}$$

Powder mixing was performed in an SPEX 8000 mill for 30 min using a stainless-steel jar and alumina balls.

An SPS 515 apparatus (Sumitomo Coal Mining Co. Ltd) was used to synthesize and simultaneously densify the $TiC-TiB_2$ composite. A schematic representation of the machine with details of the experimental setup is shown in Fig. 1. It combines a 50 kN uniaxial press with a DC-pulsed current generator (10 V, 1500 A, 300 Hz) to provide simultaneously a pulsed electric current through the sample and the graphite die containing it, together with a mechanical load through the die plungers.

About 4 g of powder mixture was first cold compacted inside the die (outside diameter, 35 mm; inside diameter, 15 mm; height, 40 mm). In order 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 made of E-940 graphite and provided by Electrodes Inc. In addition, with the aim of minimizing heat losses by thermal radiation, the die was covered with a layer of graphite felt. The die was then placed inside the reaction chamber of the SPS apparatus and the system was evacuated to 10 Pa. This step was followed by the application of a mechanical pressure of 20 MPa through the plungers.

The experiment was initiated with the application of a previously set constant value of the electric current for a given time. Temperatures were measured during synthesis by a C-type thermocouple, which was inserted inside a small hole on one side of the graphite die. Temperature, applied current, voltage, mechanical load, and the vertical displacement (δ) of the lower electrode were recorded in real time. It is worth noting that the parameter δ is a measure of compact densification. However, because of the thermal expansion of the sample as well as that one of both electrodes, graphite blocks, spacers, and plungers, the displacement δ is not exactly equal to sample shrinkage. Therefore, the real degree of consolidation was determined by measuring the density of the sample at the end of the process. For the 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 density of the product was determined by geometric and gravimetric measurements and also by the Archimedes method. Phase identification was performed using a Philips PW 1830 X-rays diffractometer (Eindhoven, the Netherlands) with CuK α radiation ($\lambda = 1.5405$ Å) and an Ni filter. The microstructure of end products was examined by scanning electron microscopy (SEM) using a Hitachi S4000 microscope (Tokyo, Japan).

Knoop microhardness measurements of the SPS composite using a 0.9806 N (100 g_f) indentation load and 15 s dwell time were also performed.

III. Results and Discussion

(1) Effect of Boron Carbide Particle Size

The influence of B_4C particles size on the TiC–TiB₂ synthesis process by the SPS method was investigated first. Specifically,

two different types of boron carbide powders, with particle sizes of 22–59 and 1–7 μ m, were investigated. Figure 2 shows the X-ray diffraction (XRD) patterns of samples obtained using the larger (a) and the smaller size (b). The synthesis in both cases was performed under SPS conditions of 800 A (total current) and a sintering/reaction time of 10 min. It was seen that, when the relatively coarse B₄C particles were used, the conversion of the initial reactants to the final products TiC and TiB₂ was not complete. In addition to the desired phases (TiC and TiB₂), the product contained unreacted B₄C as well as other, undesirable, titanium borides of TiB and Ti₃B₄. However, when the finer B₄C powder was used under the same SPS operating conditions, the XRD pattern analysis of the product revealed the presence of TiC and TiB₂ only.

The above results can be explained on the basis of the longer diffusion paths involved in the chemical transformation when relatively coarse B_4C powders are used. Therefore, in order to investigate the reaction kinetics, the finer B_4C powders (particle size 1–7 µm) were used.

(2) Kinetic Study of the Synthesis Process

The mechanism of formation of the TiC–TiB₂ composite by the SPS process was studied by simultaneously applying a constant pulsed electric current (I = 800 A) and mechanical pressure (P = 20 MPa), for different time intervals ($t_{I\neq0}$), ranging from 1 to 10 min.





Fig. 2. Effect of B_4C particle size on the composition of the final spark plasma sintering product (I = 800 A, P = 20 MPa, $t_{I\neq0} = 10 \text{ min}$): (a) 22–59 µm; (b) 1–7 µm (\blacksquare , B_4C ; \bigcirc , TiC; \triangle , TiB; \Box , Ti₃B₄; \spadesuit , TiB₂).

