Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Ceramics International 35 (2009) 397–400
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Reactive Spark Plasma Sintering of rhenium diboride

Antonio Mario Locci, Roberta Licheri, Roberto Orrù *, Giacomo Cao **

Dipartimento di Ingegneria Chimica e Materiali, Unità di Ricerca del Consorzio Interuniversitario per la Scienza e Tecnologia dei Materiali (INSTM), and Unità di Ricerca del Consorzio Nazionale delle Ricerche (CNR) – Dipartimento di Energia e Trasporti, Università degli Studi di Cagliari, Piazza d'Armi, 09123 Cagliari, Italy

Received 18 September 2007; received in revised form 30 October 2007; accepted 25 November 2007
Available online 8 April 2008

Abstract

The simultaneous synthesis and densification of rhenium diboride is investigated starting from Re and B as reactants by using the Spark Plasma Sintering (SPS) apparatus. It is shown that SPS represents an effective technique to synthesize ReB_2 bulk samples with high purity and density. In particular, a dense product with traces of secondary phases (Re_7B_3) is obtained in 35 min of total processing time by applying a maximum temperature of 1600 °C and a mechanical pressure of 20 MPa.

Keywords: A. Solid state reaction; A. Sintering; C. Hardness; D. Borides

---

1. Introduction

It is well known that super-hard materials are used for several industrial applications including abrasives, cutting tools and scratch-resistant coatings. Traditionally, diamond, which possesses the highest known hardness (70–100 GPa), is used for such applications. However, its applicability is prevented for example when cutting steel and other ferrous metals due to undesired iron carbide formation during high-speed machining. Cubic boron nitride (cBN), which is characterized by hardness value of 45–50 GPa, may be used to cut steel since the formed iron borides and nitrides are less stable than iron carbide obtained when diamonds is employed. B_6O and cubic BC_2N may also be considered as potential candidates instead of cBN due to their hardness. However, extremely high pressure and temperature, are required for the synthesis of these materials [1–3].

A potential alternative to diamond is also represented by rhenium diboride, whose ultra-incompressible and super-hard properties have been predicted from first-principle studies by Hao et al. [4]. While powders of ReB_2 have been synthesized by various methods, starting from $ReCl_3$ and MgB_2 [5] or the elements [5,6], rhenium diboride has been obtained in bulk form only by arc melting [5]. In particular, Chung et al. [5] experimentally demonstrated that rhenium diboride synthesized in bulk quantities via arc melting possesses mechanical properties to rival other materials potentially alternative to diamond. However, arc melting has the drawback to require the obtained ingots to be melted 3–5 times under argon atmosphere to ensure homogeneous mixing of the elements.

In the present study, the simultaneous synthesis and densification of rhenium diboride from elemental powders using the Spark Plasma Sintering (SPS) apparatus is investigated. The proposed method, which is based on the simultaneous application of a pulsed direct electric current and a uniaxial mechanical load through the reacting sample, has been previously adopted by the authors for the preparation of various dense, bulk materials [7,8]. In this work, it is shown that for the synthesis of bulk ReB_2 from elemental powders, the SPS technique also represents an efficient and effective method.

2. Materials and methods

Rhenium (−325 mesh, 99.99% purity, Alfa Aesar cat. No. 010313) and boron (amorphous, 95–97% purity, Fluka cat. No. 15580) powders were dry mixed in the stoichiometric ratio corresponding to the following chemical reaction:

$$Re + 2B \rightarrow ReB_2 \quad (1)$$

---

* Corresponding author. Tel.: +39 070 6755076; fax: +39 070 6755057.
** Corresponding author. Tel.: +39 070 6755058; fax: +39 070 6755057.
E-mail addresses: orru@visnu.dicm.unica.it (R. Orrù), cao@visnu.dicm.unica.it (G. Cao).

0272-8842/$34.00 © 2008 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2007.11.012

An SPS 515 apparatus (Sumitomo Coal Mining Co. Ltd.), whose characteristics are reported elsewhere [9], was used to synthesize and simultaneously sinter the ReB_2 compound. About 6.7 g of powder mixture were first cold-compacted inside a graphite die (outside diameter, 30 mm; inside diameter, 15 mm; height, 30 mm). The die was then placed inside the reaction chamber of the SPS apparatus and the system was evacuated down to 20 Pa. This step was followed by the application of 20 MPa mechanical pressure through the plungers. Further details about the experimental procedure can be found elsewhere [10].

