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In this study, the reaction sintering of boron carbide, which consists in doing reactive infiltration of molten silicon throughout a porous sample made of B_4C and carbon graphite was investigated. Thus, it has been shown that a single-mode microwave cavity can be successfully used to produce reaction-bonded B_4C–SiC composite. A specific package, consisting of a SiC based susceptor and a boron nitride based insulating container, was used to heat up the B_4C–Si system using a single-mode microwaves cavity under an Ar–H_2 atmosphere. Pore-free B_4C–SiC composite successfully produced consists of a mixture of B_4C and polygonal shaped β-SiC within a residual silicon matrix. The indentation technique permits to determine mechanical properties of the samples which are compared to those obtained conventionally. It appears that the average hardness ($H \approx 22$ GPa) value is quite constant all along the sample thickness which highlights good homogeneity of the samples obtained. Some aspects of the microstructure are also discussed and compared to those of samples conventionally obtained.

Keywords: A. Microwave processing; C. Mechanical properties; D. Carbides; E. Structural applications

1. Introduction

Boron carbide (B_4C) ceramic is a refractory material with a high melting point (≈ 2723 K), a high hardness, good mechanical properties, a low specific weight (2.52 g cm^{-3}), a high corrosion resistance to chemical agents and a high neutron absorption cross section. B_4C is currently used in many advanced technological application fields [1,2] such as the nuclear industry [3], high-temperature thermoelectricity conversion [4,5] and ballistic protections [6]. As many covalent type carbide ceramics, dense B_4C can be manufactured by a hot-pressing sintering technique at a very high temperature (about 2200 °C), which is a very costly method limited to the processing of plates or cylindrical samples. Thus, the widespread use of B_4C is restricted by the intrinsic limitations of the hot-pressing technique. Therefore, the Reaction-Bonded Sintering process (RBS-B_4C), which is much more cost-effective, represents an interesting alternative method to produce dense B_4C-based pieces [7]. RBS-B_4C is made by silicon infiltration into a porous preform, made of a B_4C and carbon graphite and shaped by uni-axial pressing. Pure silicon pieces are then put on the top of the preform and the assembly is subsequently heated up to about 1500 °C in order to melt the silicon. The molten silicon infiltrates throughout the boron carbide preform, fills the pores and reacts with graphite. The reaction between silicon and graphite mostly leads to the formation of silicon carbide [8] and, as a result, the composite is mainly made of B_4C grains, SiC grains and there may be some not reacted silicon left [9]. This pressureless and low

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temperature process significantly lowers the cost of production of B_4C-based products compared to the hot-pressing technology. To obtain high-quality reaction-bonded materials, the processing conditions, such as the starting composition, the powders morphology, and the thermal conditions, must be accurately determined [9]. The Microwaves Assisted Processing (MASS) method has been investigated in order to produce SiC–Si and SiC–(Si–Al) reaction-bonded composites in a multimode microwaves cavity [10]. This study has emphasized the fact that microwave heating can produce identical composites, in term of mechanical properties, compared to conventional heating, with substantial processing time reduction. It may be assumed that some specific features involved by microwaves [11], such as fast heating rate, selective heating or inverse thermal gradient, could have beneficial effects on the reaction-bonded materials obtained. However, few studies report the use of microwaves to produce reaction-bonded B_4C based materials. Most of them concern the multi-mode microwave processing of Si_3N_4 based material [12,13] or the microwaves joining of composites [14]. In addition, it is well established that semiconductors, such as silicon, silicon/boron carbides, couple very strongly with microwaves, especially with H field [11,15–17]. Therefore, it is expected that 2.45 GHz H-field irradiation can effectively heat up the B_4C–Si system and provide unique microstructures with improved mechanical properties. As a consequence, the aim of this work is to test this method using a single-mode microwave cavity and to investigate the feasibility of the RBS-B_4C process. A single mode microwave cavity, working at 2.45 GHz, was designed to make RBS-B_4C under Ar–H_2 atmosphere. Phase composition, microstructure and mechanical properties of the silicon infiltrated samples were then characterized. Results are discussed and compared to those usually obtained using a conventional process.