The applied current, voltage, temperature, and shrinkage displacement profiles measured during the synthesis process for the case of $t_{I\neq0} = 10$ min are shown in Fig. 3. It can be seen from Fig. 3(a) that the current increased from 0 to 800 A in about 20 s and remained constant until the end of the desired time. Cor-

respondingly, the voltage showed a rapid increase, reaching a maximum value of about 6.4 V within about 20 s, and then decreasing rapidly to a constant value of about 4.5 V (Fig. 3(b)). The decrease in voltage was a result of the increase in temperature of the reacting system, which produces an increase in its electrical conductivity. Under the given experimental conditions $(I = 800 \text{ A}, P = 20 \text{ MPa}, t_{I \neq 0} = 10 \text{ min})$, the temperature increased rapidly during the first 2 min, and then it increased at a slower rate, approaching an asymptotic value of about 1700°C after a holding time of about 5 min (Fig. 3(c)). The conditions indicate an approach to thermal equilibrium. Regarding the profile of sample displacement (Fig. 3(d)), no significant changes are observed during the first 60 s. A linear increase (to about 0.5-0.6 mm) then takes place during the next minute (60-120 s) and is followed by a steep increase (to 1.25 mm) in the time range of 120-150 s. The displacement then decreases gradually to reach an approximately constant value at about 300 s. The observed increase of δ when the application of the electric current is interrupted (Fig. 3(d)) was a manifestation of the shrinkage of the sample ensemble (die/plungers/sample) because of thermal shrinkage accompanying the cooling of the system. A qualitatively similar behavior was also observed when current values other than 800 A were applied. In order to investigate the kinetics associated with the SPS process of TiC-TiB2 composites based on Eq. (1), the reacting system composition was monitored at different time intervals ($t_{I\neq 0} = 1, 2, 3, 4, 5, 6, 7, 8$, and 10 min). The XRD patterns, including the one related to the starting powder mixture, are shown in Figs. 4(a) to (j), respectively. The range for the diffraction angle (2θ) in these patterns $(33^{\circ} \text{ and } 46^{\circ})$ includes, in addition to the main peaks of TiB₂ and TiC, the main peaks of Ti and B₄C. As the carbon was amor-



Fig. 3. Temporal profiles of spark plasma sintering outputs: (a) current intensity, (b) voltage, (c) temperature, and (d) sample displacement (I = 800 A, P = 20 MPa); $t_1 = 1$ min, $t_2 = 2$ min, $t_3 = 3$ min, $t_4 = 4$ min, $t_5 = 5$ min, $t_6 = 6$ min, $t_7 = 7$ min, $t_8 = 8$ min.



Fig. 4. X-ray diffraction (XRD) patterns of spark plasma sintering products obtained for different values of the time interval during which the pulsed electric current is applied (I = 800 A, P = 20 MPa). (a) Reactants; (b) $t_{I\neq0} = 1 \text{ min}$; (c) $t_{I\neq0} = 2 \text{ min}$; (d) $t_{I\neq0} = 3 \text{ min}$; (e) $t_{I\neq0} = 4 \text{ min}$; (f) $t_{I\neq0} = 5 \text{ min}$; (g) $t_{I\neq0} = 6 \text{ min}$; (h) $t_{I\neq0} = 7 \text{ min}$; (i) $t_{I\neq0} = 8 \text{ min}$; (j) $t_{I\neq0} = 10 \text{ min}$ (\blacklozenge , Ti; \blacksquare , B₄C; \bigcirc , TiC; \triangle , TiB; \square , Ti₃B₄; \blacklozenge , TiB₂).

phous, it was not identified by this analysis. The application of a current (800 A) for 60 s showed that no significant interaction between the reactants took place, as seen from the pattern of

Fig. 4(b), which depicts peaks for Ti and B_4C only. This observation is related to the corresponding temperature profile (Fig. 3(c)). The maximum temperature measured during this

stage of the SPS process was less than 600°C, too low to activate the solid-state diffusion processes necessary for the synthesis reaction. When the reaction time is increased to 2 min, the desired end phases, TiB₂ and TiC, were now present in the final product, particularly the latter one (Fig. 4(c)). However, a complete conversion to the desired product had not yet been achieved, as can be seen by the presence of titanium and boron carbide peaks, along with peaks of the intermediate phases of TiB and Ti₃B₄, in the XRD pattern of the SPS sample. The increase in the interaction between reactants was a result of the increase in temperature to about 1200°C (Fig. 3(c)).