The experiment is initiated with the application of the electric current in order to guarantee a previously set temperature cycle. 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 the Archimedes' method. Phase identification was performed on powdered SPS sample by using a Philips PW 1830 X-rays diffractometer with Cu K_α radiation ($\lambda = 1.5405$ Å) and a Ni filter. Vickers microhardness measurements (Zwick 3212 hardness tester) were performed on the polished SPS sample at different indentation loads with a dwell indentation time of 18 s. Fracture toughness was also obtained by means of the Palmqvist formula [11] using an indentation load equal to 98.1 N with an indentation dwell time of 18 s.

3. Results and discussion

Fig. 1 shows the temperature time profile imposed during the SPS experiments. Specifically, the temperature was increased from room temperature to 1600 °C in 32 min with a corresponding heating rate equal to about 50 °C/min. Then, the system was maintained at 1600 °C for 2.5 additional min. After 34.5 min of total processing time, the application of the current was manually interrupted and the system was subjected to natural cooling. The applied root mean squared (RMS) electric current (I) and voltage (ϕ) measured during the synthesis process are shown in Fig. 2. It can be seen that the current increased from to 0 to about 1050 A during the heating stage (cf. Fig. 1). Once the holding temperature was reached by the ensemble sample/die, the automatic PID temperature control reduced the applied current to about 1000 A, whose value was then maintained approximately constant until the end of the experiment. The associated applied voltage time profile is also reported in Fig. 2. It can be observed an increase of ϕ up to 4.2 V followed by a sudden decrease to about 4 V when the heating stage was completed (cf. Fig. 1). The slight decrease of the applied voltage during the holding time is caused by the increase in sample density, which, in turn, produces a decrease of its electrical resistivity. It is interesting to note that at $t = 825$ s, a sharp change of the current and the voltage takes place.

Fig. 3 shows the temporal profile of sample shrinkage δ, which is obtained from the experimental displacement temporal profile recorded during the process as illustrated elsewhere [12]. It can be seen that no significant changes are observed during the first 60 s. Favored by the temperature increase, a gradual augmentation of δ (up to about 0.45 mm) then takes

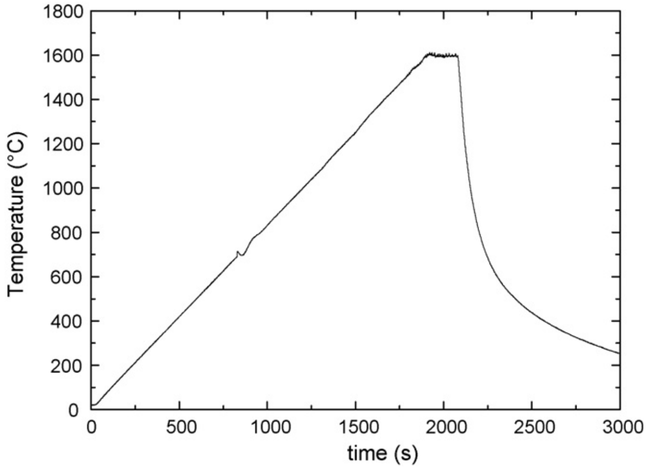

Fig. 1. Temperature temporal profile adopted during the SPS process.

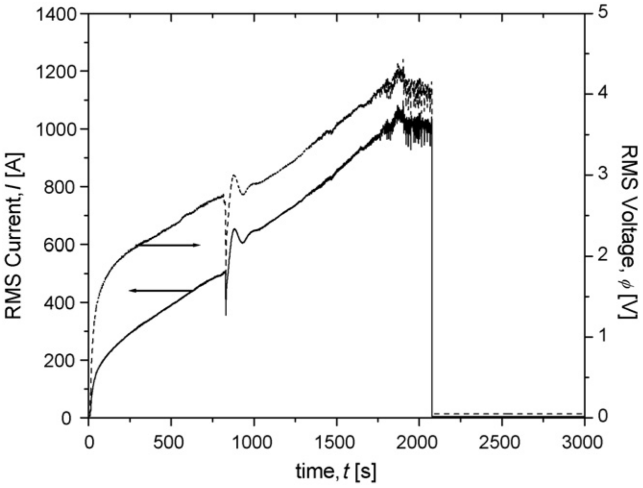

Fig. 2. Temporal profile of the RMS current and voltage applied during the SPS process.

