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Journal of Solid State Chemistry 177 (2004) 410–414

JOURNAL OF
SOLID STATE
CHEMISTRY

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The effect of the sintering atmosphere on the densification of B_4C ceramics

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Received 26 September 2002; accepted 3 February 2003

Abstract

Densification of boron carbide during sintering may be improved by a two-stage process, namely heating to 2000°C under vacuum and sintering at 2190°C under argon. This sintering regime allows achieving a relative density of the ceramic bodies fabricated from a fine powder higher than 95%. The nitrogen treatment of the boron carbide phase at 1900°C leads to the formation of the BN phase and precipitation of graphite. Vacuum treatment of these samples at 2000°C leads to decomposition of the boron nitride phase. The liberated free boron may again react with graphite to form in situ boron carbide particles. The experimental investigations of the sintering behavior of the boron carbide phase under various atmospheres supported the thermodynamic predictions regarding the phase transformation. No evidence, however, was found for enhanced sintering under a nitrogen atmosphere.

Keywords: Boron carbide; Sintering; Densification; Nitrogen atmosphere; Thermodynamic prediction

1. Introduction

The outstanding properties of B_4C, such as stiffness, hardness, and wear resistance, make it a valuable potential material for a variety of applications [1–3]. The realization of this potential is hindered, however, by two major drawbacks, namely the low fracture toughness of B_4C and the very high temperature required for its sintering, due to the covalent bonding that prevails in boron carbide. Sintering schedule at such elevated temperatures leads to rapid grain coarsening and generates equipment-related problems. Thus, there exists a very strong motivation for decreasing the temperature required to attain desired levels of density of sintered ceramics.

Sintering B_4C powder compacts is commonly performed in an inert gas medium. In the present work, we have attempted to evaluate the effect of vacuum and of nitrogen as sintering media on the densification of boron carbide powder. There are some justifications for using a vacuum medium instead of an argon atmosphere during the sintering of non-oxide ceramics. Sintering under vacuum cleans a surface from oxide contaminations, prevents further oxidation, and promotes one of the possible sintering mechanisms, namely the evaporation–condensation process. On the other hand, it is very difficult to use a vacuum medium at temperatures higher than 2000°C. The use of a nitrogen atmosphere was motivated by the possibility of having nitrogen react in a certain temperature range with boron carbide resulting in the formation of the boron nitride phase and in graphitization of B_4C. It was expected that at higher temperatures, the treatment under vacuum would lead to the dissociation of boron nitride, the formation of free boron that may again react with carbon, generating an active in situ formed B_4C. The analysis of these reactions will be discussed below.

2. Experimental

The carbide powders used in this study were supplied by H.C. Starck, Germany, grade HS, denoted “Starck” and by “Modan Jang”, a Chinese Company, denoted “MJ”. The sintering behavior of B_4C powders is affected very significantly by its composition, in

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doi:10.1016/j.jssc.2003.02.001

Table 1
Chemical compositions of the boron carbide powder (wt%)

Element or compounds	B_2O_3	Si	N	O	C			B	Total[a]
					Combined	Free	Total		
Starck	0.46	0.09	0.426	2.04	20.69	1.28	21.97	74.96	99.946
MJ	0.05	0.7	0.12	0.6	19.80	0.90	20.5	77.8	99.770

[a] The balance consists of Al, Fe, Ca, and other unidentified impurities.

particular, the presence of excess free carbon is an important factor. The chemical compositions of the powders determined by ICP-OE method are shown in Table 1. The average particle size, the B/C ratio and the specific surface area (BET), as determined by the supplier for the Starck powder, were 0.8 μm, 3.7–3.8, and 15–20 m^2/g, respectively. These values for the MJ powder were 4.5 μm, 3.9–4.1, and 1.5 m^2/g, respectively.

