Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 33 (2013) 2375–2390

www.elsevier.com/locate/jeurceramsoc

B_6O materials with Al_2O_3/Y_2O_3 additives densified by FAST/SPS and HIP

M. Thiele [a,*], M. Herrmann [a,1], A. Michaelis [b,2]

[a] Fraunhofer Institute for Ceramic Technologies and Systems, Winterbergstraße 28, 01277 Dresden, Germany

[b] University of Technology, Dresden, Fakultät Maschinenwesen, Institut für Werkstoffwissenschaft (IfWW), Professur für Anorganisch-Nichtmetallische Werkstoffe (ANW), 01062 Dresden, Germany

Received 29 October 2012; received in revised form 29 April 2013; accepted 4 May 2013
Available online 3 June 2013

Abstract

Fully densified B_6O materials with Al_2O_3/Y_2O_3 sintering additives amounts systematically varied between 0 and 15 vol.% and $Al_2O_3/(Al_2O_3 + Y_2O_3)$ molar ratios of 0.05–1 were prepared by FAST/SPS and HIP at sintering temperatures between 1725 °C and 1900 °C. Their densification and microstructure were correlated with measured mechanical properties. The addition of low additive amounts in the range of 2–3 vol.% was found to increase the fracture toughness and strength from 2.0 MPa $m^{1/2}$ (SEVNB) and 420 MPa for pure B_6O to about 3.0 MPa $m^{1/2}$ and 540 MPa, but it had no effect on the hardness, which remained at a high level of 30–36 GPa ($HV_{0.4}$). Higher additive contents did not yield a further improvement in the toughness but resulted in a reduction in hardness and strength.

Keywords: Boron suboxide; Mechanical properties; Microstructure-final; Wear parts

1. Introduction

With a reported hardness of up to 45 GPa, comparable with that of cubic boron nitride (cBN), as well as a toughness similar to that of diamond,[1] single-crystal boron suboxide (B_6O) possesses excellent mechanical properties. Therefore, materials on the basis of B_6O qualify as potential candidates for applications with a high demand in wear resistance i.e. cutting tools, abrasives and protective hard coatings. Although B_6O can be cost-effectively synthesized at ambient pressure, its commercial use is actually prevented by its poor sinterability due to low diffusion coefficients and a high vapor pressure as well as the low fracture toughness of polycrystalline materials. Usually high pressures of 1–5 GPa are required for complete densification, but the resulting fracture toughness does not exceed 2 MPa $m^{1/2}$.[2–4] Even efforts to improve the fracture toughness by forming composites with other superhard materials such as diamond,[5] cBN,[6] and boron carbide[7] yield only materials with a high hardness of up to 46 GPa but a fracture toughness of less than 1.8 MPa $m^{1/2}$.

Current research is focused on improving the densification and toughness of B_6O materials by the use of liquid-forming sintering additives. Thermodynamic calculations[8] as well as experimental investigations[8–13] determined oxides of the groups 1–4 in the periodic table as well as rare earth oxides as suitable sintering additives, which form stable oxide liquids during sintering. Moreover, boride-forming transition metals and the associated oxides from the groups 4–8 in the periodic table gained attention since some of these borides are liquid under sintering conditions (Fe, Co, Ni, and Pt group elements).[8,14–16] Even low additive amounts in the range of 2–4 vol.% are reported to enable full densification of B_6O by low-pressure sintering techniques such as hot pressing[9–11,14–16] or field-assisted sintering technology/spark plasma sintering (FAST/SPS).[8,12,17] In comparison to sintered pure B_6O, for example, materials densified with Al_2O_3 or Al_2O_3/Y_2O_3 addition showed only marginally lower hardness values, in the range of 30–35 GPa ($HV_{0.4–0.5}$).[8–10,12] A simultaneously higher fracture toughness in the range of 3–4 MPa $m^{1/2}$[9,11,12] and a high strength of up to 510 MPa[12] reveal a promising overall performance for

* Corresponding author. Tel.: +49 351 2553 7546.
E-mail addresses: maik.thiele@ikts.fraunhofer.de (M. Thiele), Mathias.Herrmann@ikts.fraunhofer.de (M. Herrmann), Alexander.Michaelis@ikts.fraunhofer.de (A. Michaelis).
[1] Tel.: +49 351 2553 7527; fax: +49 351 2554 122.
[2] Tel.: +49 351 2553 7512; fax: +49 351 2554 300.

0955-2219/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jeurceramsoc.2013.05.002