2. Experimental

85 wt% of B_4C (F20 Metabap 5003) and 15 wt% of C graphite powders (Alfa Aesar 99.9995%, D50 ~ 74 μm) were thoroughly mixed in an agate mortar under dry condition. An organic binder (Rhodoviol 4%, Prolabo) was added to the mixture powder and cylindrical samples (6.5 mm diameter and 5.4 mm thickness) were made using a 30.6 kN uni-axial load. Green pellets have an apparent specific weight of about 1.6 g cm^{-3}, which is roughly 65% of the theoretical value of the B_4C–C mixture ($\approx$ 2.47 g cm^{-3}). Cylindrical samples ($m \approx 0.15$ g, 6.5 mm diameter and 3 mm thickness) of Si powder (Alfa Aesar 99.9%, 0.149 mm) were also made using the same process. The amount of silicon was calculated in order to fully fill the pores of the B_4C–C preform. Assuming that the silicon infiltrates throughout the preform and subsequently fully reacts with graphite to form SiC, the final composition theoretically expected is made of 56% B_4C, 32.5% SiC and 11.5% Si by weight, and the theoretical density of this final mixture is about 2.72 g cm^{-3}. It must be noted that this composition is not optimized to reduce the final amount of residual silicon (to do so, the amount of graphite should be higher). However, this silicon amount is large enough to totally fill the pores and thus, it is suitable to investigate the reactivity between B_4C, C and Si in our experimental conditions. The microwaves heating system consists of a microwaves generator (SAIREM GMP 20 KSM, 2.45 GHz), which delivers a variable power up to 2 kW along a standard R26 rectangular waveguide (section of 86.36×43.18 mm^2) equipped with two circulators and ended by a TE_{10M} rectangular microwaves cavity. The cavity can be tuned in both modes TE_{10m} ($m = 2$ or 3) by adjusting the length between the coupling iris and the short circuit piston [18,19]. The temperature was measured using an infrared pyrometer (Ircon, Modline 5, 350–2000 °C) vertically positioned on the top of the cavity and focused on the top of the samples surface [19]. The scheme of the overall assembly is illustrated in Fig. 1. A cylindrical SiC susceptor was used to limit the radiation losses from the sample surface. Moreover, thermal insulation was ensured using BN powder placed between the SiC susceptor and the BN crucible, as shown in Fig. 1. The process consists in (i) putting a silicon cylinder on the top of the B_4C–C graphite cylinder, (ii) putting the double-layer sample inside the specifically designed crucible, and (iii) putting the assembly inside the cavity at the appropriate location. Then, the sample was heated up by raising the power by 50 W steps every 10 min until 650 W to reach a temperature of about 1500 °C and a 10 min dwell time was imposed at the final temperature. The heating was investigated in the TE_{102} mode at H field maximum in order to minimize the risk of plasma formation and arcing, especially when semiconducting materials are heated using

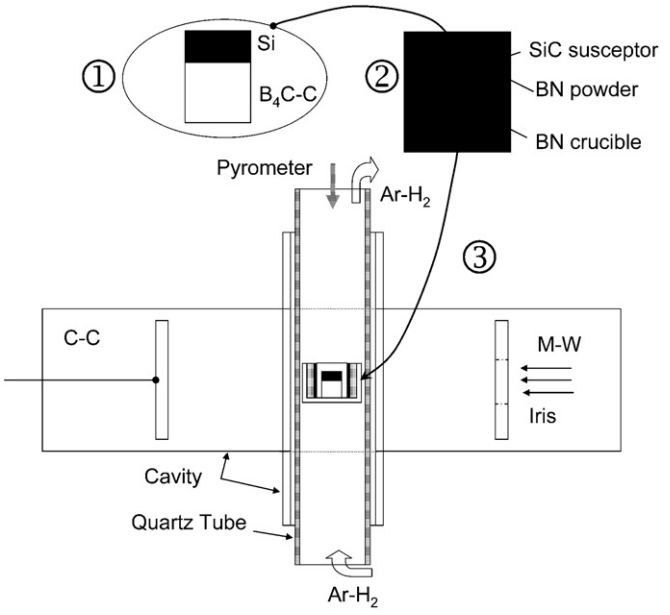

Fig. 1. Scheme of the microwaves TE_{10m} single-mode cavity, representing the used process and a picture of the home-designed crucible.

microwaves [16]. Afterwards, the assembly was cooled down to RT during 30 min. The entire heating cycle was conducted under a gas flow made of 95% Ar + 5% H_2. The crystalline phases were identified by X-Ray diffraction (XRD) using Cu K_α radiation (Philips X'Pert diffractometer). The sintered samples were coated in a carbon resin (Struers Polyfast), polished (Struers Tegra-Pol 31) and observed by a scanning electron microscopy (Zeiss Supra 55). Chemical composition was checked by SEM and energy dispersive microscopy (EDAX–EDS). Hardness was determined using a Vickers type micro-durometer with an applying force of 1 kgf and Young's modulus was determined using a nanoindenter (MTS XP), equipped with a Berkovich tip, for a 10,000 nm indentation depth.