Green tablet-shaped preforms of boron carbide ($\varnothing$ $20 \times 7\,mm^2$) were prepared by uniaxial compacting the powders with 5–6% paraffin wax at 100 MPa. The sintering process was performed in an "ASTRO" furnace with graphite heating elements. High-purity (99.99%) argon and nitrogen were used in this work.

The density of the sintered preforms was measured by the liquid displacement method in distilled water. Phase composition of the ceramic bodies was determined by X-ray diffraction ("Rigaku", RINT-2100, Cu$K\alpha$ line). A scanning electron microscope (SEM, JEOL-35) was used for the microstructural studies.

3. Results and discussion

3.1. Sintering under a combined vacuum–argon atmosphere

The use of vacuum for sintering above 2000°C is usually limited by the specific characteristics of high-temperature furnace. The internal parts of these equipments are made of graphite and ultraporous carbon material that are considered to be incompatible with high vacuum demands. We were able, however, to run the furnace up to 2000°C in a vacuum with residual pressure of 13–6.5 Pa. At higher temperature, an inert gas must be applied in order to eliminate electric arcing. Thus, heating up to 2000°C was conducted under vacuum and a higher temperature treatment at 2190°C for 1 h was carried out under argon. This treatment yielded 94% and 80% relative density for the Starck and the MJ powder, respectively. A similar treatment under a continuous flow of argon up to 2190°C, yielded samples with 83% and 70% relative density.

3.2. Sintering under a nitrogen atmosphere

3.2.1. Theoretical background

As mentioned above, an underlying premise of this work that by varying the sintering atmosphere it might be possible to decrease the sintering temperature. Reduction of the sintering temperature may be due to a chemical interaction between the solid and gaseous phases that may lead to the partial decomposition of the carbide phase and formation of additional phases. At a relatively low temperature, sintering under nitrogen may lead to the formation of BN and pure carbon. At a higher temperature, however, sintering under vacuum allows the decomposition of the nitride phase, removal of the nitrogen from the sample and formation of pure boron. The interaction between boron and the previously formed carbon could lead to the formation of very fine carbide particles that may enhance the rate of sintering.

A thermodynamic analysis of the B–C–N system allows defining the appropriate temperature regimes for sintering the boron carbide phase.

The interaction of the boron carbide phase with nitrogen can be expressed as

$$B_4C + 2N_2 = 4BN + C. \quad (1)$$

We can evaluate the free Gibbs energy of reaction (1) from the standard values of the following reactions:

$$4B + C = B_4C, \quad (2)$$

$$BN = B + 0.5N_2. \quad (3)$$

The standard free energy of formation (J/mol) for these reactions are [4]

$$\Delta G^0(2) = -67\,496 + 7.78\,T, \quad (4)$$

$$\Delta G^0(3) = 25\,117 - 87.61\,T. \quad (5)$$

For reaction (1) we have

$$\Delta G^0(1) = -937184 + 342.66\,T. \quad (6)$$

The equilibrium constant of reaction (1) may be expressed by Eq. (7). Notice that in this and the following Eq. (8), the pressure is expressed in units of atms,

$$\ln K(1) = -2\ln P_{\mathrm{N}_2} = \frac{112\,784}{T} - 42.22. \tag{7}$$

From Eq. (7), we can conclude that the equilibrium nitrogen pressure is very low and up to 2671 K, boron nitride is the stable phase under a nitrogen atmosphere of 10^5 Pa. At 2000 K, for instance, the nitrogen pressure, which leads to decomposition of boron carbide, is 50 Pa.

Under vacuum, decomposition of boron nitride occurs and the lowest total pressure in the furnace chamber may be estimated from reaction (3). For reaction (3) we may write

$$0.5\ln P_{\mathrm{N}_2} = -\frac{30\,210}{T} + 10.54. \tag{8}$$

According to Eq. (8) at 2200 K, the equilibrium nitrogen partial pressure is 170 Pa. Thus, poor vacuum conditions in the system must lead to the decomposition of the boron nitride phase and formation of pure boron.