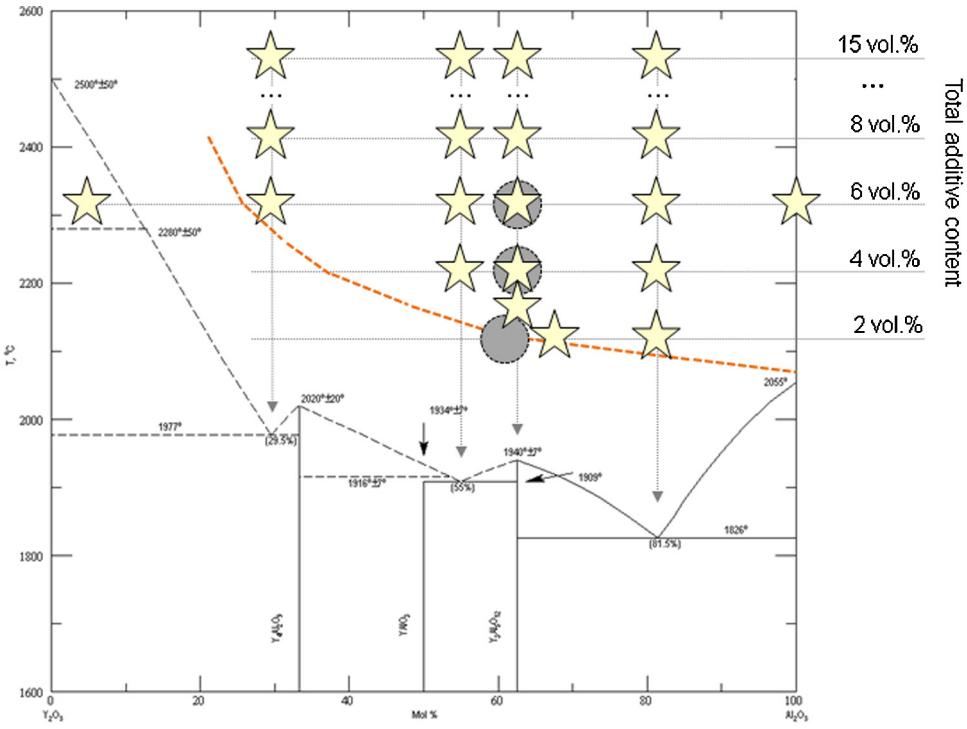

Fig. 1. Overview of the additive compositions used for the preparation of B_6O materials by FAST/SPS (stars) or HIP (circles) illustrated in the binary system Y_2O_3–Al_2O_3 of Mah and Petry.[24] The dashed line approximates the lowest possible $Al_2O_3/(Al_2O_3 + Y_2O_3)$ molar ratio as a function of the total additive content that can be obtained in the used batch preparation setup by attrition milling due to the wear of the alumina milling balls and impurities in the B_6O starting powder.

these materials for their potential use in cutting and wear applications.

Microstructural investigations show that the oxide liquid contains additional B_2O_3 from the B_6O surface and forms an amorphous phase in the triple junctions upon cooling. The B_6O grain contacts are non-wetted and clean.[10,12] For materials sintered with Al_2O_3 additives, the partial devitrification of the glass results in additional formation of borates and nano-sized pores, which are thought to act as crack-arresting sites and to be at least partially responsible for the observed increase in fracture resistance. However, in contrast to recently reported B_6O–TiB_2 composites,[18] the toughening mechanisms in liquid phase sintered B_6O materials remain uncertain.

An understanding of the role of sintering additives on the sintering behavior and the resulting microstructures is essential for specific tailoring and optimization of the physical properties of B_6O materials. For Al_2O_3/Y_2O_3 sintering additives, the recently published literature data only covers materials with a relatively restricted range of additive compositions not exceeding 2–3 vol.% in total and narrow molar $Al_2O_3/(Al_2O_3 + Y_2O_3)$ ratios of 0.6–0.7 or 1.[8–12] Therefore, in this study, B_6O materials with a broad compositional range of Al_2O_3/Y_2O_3 sintering additives (0–15 vol.%; $Al_2O_3/(Al_2O_3 + Y_2O_3) = 0.05$–1) were prepared by FAST/SPS and their densification as well as their phase and microstructure formation correlated with the resulting mechanical properties. In addition, data for the densification of B_6O by hot isostatic pressing (HIP) are presented, and the resultant materials are compared with materials with similar compositions densified by FAST/SPS.

2. Experimental and analytical methods

2.1. Experimental techniques

2.1.1. Powder preparation

Boron suboxide powder was fabricated by reducing boron oxide B_2O_3 (Merck, Germany) with amorphous boron (Grade I, H.C. Starck, Germany) in a furnace with tungsten heaters (FSW 315/400-1600-NE, FCT, Germany) at 1300 °C for 6 h in a flowing argon atmosphere according to methods reported in the literature.[4–7,11] The resulting product was milled in a jaw crusher and a jet mill and afterwards washed in ethanol for the removal of residual B_2O_3 remaining from the synthesis. The average grain size (d_{50}) of the final B_6O powder obtained with a Mastersizer 2000 (Malvern Instruments Ltd., UK) was 2.34 μm. Chemical analysis by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 6000, Thermo Scientific, USA) identified minor impurities of Mg (0.35%), Al (0.26%), and Fe (0.07%), which were introduced through the starting materials (Mg and Al) as well as the powder preparation procedure (Fe). The determination of the residual B_2O_3 content in the B_6O powder is difficult due to an oxygen-deficient composition of B_6O synthesized at low-pressure/low-temperature conditions.[2,19–23] Therefore simple oxide analysis does not allow a calculation of the B_2O_3 content. Also a determination of the stoichiometry based on the lattice parameters gives only an estimate. However, for the synthesized B_6O material used, lattice parameters of $a = 0.5354(1)$ nm and $c = 1.2339(2)$ nm were refined on the basis of X-ray powder diffraction, indicating an x value for B_6O_x in the range of 0.78–0.85. Based on hot gas extraction