On the basis of the results described above, it can be concluded that the main reaction taking place during the first stage of the SPS process was the interaction between titanium and amorphous carbon to form TiC.

As the reaction time is increased to 3 min (Fig. 4(d)), the product contained large amounts of both TiC and TiB₂, with only small traces of B₄C and the secondary products TiB and Ti₃B₄. Elemental titanium was not present in the product as judged by the XRD pattern. This result is in good agreement with the experimental evidences reported by Zhao and Cheng,⁶ who investigated the formation of TiC–TiB₂ composites by reactive sintering. In fact, they found that the interaction between Ti and B₄C becomes significant only when T > 1300°C. Accordingly, our results show that the complete conversion of titanium takes place in the time interval of 2–3 min, during which this temperature threshold (1300°C) is reached (cf. Fig. 3(c)). In addition, as the corresponding temperature for this stage is considerably lower than the melting point of Ti, this observation indicates that the synthesis reaction is a solid-state process.

With an increase in reaction time to 4 min (Fig. 4(e)), the relative amount of TiB_2 increased while the TiB phase appeared to decrease and the Ti_3B_4 increased. In addition, traces of B_4C were still found in the product.

When the synthesis time was increased to 5 min, B_4C was not detected in the XRD pattern (Fig. 4(f)) and the amounts of TiB₂ and Ti₃B₄ still increased at the cost of TiB. The monoboride (TiB) completely disappeared when the reaction time was increased to 6 min (Fig. 4(g)). Moreover, and in contrast to the previous reaction times, the relative abundance of the phase Ti₃B₄ is now lower with only small amounts present in the product. This trend continues as the reaction time was increased to 7 min, with only a trace of Ti₃B₄ found in the product (Fig. 4(h)). Ti₃B₄ disappeared when the reaction time was increased to 8 min, with the XRD pattern now showing peaks for TiC and TiB₂ only (Fig. 4(i)).

As the results presented above indicate, the composition of the product depends on the reaction time under the influence of the pulsed electric current. In addition, the rate of conversion of the starting reactants is different for the two ceramic components of the composite. Under the experimental conditions utilized, titanium reacted completely while in the solid state. This observation, along with the fact that the maximum temperature measured during the process was about 1800° C and that the eutectic temperature of the TiC–TiB₂ system was approximately 2500° C,²⁰ allows us to conclude that the formation of the desired composite by the SPS process is governed by a solid-state diffusion mechanism.

By studying the formation of the 2TiB_2 -TiC composite by reactive sintering based on the following reaction:

$$3\mathrm{Ti} + \mathrm{B}_4\mathrm{C} \to 2\mathrm{Ti}\mathrm{B}_2 + \mathrm{Ti}\mathrm{C}$$
 (2)

Zhao and Cheng⁶ suggested that the first step occurring during the transition from the starting powders to the final composites is represented by the formation of TiB and TiC, through the following reaction:

$$5Ti + B_4C \rightarrow 4TiB + TiC$$
 (3)

Then, two reactions are proposed as possible paths. The first involves the formation of Ti_3B_4 and its subsequent transforma-

tion to TiB_2 through two reaction steps, as follows:

$$16\text{TiB} + B_4\text{C} \rightarrow 5\text{Ti}_3B_4 + \text{TiC} \tag{4}$$

$$3\text{Ti}_3\text{B}_4 + \text{B}_4\text{C} \rightarrow 8\text{Ti}\text{B}_2 + \text{Ti}\text{C}$$
 (5)

In the second path, titanium monoboride is directly converted into the diboride phase according to

$$6\mathrm{Ti}\mathbf{B} + \mathbf{B}_4\mathbf{C} \to 5\mathrm{Ti}\mathbf{B}_2 + \mathrm{Ti}\mathbf{C} \tag{6}$$

Both reaction paths, i.e. Eqs. (3)–(5) and the one involving Eqs. (3) and (6), give rise to the same final composite.