On the basis of the above analysis, we suggested a four-step process for sintering boron carbide. The first step up to 1900°C is to be performed in vacuum (5–10 Pa), the second step at the same temperature under nitrogen atmosphere, the third steps in vacuum of 50 Pa at about 2000°C, and the final stage of the sintering process should be conducted at a still higher temperature for improved densification of the ceramic preforms.

The duration of the various steps of the process is strongly affected by kinetic factors and must be established by an appropriate experimental investigation.

3.2.2. Experimental verification

Previous experiments have shown that sintering under combined atmosphere at 2190°C allows reaching approximately 94–95% of the theoretical density (TD) for the Starck powder and at most 78–80% of TD, for MJ powder specimens. Thus, the second step in the four-step process at 1900°C was conducted under a nitrogen treatment for duration from 5 to 60 min. The next step under vacuum at 2000°C was conducted under vacuum for 30 min and finally the sample was heated under an argon atmosphere and maintained at 2190°C for 1 h.

The specimens underwent a change of weight during the combined nitrogen vacuum treatment as shown in Fig. 1.

The formation of the BN phase is associated with an increase of the specimen weight, according to reaction (1), and the longer the treatment, the larger the weight increase. The rate of the new phase formation for the fine Starck powder was significantly higher than that for the relatively coarse MJ powder. This feature may be attributed to the higher specific surface of the fine particles. The heating of the specimens after nitridation under vacuum, as expected, leads to a mass loss, which may be attributed to the decomposition of the boron nitride (reaction (3)).

It must be noted that the weights of the preforms treated in vacuum are higher than the initial weights of the sample before treatment in the nitrogen atmosphere. Obviously, only partial decomposition of the BN took place during the applied vacuum treatment. The final weight loss after sintering under argon at 2190°C is negligible, thus the decomposition of the BN takes place only under vacuum, and a residual BN is present within the sintered preforms.

The occurrence of the phase transformation in the boron carbide preforms was confirmed by XRD analysis (Figs. 2 and 3). There are some intrinsic difficulties for evaluating the XRD patterns. The main peaks of BN are located at 26.717° (100%), 42.620° (13%), and 45.566° (7%). The corresponding peaks that can be attributed to carbon are at 26.603 (100%), 42.464 (3%), and 44.669 (13%). A partial overlap of the reflections takes place

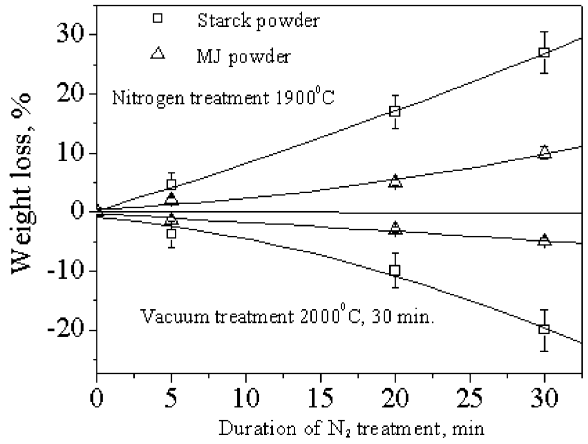

Fig. 1. Weight changes during nitrogen and vacuum treatments for Starck and MJ powders.

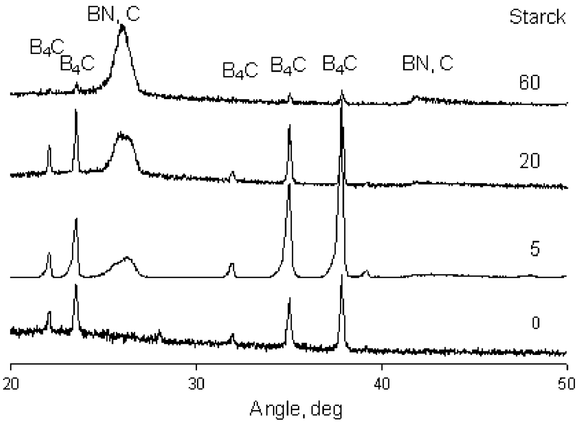

Fig. 2. Phase composition of the sample treated in nitrogen for various times. The figures on the legend denote the duration of the treatment, 0—non-treated sample, 5, 20, and 60—duration of the treatment in minutes (Starck powder).

and a very broad, undefined peak is present in the 26–27° angle range. This feature suggests the simultaneous presence of both BN and a carbon phase.

