Journal of the European Ceramic Society xxx (2017) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Full Length Article

Comminution of B_4C powders with a high-energy mill operated in air in dry or wet conditions and its effect on their spark-plasma sinterability

Angel L. Ortiz [a,*], Florentino Sánchez-Bajo [b], Victor M. Candelario [c,d], Fernando Guiberteau [a]

[a] Departamento de Ingeniería Mecánica, Energética y de los Materiales Universidad de Extremadura, 06006 Badajoz, Spain
[b] Departamento de Física Aplicada, Universidad de Extremadura, 06006 Badajoz, Spain
[c] LiqTech International AS,Industriparken 22C, 2750 Ballerup, Denmark
[d] Department of Energy Conversion and Storage, Technical University of Denmark, Risø Campus, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

ARTICLE INFO

Article history:
Received 17 January 2017
Received in revised form 15 May 2017
Accepted 17 May 2017
Available online xxx

Keywords:
B_4C
Comminution
Ball-milling
Spark-plasma sintering

ABSTRACT

The comminution of a typical submicrometre B_4C powder with a high-energy mill (i.e., a shaker mill) operated in air in either a dry or a wet environment was investigated. It was found that dry shaker milling (i.e., high-energy ball-milling) is able to progressively refine the B_4C particles to the nanoscale. While this is accompanied by oxidation and aggregation, these are not serious drawbacks. Wet shaker milling in methanol (i.e., conventional ball-milling) resulted only in a moderate B_4C particle refinement with greater contamination by the milling tools, which limits its usefulness. It was also found that both dry and wet milling modify the B_4C crystal structure, attributable to carbon enrichment. Consequently, dry shaker milling was found to be more recommendable than wet shaker milling to provide B_4C starting powders with superior sinterability. A comparative densification study by spark-plasma sintering confirmed this recommendation, and also showed the usefulness of dry shaker milling to obtain refined B_4C microstructures for structural applications.

1. Introduction

B_4C is an engineering ceramic with great appeal for structural applications requiring ultrahigh hardness and lightness [1–6]. Ceramic armours and tribocomponents are two representative examples of such applications. Unfortunately, one serious problem that has plagued B_4C is that it is not densifiable in the pure state by conventional solid-state sintering (i.e., pressureless sintering or hot-pressing) unless very demanding sintering conditions are used [2]. The undesirable consequence is that B_4C ceramics have poorer mechanical properties than expected because they are either porous or possess coarse-grained microstructures [2,7–10], and this conditions their great potential as structural ceramics. It is then understandable that liquid-phase sintering additives have been used to densify B_4C, ideally seeking dense fine-grained microstructures. Unfortunately, however, the resulting ceramics are much softer [2].

It is well established that the finer the particles in the ceramic's starting powder, the greater its solid-state sinterability [11]. Certainly, this has been observed for B_4C [12]. A common practice within the ceramics community to promote densification is therefore to refine the starting powders by some type of mechanical milling. Generally, either conventional ball-milling or attrition milling is used, but high-energy ball-milling is potentially capable of producing much finer particles [13–16]. This option would thus seem to in principle be more desirable with a view to assist in B_4C sintering, a long sought for objective for these advanced ceramics.

With this premise in mind, the present study had two objectives. The first was to investigate the high-energy ball-milling behaviour of a typical B_4C starting powder. The underlying motivation was to elucidate the milling conditions that would lead to effective B_4C comminution. For this purpose, we subjected the same submicrometre B_4C powder to shaker milling in air in either a dry or a wet environment for different times (from a few minutes to one day), and characterized the resulting powders in detail. The second was to evaluate the effect of the prolonged milling on the spark-plasma sinterability of B_4C. The underlying motivation here was to identify fabrication strategies that might help in the forthcoming

* Corresponding author.
E-mail address: alortiz@unex.es (A.L. Ortiz).

http://dx.doi.org/10.1016/j.jeurceramsoc.2017.05.034
0955-2219/

challenge of obtaining B_4C nanoceramics [17–21]. For this purpose, we compared the densification under the same conditions of spark-plasma sintering (SPS) of the as-received B_4C powder and of the B_4C powders milled for 600 min in dry or wet conditions.

2. Experimental procedure

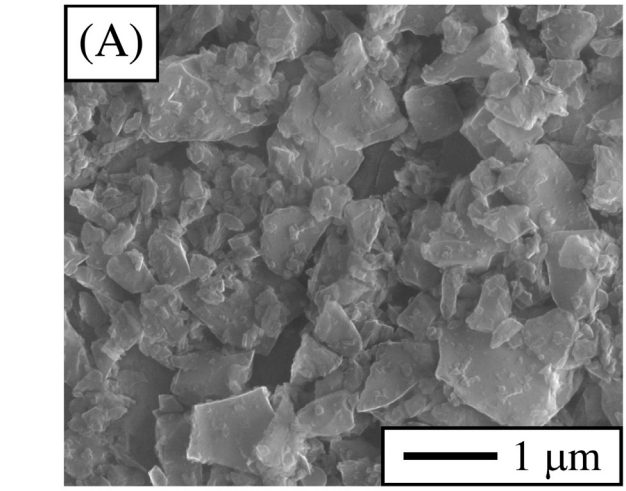
The starting material was a commercially available B_4C powder (Grade HD20, H.C. Starck, Germany). According to the manufacturer's specifications, this powder has an average particle size of ~0.6 μm. Its comminution was performed using a shaker mill (Spex D8000, Spex CertiPrep, USA) whose operating principle is to shake the milling container in a complex three-dimensional trajectory at about 1060 back-and-forth cycles per minute. The milling was carried out in air using cylindrical WC containers in turn loaded with 5 WC-Co balls of 6.7 mm in diameter and 3 g of B_4C powder (so that the ball-to-powder weight ratio is ~4), for different times in the range 3–1440 min taken as the values of a comminution variable whose influence on the powder's features was to be investigated. In addition, two types of milling were implemented, one in dry conditions and the other in wet conditions, this latter by pouring 30 ml of methanol into the milling container (filling ~ one-third of the volume), which was taken to be another comminution variable. Methanol was chosen because it is known that methylation of B_4C removes the oxidic impurities that are particularly detrimental for its sinterability [21–23].