Although the reaction investigated by Zhao and Cheng⁶ was different from that examined in the present work (cf. Eq. (1)) the latter one can be considered as the sum of Eq. (2) and the following:

$$\Gamma i + C \to T i C$$
 (7)

which represents the direct carburization of elemental Ti by amorphous carbon.

Based on the results obtained during the kinetic investigation of the SPS process, it is possible to postulate that Eq. (7) is the first step during the spark plasma synthesis of TiC–TiB₂. Moreover, Eqs. (3)–(5) are more likely responsible for the subsequent TiB₂ formation, as well as the intermediate phases, i.e. TiB and Ti₃B₄, detected before the synthesis reaction was completed. In fact, while the possibility of Ti₃B₄ formation is excluded by Eq. (6), this phase was the last to disappear from the product (Figs. 4(g)–(h)), suggesting that the sequence of Eqs. (4) and (5) is the likely path in the synthesis of the composite.

The presence of B_4C is then required to guarantee the complete transformation of TiB and Ti₃B₄ into TiB₂. The fact that boron carbide was not detected by XRD for $t \ge 5$ min is consistent with its relatively low peak intensity even when the corresponding content was maximum, i.e. in the starting mixture (cf. Fig. 4(a)).

It is now possible to correlate the results shown in Fig. 4 with those reported in Fig. 3(d), where the displacement profile measured during the synthesis/densification process is reported. In particular, the linear increase in δ , observed in the range 60–120 s, corresponds to the formation of titanium carbide. Therefore, the sample displacement recorded during this stage can be related primarily to the carburization process of elemental titanium by amorphous carbon. Although the first evidence of formation of titanium borides (TiB, Ti₃B₄, and TiB₂) was indicated, it was at a much limited level.

In addition, it should be noted that this stage corresponds to the maximum transformation rate of the starting reactants. However, this does not lead to the complete conversion into the desired phases, which is reached only when the slow conversion of the titanium borides TiB and Ti_3B_4 to the desired TiB₂ takes place. The completion of such a conversion occurs at 8 min (cf. Fig. 4(i)), which therefore represents the required duration of current application leading to the formation of the desired compounds, i.e. TiC and TiB₂. This aspect will be further examined in the next section, where different current levels have been applied.

(3) Effect of Current Intensity

The influence of the pulsed electric current intensity (*I*) on the simultaneous synthesis and densification of the TiC–TiB₂ composite was investigated in the range 700–1100 A, while the mechanical pressure was maintained constant at 20 MPa in all SPS experiments. In particular, the dependence of the synthesis time, i.e. the minimum time interval during which the applied current results in complete conversion, on the current intensity was investigated first. To this aim, the same approach described in the previous paragraph, i.e. monitoring the evolution of the synthesis process through quenched reactions at different intervals (cf. Figs. 3 and 4), was adopted in the range 700–1100 A.



Fig. 5. Effect of the applied current on the time needed to obtain the full conversion of the initial reactants into the final desired product (P = 20 MPa).

This procedure allowed us to identify the minimum time interval needed to achieve the full conversion, hereafter referred to with the symbol t^* . For instance, as observed previously, for the case of I = 800 A, t^* was found to be equal to 480 s. The effect of the applied current intensity on t^* is shown in Fig. 5. It can be seen that the conversion time decreased monotonically as the applied current level increased. Full conversion times decreased from 960 to 180 s as the current intensity increased from 700 to 1100 A.

This finding may be explained on the basis of the different temperature conditions observed when applying different current intensities. In fact, the increase of the applied current resulted in both higher heating rate and temperature levels reached, both of which accelerate synthesis processes.