The interaction of the fine B_4C powder (Starck) with N_2 appears to be very rapid and even a few minutes of nitrogen treatment resulted in the formation of a mixture of B_4C, BN, and carbon. The samples that were treated for 1 h had BN as the predominant component (Fig. 2). For the MJ powder, the rate of nitridation was significantly lower due to its larger grain size (Fig. 3). The new phase formation was clearly detected only after 60 min of N_2 treatment. This observation is in accordance with the weight changes of the samples fabricated from MJ powder.

The XRD patterns of the samples after nitridation, which were treated under vacuum at 2000°C and sintered at 2190°C under argon, are similar to the initial patterns of the boron carbide powders with small peaks corresponding to the residual BN and carbon phase (Fig. 4)

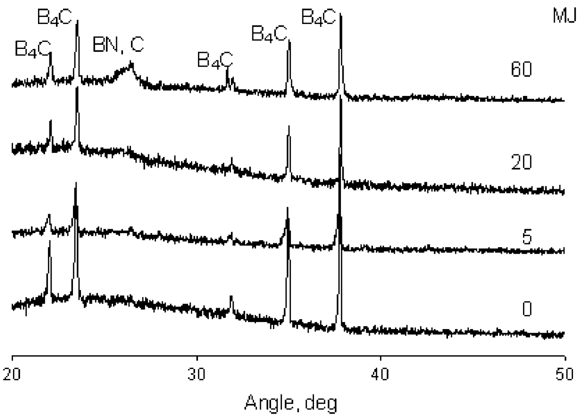

Fig. 3. Phase composition of the sample treated in nitrogen for various times. The figures on the legend denote the duration of the treatment, 0—non-treated sample, 5, 20, and 60—duration of the treatment in minutes (MJ powder).

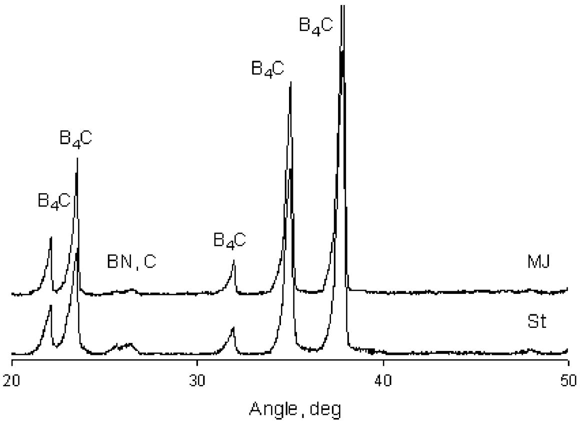

Fig. 4. The XRD patterns of the samples after nitridation, vacuum treatment at 2000°C and sintering at 2190°C under argon.

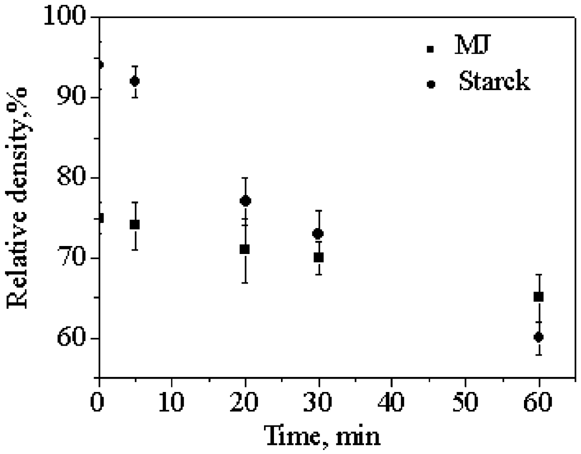

Fig. 5. Relative density of boron carbide specimens vs. duration of nitrogen treatment at 1900°C, the final sintering temperature was 2190°C.

