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Densification and properties of superhard B_6O materials with cobalt additions

O.T. Johnson [a,*], I. Sigalas [a], M. Herrmann [b], H.J. Kleebe [c]

[a] School of Chemical and Metallurgical Engineering, University of the Witwatersrand, P/Bag 3, Wits, 2050 Johannesburg, South Africa
[b] Fraunhofer Institute of Ceramic Technologies and Systems, Winterbergstrasse 28, D-01277 Dresden, Germany
[c] Technische Universität Darmstadt, Institute for Applied Geosciences, Schnittspahnstr. 9, D-64287 Darmstadt, Germany

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Abstract

The search for suitable additives for boron suboxide (B_6O) materials which could improve densification, reduce sintering temperature and tailor the microstructure has been productive. B_6O materials doped with 0–5 vol% cobalt addition were sintered at temperatures up to 1850 °C and pressure of 50 MPa for 20 min. Relationships between the formed phases, microstructures and mechanical properties of the sintered materials were investigated as a function of sintering conditions and added cobalt content. The hardness of the sintered B_6O materials increases with sintering temperature, while the fracture toughness increases with increasing cobalt content and reduces with increasing sintering temperature.

Keywords: Boron suboxide (B_6O); Microstructure- final; Sintering; Mechanical properties

1. Introduction

B_6O powders can be produced without any pressure applied, at 1300 °C, under argon, by reducing B_2O_3 with B or by oxidation of boron with zinc oxide or other oxidants.[1–5] However, it has been established that boron suboxide powders formed at or near ambient pressures are generally oxygen deficient (B_6O_x, $x < 0.9$). They also have poor crystallinity and very small grain sizes. However, it was reported that application of high pressure during the synthesis of B_6O can significantly increase the crystallinity, oxygen stoichiometry, and crystal size of the products.[1–3]

In addition, it is very difficult to sinter B_6O powders to full density, but a careful selection of additives combined with controlled sintering conditions could result in dense B_6O materials. Previous hot pressing studies concerning the densification of boron suboxide powders, made from mixing amorphous boron with boron oxide or with zinc oxide, have produced B_6O materials with densities in the range of 85–97% of theoretical density. These materials were hot pressed either under vacuum or argon at temperatures in the range of 1600–2200 °C. Although, an average Knoop hardness (100 g load) between 30 and 38 GPa was measured, the fracture toughness values were low ($\leq$2 MPa $m^{0.5}$) or sometimes not reported.[6–10]

Efforts have been made to enhance the mechanical properties of B_6O, especially its fracture toughness, by forming B_6O composites with other hard materials such as diamond,[4] boron carbide,[2] and c-BN.[3] Even though high hardness values were recorded for the composites ($H_v \sim 46$ GPa), again, fracture toughness values did not exceed 1.8 MPa $m^{0.5}$.[2–4]

Recently it was shown that B_6O materials with the addition of Al_2O_3 and rare earth oxides can be hot pressed or densified by the hot pressing or SPS/FAST technique at 1800–1900 °C. The resulting sintered materials had improved fracture toughness (3–5 MPa $m^{0.5}$) and only a slight reduction in Vickers microhardness (31 GPa under 500 g load) in comparison to pure B_6O-materials (34 GPa).[11–16] The investigation of the microstructure reveals that the material was densified predominantly by liquid phase sintering. Additionally, it was shown that

* Corresponding author at: DST/NRF Centre of Excellence in Strong Materials, School of Chemical and Metallurgical Engineering, University of Witwatersrand, P/Bag 3, Wits, 2050 Johannesburg, South Africa.
Tel.: +27 11 717 7515; fax: +27 86 553 6449.
E-mail addresses: Oluwagbenga.johnson@wits.ac.za, johnson.gbenga@gmail.com (O.T. Johnson).

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transition metals can be used as sintering additives too. Independently of the starting nature – of the additives, oxide or metal, during sintering they form borides.[17]

The present authors have reported previously on the chemical interaction between B_6O and cobalt by heat treating a reaction couple consisting of a cobalt sheet sandwiched between sintered and porous B_6O compacts.[18] The study shows that B_6O reacts with cobalt to form cobalt boride and some B_2O_3, which mostly evaporates.

$$Co + 0.1875B_6O \rightarrow 0.0625B_2O_{3(l,g)} + CoB \quad (1)$$

In addition, the results revealed that the liquid boride infiltrates the dense B_6O material, which is a strong indication that the B_6O is wetted by the melt. The data also suggested that the solubility of B_6O is not very high in the melt. Hence, the existence of wettability and solubility prove that the sintering of B_6O with transition metal borides like Ni, Fe and Co is a liquid phase sintering process.

In this paper, the densification behaviour of B_6O materials doped with different cobalt content using hot press was studied, and the resulting microstructure and mechanical properties were investigated.