3. Results and discussion

Fig. 2A shows a typical cross-section of a sample obtained using the microwave reaction-bonded process. It is clearly shown that the molten silicon has fully infiltrated the porous body. The apparent density is about 2.6 g cm^{-3}, which is very close to the expected value ($\approx$ 2.72 g cm^3), assuming a complete reaction between graphite and silicon. The sample dimension changes are about 0% and about −5.1% along respectively, the diameter and the height. Compared to the classic sintering process, which leads to shrinkage values ranged between 15% and 20%, it is observed that the reaction-bonded process is a near net shape technique, which is a great advantage compared to the conventional sintering process. The anisotropy of the samples shrinkage observed is not clearly understood yet. It may be due to the fact that the preform has been uni-axialy pressed. The SEM microstructure (Fig. 2B) reveals, as expected, a composite microstructure consisting of B_4C and SiC grains, embedded within a silicon matrix. The SiC grains have mostly a polygonal shape, which is very similar to the microstructure reported by Hayun et al. [20] in free carbon added reaction-bonded boron carbide composite. Moreover, the microstructure presents very few pores, which confirms that the infiltration process was successfully completed. SEM observations at various locations of the pellets reveal a quite uniform and homogeneous microstructure at large scale throughout the sample. The XRD pattern performed on a crushed sample is shown in Fig. 3. It appears that the sample seems to be made of B_4C, β-SiC and residual silicon. Hayun et al. [20,21] have deeply studied the microstructure of the reaction-bonded boron carbide made using a conventional method. They used the silicon infiltration process in vacuum (10^{-5} Torr) using preform of B_4C with or without carbon addition. They reported that the reaction-bonded boron carbide composite microstructure consists of core-rimed boron carbide particles, β-SiC and residual Si. They explained that the molten silicon is saturated with free carbon and boron; hence, a reaction due to a secondary equilibrium of the ternary system occurs. The newly formed equilibrium phase, i.e. $B_{12}(B,C,Si)_3$, precipitates at the interface with the initial boron carbide particles and forms the rim regions. The rim region can be seen using SEM and/or in

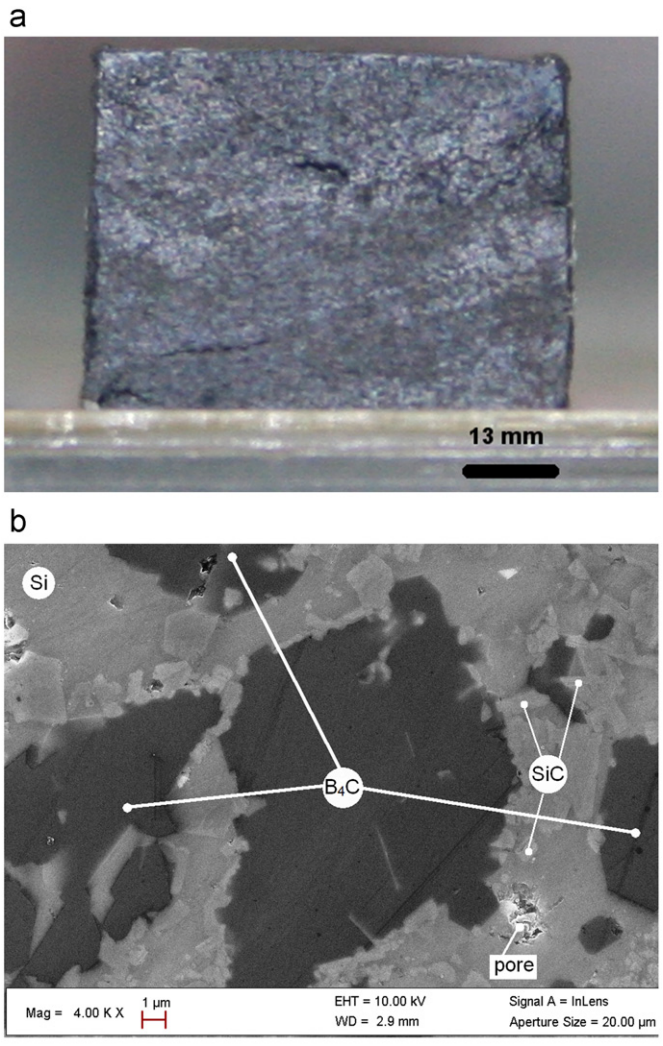

Fig. 2. (a) Cross section of a typical RB B_4C–SiC sample processed using microwaves and (b) its typical microstructure observed using SEM.