Unfortunately, all specimens subjected to the N_2 treatment, displayed a decrease of density (Fig. 5). The longer the duration of the N_2 stage, the larger the density decrease.

For instance, a 1 h nitrogen treatment results in a relative density of 60% as compared to 94% for Starck B_4C. The density of the other samples from MJ powder was also reduced by 12–16% after the nitrogen treatment. This effect may be attributed to the influence of the residual BN phase on the sintering of boron carbide.

The fracture surfaces of the partially sintered preforms from Starck powder, which were obtained under the various conditions, are shown in Fig. 6.

There is no evidence of sintering and of initial neck formation after a nitrogen treatment at 1900°C (Fig. 6a). This may be attributed to BN formation and carbon precipitation on the B_4C particles. The final sintering at elevated temperature leads to only a slight increase of the density of the sintered preforms (Fig. 6b). The structure of the sintered samples with no nitrogen treatment displays a very high density, without any accompanying significant grain growth (Fig. 6c). Thus, in general, under the conditions that were investigated in the present work, there is no advantage in applying a nitrogen treatment.

4. Conclusions

Sintering under a combined vacuum–argon atmosphere leads to remarkable improvement of boron carbide densification and allows to reach 94–95% relative density for powder supplied by H.C. Starck. The results of the nitrogen treatment are strongly affected by kinetic factors. Under the specific conditions used in this investigation there appears no advantage in the use of a nitrogen treatment. Nevertheless, the

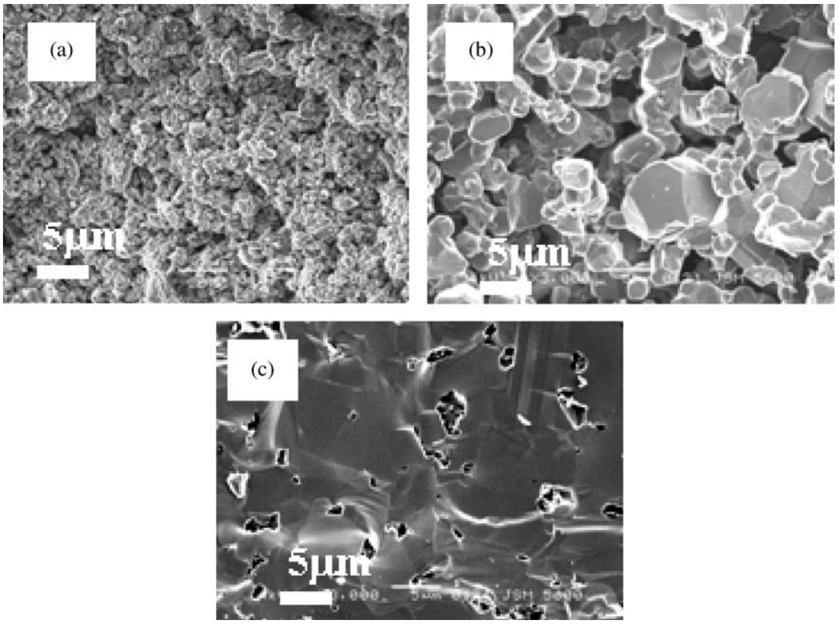

Fig 6. Microstructure of the fracture surface of B_4C ceramic preforms (Starck): (a) after a nitrogen treatment for 1 h at 1900°C; (b) the same sample after a further vacuum treatment at 2000°C for 1 h and at 2190°C in argon for 1 h; and (c) reference sample sintered under vacuum at 2000°C and in argon at 2190°C.

determination of the appropriate external conditions for improving the sintering rate of boron carbide must be pursued.

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