The results reported in Fig. 5 can be used as a basis for evaluating energy costs for the production of a TiC–TiB₂ ceramic composite by the SPS process using Ti, B₄C, and C powders as reactants. Using the electric current (*I*) and the corresponding minimum application time (t^*) from Fig. 5, it is possible to calculate the energy consumed during the reaction synthesis through the following expression:

$$E = \int_0^{t^*} I(t)V(t)\mathrm{d}t \tag{8}$$

where V is the voltage, whose time profile is known (Fig. 3(b) for the case of I = 800 A). Therefore, the minimum energy required to obtain the desired composite can be calculated from Eq. (8) for each current level. Besides the total energy requirement for the synthesis process, another parameter that can be considered useful is the averaged electrical power evaluated as follows:

$$\bar{W} = \frac{1}{t^*} \int_0^{t^*} I(t) V(t) dt$$
(9)

i.e. the total energy supplied divided by the time t^* needed for obtaining the complete conversion. Both the parameters defined above in Eq. (8) and Eq. (9) are reported in Fig. 6 as a function of the applied current. It can be clearly seen that the total electrical energy *E* necessary to obtain the complete conversion of the reactants to the desired phases decreased as the current level increased. This was a consequence of the corresponding reduction of t^* . On the other hand, \overline{W} increased as *I* increased. This result is consistent with the relatively higher heating rates and temperature levels reached during the process, and clearly justifies the corresponding shorter synthesis time, i.e. higher reaction rates, observed experimentally.

The effect of the applied electric current on product densification was also investigated. Figure 7 shows the relative density



Fig. 6. Effect of applied current on the total energy (Eq. (8)) and the average power (Eq. (9)) needed to achieve the full conversion of the initial reactants into the final desired product (P = 20 MPa).

of the SPS samples (theoretical value equal to 4.678 g/cm³) obtained by applying the electric current *I* for the corresponding minimum time t^* . It can be seen that higher applied currents produced denser TiC–TiB₂ composites. Specifically, while the relative density of the end-product obtained when a current intensity of 800 A is applied for 8 min is about 84%, it increases up to 87% when a current intensity of 1100 A is applied for 3 min. This result may be justified on the basis of the considerations made above, and related to the synthesis time. In fact, when relatively higher current densities are applied, the averaged electrical power, \overline{W} , supplied to the system increases, thus increasing its temperature level and the heating rate, which would enhance the sintering process.

(4) Effect of SPS Processing Time on Product Densification

From the results shown above, it can be seen that the product densities are relatively low (the maximum value reached was about 87%). Regarding this aspect, it should be noted that a further increase in the current was not considered, as it would cause several practical problems, particularly related to safety, because of higher process temperatures, as well as difficulties in sample extraction from the graphite die, and increased wear of the die itself. However, with the aim of improving the densification of the TiC–TiB₂ composite, the influence of the time interval during which the pulsed current is applied on the final density of the SPS product was then investigated.



Fig. 7. Effect of applied electric current on the density of the obtained spark plasma sintering samples (P = 20 MPa, theoretical density = 4.678 g/cm³).



Fig. 8. Densities of end products obtained by spark plasma sintering as a function of the application time of the applied current (I = 1100 A, P = 20 MPa).

Based on the results obtained previously, this study has been carried out using an electric current equal to 1100 A, because it corresponded to the higher relative density reached at this stage (Fig. 7). In particular, as under this current level condition the desired composition was reached after 3 min (Fig. 5), the time interval investigated for densification purposes was in the range 3–8 min. The results are reported in Fig. 8. It can be seen that as the time was increased from 3 to 4 min, the relative density of the product increased markedly, from 87% to about 98%. A further increase of the synthesis time up to 8 min did not result in significant changes in the product density.