2. Experimental procedure

The starting B_6O-powder was prepared by the reaction of B with B_2O_3 as described elsewhere.[5,11,13] The powder produced was jet milled up to a grain size of 2.5 μm and then attrition milled for 30 h with 2.5 mm steel balls at a speed of 200 rpm. The mean particle size of the powder was 0.5 μm measured using a Mastersizer 2000 (Malvern Instruments, Germany). The milled B_6O powder was repeatedly washed in 1 M HCl until the liquid colour changes from semi-transparent dirty yellow to colourless with the removal of contaminant from the steel balls, followed by washing in ethanol to remove remaining $H_3B_3O_3$. 0.09 wt% Fe and 0.01 wt% Cr were found as impurities after washing (ICP-OES SPECTRO CIRUS CCD, Spectro analytical Instrument (Pty) Ltd., South Africa).

Cobalt additives were precipitated on the B_6O powder from the reaction of $Co(NO_3)_2{\cdot}6H_2O$ and alkaline solution at 74 °C (Eq. (2.1)). The metallic oxide was then reduced in an H_2/Ar atmosphere at 800 °C (Eq. (2.2)). The Co contents precipitated were 0.5, 1, 2.5 and 5 vol%, respectively.

$$Co(NO_3)_2 \cdot 6H_2O_{(s)} + Na_2CO_{3(s)} \xrightarrow{74\,^\circ C} CoO_{(s)} + 2NaNO_{3(l)} + CO_{2(g)} + 6H_2O_{(l)} \quad (2.1)$$

$$CoO_{(s)} \xrightarrow{H_2/Ar/800\,^\circ C} Co_{(s)} \quad (2.2)$$

Pure B_6O powder was hot pressed (HP20 Thermal Technology) in hBN-lined-graphite dies in argon at 1900 °C and a pressure of 50 MPa for 20 min, while the powders with cobalt additions were sintered at temperatures between 1750 °C and 1850 °C, at the same pressure and isothermal sintering time. Hot-pressed samples were 18 mm in diameter and 3–4 mm in thickness. The pure B_6O powder densified at 1850 °C had shown only a density of less than 90% of theoretical density.[13]

After sintering the materials were ground to clean their surface from reaction products with the hBN lining. The density of the samples was determined using Archimedes principle. The theoretical densities were calculated on the basis of the rule of mixtures of the phases formed [the value of 2.55 g/cm^3 was used as the density of boron suboxide].[13] Cross-sections of the materials were polished using diamond slurry and were characterized using X-ray diffraction (PW1830; Philips; Cu Kα radiation, 2θ range: 10–80°, step size 0.02°). Microstructure observations were carried out using scanning electron microscopy (Philips, XL30 SERIES) with attached EDX system. TEM characterization was performed on the material containing precipitated Co. TEM foil preparation followed standard ceramographic techniques, including cutting, grinding, polishing and dimpling down to 10 μm. The dimpled discs were ion beam thinned with a Gatan Duo Mill 600 into two steps to electron transparency. During the first step, the acceleration voltage was set to 5 kV and the angle of incidence to 15°. This condition was maintained until the first transparent area was observed under an optical microscope. Then, the acceleration voltage was lowered to 2.5 kV and the angle of incidence to 12°. The thinned samples were lightly coated with carbon (Edwards Auto 306) to minimize charging under the incident electron beam. TEM characterization was performed with a FEI CM20 microscope (FEI, Eindhoven, The Netherlands) operating at 200 kV.

The Vickers hardness (H_v) and fracture toughness (K_{IC}) were measured using indentation techniques under a load of 1 kg. The average of five measurements was used to determine the properties of the samples. The K_{IC} was determined via the direct crack measurement method using Anstis's equation,[18] with the calibration constant $\xi = 0.016$ and elastic constant $E = 470$ GPa.[19]

3. Results and discussion

3.1. Densification and microstructure of B_6O materials

The B_6O material hot pressed without additives at temperature of 1900 °C resulted in a material having 96.5% of the theoretical density, which agrees with the value obtained by Kayhan and Inal.[20] An ultra-high pressure high temperature study, concerning the sintering of B_6O at pressures in the range of 3-5 GPa, done by Itoh et al.[21] also did not produce fully dense material. The density of the material was reported to be above 95% of theoretical. Therefore, the use of ultra-high pressures does not guarantee a completely dense material. Phase analysis of the sintered pure B_6O sample reveals only B_6O. TEM analysis of hot pressed B_6O sample in Fig. 1a and b shows that the hot pressed B_6O sample has stacking faults and plastically deformed grains. Deformation occurs as a result of pressure applied during hot pressing while the stacking faults are characteristic for structures based on B_{12} units, i.e. boron carbide structure.[22]

Densification of B_6O powder coated with different volume percent of cobalt using the precipitation method was carried out in the hot press at different temperatures within 1750–1850 °C and pressure of 50 MPa. Table 1 gives the full list of all the