The as-received and the two sets of milled powders were selectively characterized using a wide battery of characterization techniques, including high-resolution X-ray diffractometry (XRD; D8 Advanced, Bruker AXS, Germany), field-emission scanning electron microscopy (FE-SEM; Quanta 3D FEG, FEI, The Netherlands), laser scattering (LS; Mastersizer 2000, Malvern Instruments, UK), X-ray photoemission spectroscopy (XPS; K-Alpha, Thermo Scientific, UK), and transmission electron microscopy (TEM; Tecnai G^2-20 Twin, FEI, The Netherlands) together with selected area electron diffractometry (SAED). The protocols of sample preparation for each of these techniques followed standard procedures for ceramic powders, and therefore are not described here.

Finally, the as-received powder and the powders milled for 600 min in dry or wet conditions were densified by SPS (HP D 10, FCT Systeme GmbH, Germany) in a dynamic vacuum atmosphere at temperature of 1700 °C (as measured by an optical pyrometer focused vertically on a hole machined across the upper graphite punch) for 3 min under 75 MPa pressure, with a heating ramp of 100 °C min^{-1}. The 75 MPa pressure was applied at room temperature (in 2 min), followed by the heating cycle. After the completion of the SPS cycle, the pressure was released and the electrical power was shut off to allow rapid cooling (i.e., in 1–2 min) to room temperature. The SPS-ed samples were then broken, and their fracture surface observed by FE-SEM. They were also polished to 1-μm finish using conventional ceramographic methods, and mechanically characterized by Vickers indentation tests (MV-1, Matsuzawa, Japan) at 9.81 N load (ten indentations per specimen).

3. Results and discussion

Fig. 1 shows a representative FE-SEM image and the XRD pattern of the as-received B_4C powder. It can be seen in Fig. 1A that the FE-SEM observations confirm the average particle size in the submicrometre range indicated by the manufacturer (i.e., ~0.6 μm), and also show that the particles are equiaxed and faceted. According to its XRD pattern shown in Fig. 1B, this powder contains not only B_4C but also H_3BO_3 and graphite impurities, which is not a surprise for B_4C prepared by carbothermic reduction [24].



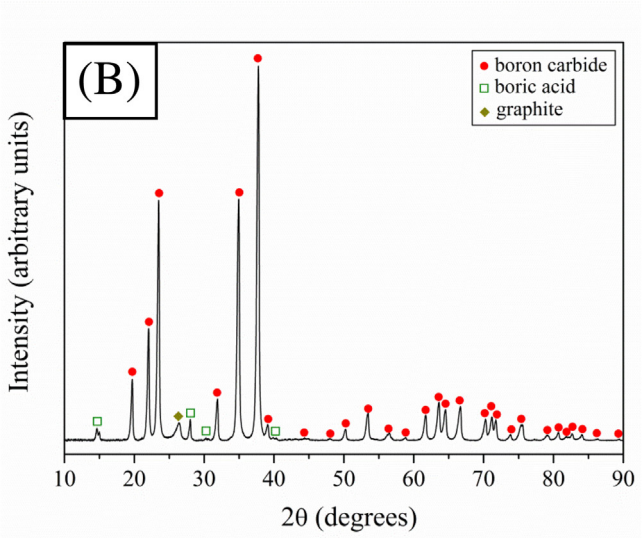


Fig. 1. (A) Representative FE-SEM micrograph and (B) XRD pattern (peak assignations are included for relevant peaks) of the as-received B_4C powder.

Figs. 2 and 3 show selected sequences of representative FE-SEM images of the B_4C powders milled for different times under dry and wet conditions, respectively. Relative to the as-received powder in Fig. 1A, it can be seen in Fig. 2A–F that dry milling progressively refined the primary particle size to the nanoscale by brittle fracture, in the long term with formation by cold-welding of submicrometre and micrometre aggregates as seen in Fig. 1D–F. This SEM observation was confirmed by LS. For example, the particle size (D_{50}) was found to be 0.64 μm in the as-received powder, but 3.04 μm after the dry milling for 600 min. Also note in Fig. 2 the faceted morphology of the single-crystal particles in the powders for the short- and moderate-term millings, and the rounded morphology of the aggregates with smoother-surfaced nanoparticles in their interior for the long-term millings. Occasionally, sparse ultrafine or nanoscale WC particles were also observed within the aggregates. These are debris from the wear of the milling tools. Cold-welding is possible because during high-energy ball-milling there is a local temperature spike at the collision site (~300–500 °C) with the presence of high compressive stresses (~6 GPa) of very short duration (~10^{-6}–10^{-5} s) [25,26], conditions at which the B_4C nanoparticles behave in a ductile manner. The same dry milling behaviour has indeed been observed for other brittle borides [14–16] and carbides [27]. In contrast, it can be seen in Fig. 3A–F that wet milling caused

Please cite this article in press as: A.L. Ortiz, et al., Comminution of B_4C powders with a high-energy mill operated in air in dry or wet conditions and its effect on their spark-plasma sinterability, *J Eur Ceram Soc* (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.05.034