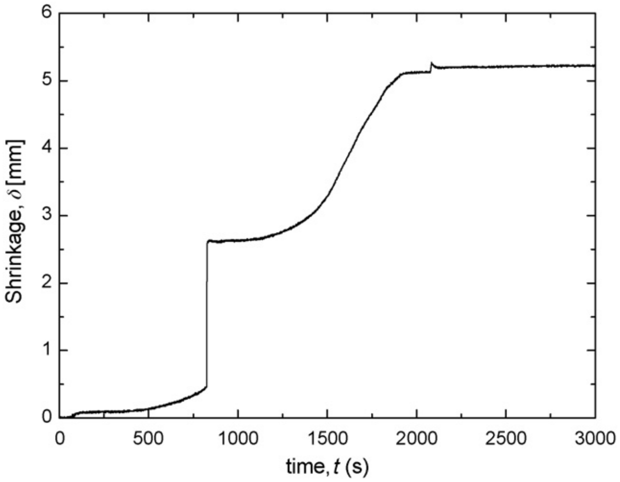

Fig. 3. Temporal profile of sample shrinkage taking place during the SPS process.

place during the interval 60–825 s. When the system temperature is about 690 °C (cf. Fig. 1), the sample shrinkage undergoes a steep increase (to 2.6 mm) in a very short time (less than 0.5 s). It should be noted that this event corresponds to the sharp change of current and voltage shown in Fig. 2. The parameter δ then remains approximately constant up to about 17 min of current application, when the system temperature is about 850 °C. At this time δ starts again to increase showing a maximum shrinkage rate when the temperature is about 1380 °C (cf. Fig. 1). Finally, δ reaches a plateau value equal to about 5.13 mm when the processing time approaches the final value (i.e. 34.5 min).

In order to get some insights into the peculiar shrinkage behavior shown in Fig. 3, a specific experiment was performed where the application of the current is manually interrupted immediately after the abrupt shrinkage variation. The XRD analysis results of the obtained sample are reported in Fig. 4 along with the XRD pattern of the starting powders. The intensity is plotted by adopting a square root scale in order to evidence the presence, even in small traces, of minor phases. In Fig. 4a, only signals pertaining to rhenium are present, being the boron powders in amorphous form, while diffraction peaks of ReB_2, Re_3B_7, and C are the only revealed in Fig. 4b. By comparing Fig. 3 and Fig. 4a and b, it is apparent that complete conversion of the starting reactants to the desired phase ReB_2 along with small traces of the compound Re_7B_3, can be associated to the rapid shrinkage variation of the sample. Therefore, the change of δ represents in this case an indication of the occurrence of the synthesis reaction (1). Fig. 4c reports the XRD pattern of the SPS sample obtained when the entire temperature temporal profile shown in Fig. 1 was imposed to the system. It can be seen that, from the compositional point of view, there are no significant differences between the two samples. Traces of Re_7B_3 revealed in the SPS sample may be due to the low purity of the boron powders used which in turn gives a slightly rhenium-rich stoichiometry with respect to the theoretical one (cf. Eq. (1)). In addition, graphite found in the final sample is a consequence of C diffusion from die and plungers.

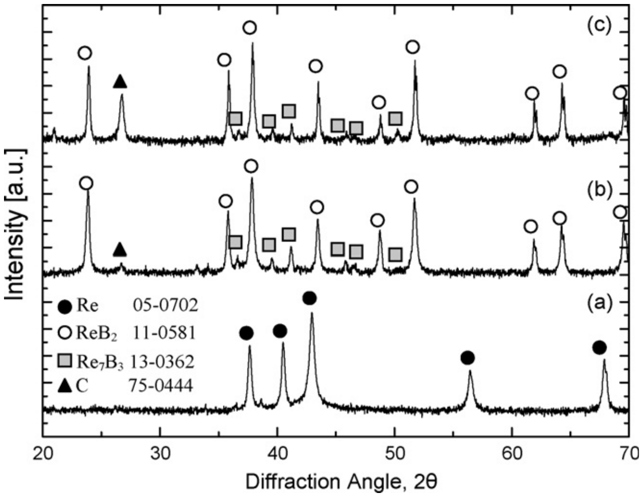

Fig. 4. XRD patterns of (a) starting powders, (b) SPS sample obtained by interrupting the current application immediately after the occurrence of the combustion reaction, (c) SPS sample obtained at end of the total processing time.