These observations are important as they provide evidence that the conversion into the product contributes only modestly to the densification. The goal of higher density is achieved 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. If a liquid had been present during the reaction, significant densification would have been observed during that stage. The observation in this study is quite different from the one that was found recently when synthesizing dense WC-6%Co by SPS,²¹ where synthesis and densification phenomena to produce fully dense composites were observed to occur simultaneously, and the complete conversion of starting reactants to the carbide phase corresponded to the production of a fully dense material. Two back-scattered SEM micrographs at different magnifications of the SPS composite synthesized by applying a pulsed electric current of intensity of 1100 A for 4 min are shown in Fig. 9. Two different regions can be observed easily. Specifically, the dark one corresponds to the TiB₂ phase, while the light one is TiC.

Knoop microhardness measurements using a 0.9806 N indentation load and a 15 s load duration time were performed for the case of the TiC–TiB₂ composite synthesized under the following SPS conditions: I = 1100 A, $t_{I\neq0} = 4$ min, and P = 20MPa. The hardness value obtained in this work, 2500 ± 100 HK, was compared with the corresponding values available in the literature. Specifically, our result is in good agreement with the reported values of the two ceramic constituents of the synthesized composite, i.e. 2470 HK for TiC and 2710–3000 HK for TiB₂,²² both obtained using a 100 g_f indentation load as in our case.

Moreover, the obtained values are very similar to, and in some cases higher than, the best results reported in the literature for TiC-TiB₂ dense composites having the same stoichiometry. In fact, the hardness of the synthesized SPS material is significantly higher than the values reported by Zhang et al.² and Lee et al.¹⁴ The observed differences may be explained on the basis of the higher product density achieved during the present investigation, i.e. about 98% of the theoretical value. The densities of the samples reported by Zhang et al.² and Lee et al.¹⁴ were about 91% and less than 96.5%, respectively. On the other hand, Yuan *et al.*²³ have produced TiC–TiB₂ composites characterized by a very high density (99.8%) and hardness. However, the synthesis method suggested in this case is very complex and involves three different steps, i.e. thermite-type SHS of TiC/TiB₂/oxides powder mixture, leaching to remove the oxide phases, and subsequent hot pressing (HP) of the leached powders. Therefore, the above comparison suggests that through the SPS method, it is possible to obtain a dense TiC-TiB₂ composite characterized by superior hardness properties using a one-step synthesis process.

IV. Concluding Remarks

A TiC–TiB₂ dense composite has been synthesized starting with Ti, B_4C , and C by a one-step process using the SPS apparatus. It was shown that the use of a finer B_4C powder resulted in higher conversion levels to the desired product.

An investigation of the evolution of the synthesis process (through quenched reactions at different intervals) provided an insight into the mechanism of product formation. It was seen that TiC is the first phase formed during the process as a consequence of the carburization of Ti, while TiB_2 formation took place subsequently. In addition, by examining product compositional changes with sample displacement in parallel, it was found that the latter stage was associated with the most rapid and significant sample shrinkage. Two intermediate boride phases, i.e. TiB and Ti_3B_4 , were also formed but, as the SPS



Fig. 9. Scanning electron microscopy back-scattered micrograph of spark plasma sintering end product at different magnifications: (a) \times 200 and (b) \times 1500 (I = 1100 A, $t_{I \neq 0} = 4$ min, P = 20 MPa).

holding time was increased, they were gradually converted to TiB₂. Moreover, because of the relatively low temperature levels recorded during the entire process, it is possible to conclude that all transformations during the synthesis of the desired composite by SPS are governed by a solid-state diffusion mechanism.

A systematic investigation of the effect of the electric current on the synthesis process made it possible to identify the optimal time intervals during which the pulsed current is applied, thus leading to the achievement of full conversion for all current intensity levels considered. Specifically, it was found that the application of relatively higher currents produces not only the reduction of the time intervals mentioned above but also a decrease of the corresponding energy provided to the reacting system for the synthesis, as well as the fabrication of denser material. However, in order to obtain a relatively high-density product, the electric current needs to be applied for time intervals longer than those required for obtaining complete conversion. A pure dense product (relative density of about 98%) was obtained when an electric pulsed current of 1100 A and a mechanical pressure of 20 MPa were applied for about 4 min, i.e. 1 min after full conversion was achieved.

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