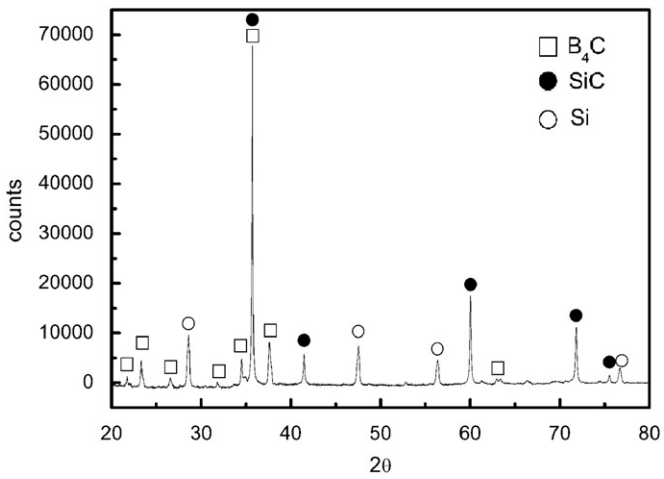

Fig. 3. XRD pattern of a crushed RB B_4C–SiC composite sample.

the XRD pattern, in which a slight split of the 'B_4C' peaks is observed. In reaction-bonded sample obtained using microwave sintering, the XRD pattern does not reveal any peak split (Fig. 3). This confirmed that the composite is mainly made of B_4C, β-SiC and residual silicon. It may be assumed that the rapid heating generated by microwaves and the fact that the infiltration process has been done under an $Ar–H_2$ gas flow at atmospheric pressure may prevent the secondary reaction. Young's modulus was calculated by nano-indentation along the z-axis of the sample and plotted against z (depth) in Fig. 4. Measurements were carried out as a matrix 12×4 (vertical $\times$ horizontal) with an indentation depth of 10,000 nm to obtain large imprints in order to test an area which has a quite homogeneous composition. So, for each depth values, four values of Young's modulus and hardness were obtained and measurement points were separated by 400 μm. Finally, it appears that the average Young's modulus is about 309 ± 4 GPa. In addition, the hardness was determined using a Vickers type micro-durometer along the z-axis of the sample and plotted against z in Fig. 4. Measurements were carried out as a matrix 9×4 and the measurement points were separated by 500 μm. Results show an average hardness value of 22 ± 0.5 GPa. It is noted that these mechanical properties are constant throughout the sample, which confirms the microstructure homogeneity and the uniform composition throughout the sample. Because of (i) the obtained microstructure slightly different from the one obtained by conventional process [20,21], since the core-rimed region has not been observed and because of (ii) the quite large residual silicon phase amount (estimated by calculations to, at least 12.7 vol% if we assumed that all the graphite has reacted but, as the composition was not experimentally determined, it is possible that this amount is underestimated), the average value of Young's modulus is slightly lower than the one obtained using the conventional process, which is about 360 GPa [22]. However, the average hardness value obtained in the experiment ($H \approx 22$ GPa) is comparable to the reported value obtained by a conventional reaction-bonded process (about 20–22 GPa) [21]. It can also be noted that those mechanical properties can be improved by adjusting the initial composition to reduce the residual amount of silicon.

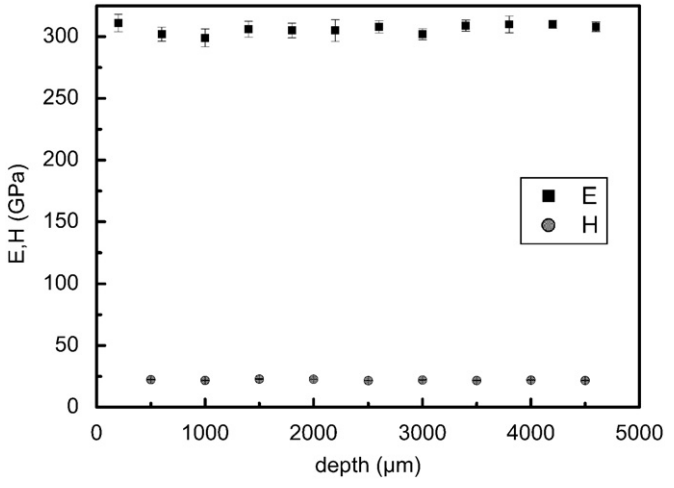

Fig. 4. Representation of Young's modulus (E) and hardness (H) values as a function of the depth z.

4. Conclusion

An original assembly made of a silicon carbide susceptor and a boron nitride based insulating crucible, was designed to produce reaction-bonded boron carbide samples, using a TE_{102} single-mode microwaves cavity. The heating process was successfully carried out, under a flowing $Ar–H_2$ atmosphere, without noticing any undesirable effects such as arcing or plasma formation. In this study, we have successfully produced a pore free reaction-bonded B_4C–SiC composite, owing to the good silicon infiltration throughout the preform. The final microstructure results in a mixture of B_4C and polygonal shaped β-SiC in a residual silicon matrix. The mechanical properties are comparable to those obtained conventionally and the average hardness value (about 22 GPa) is quite constant all along the sample z-axis. In order to produce larger samples, experiments in a multimode microwave system are in progress.

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