Typically, rapid changes of the sample shrinkage during SPS processes may be associated with melting of reactants or products, or to the occurrence of combustion reactions, because they are both accompanied by a considerable sample shrinkage in the presence of mechanical load. Since the temperature of the die corresponding to the abrupt shrinkage is much lower than the melting point of elements (3180 °C and 2300 °C for rhenium and boron, respectively) and the lowest eutectic point of the Re–B system, i.e. about 1800 °C [13], the presence of molten phases can be excluded, and therefore combustion reactions are likely to take place. The occurrence of the combustion reaction (1) also explains the corresponding rapid variation of the applied current and voltage shown in Fig. 2. In fact, since the reaction between rhenium and boron is strongly exothermic [14], the corresponding heat released forces the PID temperature controller to reduce the applied RMS current. Then, as the effect of the heat liberated during the reaction vanishes, the PID controller increases the applied current so that the system follows the set temperature temporal profile. It should be mentioned that a similar behavior (fast reaction and abrupt shrinkage occurring at low temperature) was already observed for instance during the synthesis and simultaneous densification of $MoSi_2$ or the composite TiC/TiB_2 by SPS, when starting from mechanically activated elemental reactants [12,15].

The combustion behavior of the Re–B system has also been reported by Otani et al. [6] who took advantage of the self-propagating character of the reaction between Re and B to produce rhenium diboride powders. It is interesting to note that the reaction was observed to occur at about 1100 °C, i.e. higher than the apparent ignition temperature recorded in this work, 690 °C (cf. Figs. 1 and 3). This significant discrepancy can be due not only to the different heating rate and procedure adopted, but also to the finer rhenium powders used as starting material in this work. It is worth noting that Chung et al. [5] heated in a furnace up to 1000 °C for 5 days rhenium powders, as fine as the ones used in this work with high purity boron. However, no information about the occurrence of combustion reactions is provided. Therefore, it cannot be excluded that the presence of an electric current may influence the ignition temperature of the reaction (1).

Density measurements were performed on both samples whose XRD are shown in Fig. 4b and c. It was found that while the sample obtained after 34.5 min of processing time shows a density of 12.67 g/cm^3 (close to the theoretical density of ReB_2, i.e. 12.673 g/cm^3), the density of the sample obtained when interrupting the process immediately after the combustion reaction has occurred was found to be only 8.7 g/cm^3. These observations are important as they provide evidence that the conversion to the product contributes only modestly to the densification. The goal of reaching higher density values is achieved after the completion of the reaction through product sintering. This is another, albeit indirect, evidence of the occurrence of the synthesis reaction between solid state phases.

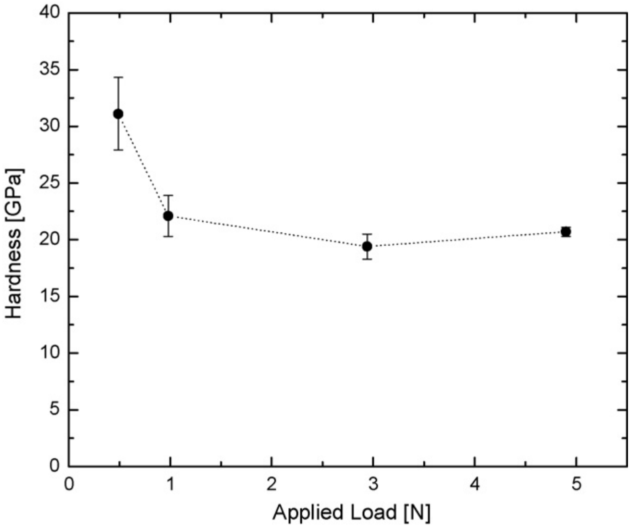

Fig. 5. Vickers microhardness of ReB_2 SPS sample as a function of the applied indentation load.

If a liquid had been present during the reaction, significant densification would have been observed during that stage.

Fig. 5 shows the Vickers microhardness measurements performed on the dense sample at different loads in the range 0.49–4.9 N. The observed inverse relationship of applied load to hardness is due to the well-known indentation size effect. The obtained microhardness values are lower than the corresponding values reported by Chung et al. [5]. This may be due the fact that while Chung et al. [5] took advantage of a casting technique, in this work bulk ReB_2 was obtained through sintering. In addition, the higher purity of boron powders used by Chung et al. [5], as well as the presence of traces of Re_3B_7 and graphite in the samples obtained in this work, may also contribute to the hardness differences. Fracture toughness tests were also performed on the same sample, and a value of 7.36 ± 0.69 MPa $m^{1/2}$ was obtained.

4. Conclusions

In summary, the following conclusions can be made:

(1) ReB_2 has been successfully produced by means of the SPS apparatus starting from the elements by applying a mechanical pressure of 20 MPa and a maximum temperature of 1600 °C in 34.5 min of total processing time.
(2) The obtained sample is highly dense, with no unreacted starting powders and with traces of Re_7B_3.
(3) The complete conversion of the initial powders is found to occur through a combustion reaction. However, the conversion to the final product contributes only modestly to the densification. The goal of reaching higher density is achieved after the completion of the reaction through the sintering of the product.
(4) The Vickers microhardness value of the obtained sample ranges in the interval 20.7–31.1 GPa depending on the applied indentation load, while the fracture toughness is 7.36 ± 0.69 MPa $m^{1/2}$.
(5) It is shown that the SPS technique represents an efficient and effective method to synthesized ReB_2 from elemental powders.

Acknowledgements

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

References

[1] V.L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar, D.C. Rubie, Synthesis of superhard BC_2N, Appl. Phys. Lett. 78 (10) (2001) 1385–1387.
[2] D. He, Y. Zhao, L. Daemen, J. Qian, T.D. Shen, T.W. Zerda, Boron suboxide: as hard as cubic boron nitride, Appl. Phys. Lett. 81 (4) (2002) 643–645.
[3] P.F. McMillan, New material from high-pressure experiments, Nat. Mater. 1 (2002) 19–25.
[4] X. Hao, Y. Hu, Z. Wu, D. Zhou, X. Liu, X. Cao, J. Meng, Low-compressibility and hard materials ReB_2 and WB_2: prediction from first-principles study, Phys. Rev. B: Condensed Matter Mater. Phys. 74 (2006) 224112–224116.
[5] H.Y. Chung, M.B. Weinberger, J.B. Levine, A. Kavner, J.M. Yang, S.H. Tolbert, R.B. Kaner, Synthesis of ultra-incompressible superhard rhenium diboride at ambient pressure, Science 316 (2007) 436–439.
[6] S. Otani, T. Aizawa, Y. Ishizawa, Preparation of ReB_2 single crystals by the floating zone method, J. Alloys Compd. 252 (1997) L19–L21.
[7] A.M. Locci, R. Licheri, R. Orrù, A. Cincotti, G. Cao, Synthesis/sintering of dense carbides-, borides- and perovskites- based materials by SPS, Ceram. Transact. 194 (2006) 173–188.
[8] A.M. Locci, R. Licheri, R. Orrù, A. Cincotti, G. Cao, Mechanical and electric current activation of solid-solid reactions for the synthesis of fully dense advanced materials, Chem. Eng. Sci. 62 (18–20) (2007) 4885–4890.
[9] A.M. Locci, R. Orrù, G. Cao, Simultaneous Spark Plasma Synthesis and consolidation of WC/Co composites, J. Mater. Res. 20 (3) (2005) 734–741.
[10] A.M. Locci, R. Orrù, G. Cao, Z.A. Munir, Simultaneous Spark Plasma Synthesis and densification of TiC-TiB_2 composites, J. Am. Ceram. Soc. 89 (3) (2006) 848–855.
[11] D.K. Shetty, I.G. Wright, P.N. Mincer, A.H. Clauer, Indentation fracture of WC-Co cermets, J. Mater. Sci. 20 (5) (1985) 1873–1882.
[12] A.M. Locci, R. Orrù, G. Cao, Z.A. Munir, Effect of ball milling on simultaneous spark plasma synthesis and densification of TiC-TiB_2 composites, Mater. Sci. Eng. A 434 (1–2) (2006) 23–29.
[13] K.I. Portnoi, V.M. Romashov, Binary constitution diagrams of systems composed of various elements and boron. A review, Soviet Powder Metallurgy Metal Ceram. 11 (5) (1972) 378–384.
[14] S.V. Meschel, O.J. Kleppa, Standard enthalpies of formation of NbB_2, MoB, ReB_2 by high-temperature direct synthesis calorimetry, Metallurgical Transact. A 24 (4) (1993) 947–950.
[15] R. Orrù, J.N. Woolman, G. Cao, Z.A. Munir, The synthesis of dense nanometric $MoSi_2$ through mechanical and field activation, J. Mater. Res. 16 (6) (2001) 1439–1448.