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Densification and properties of superhard B_6O materials with cobalt additions

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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 (≤ 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

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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.

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

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.

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

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

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

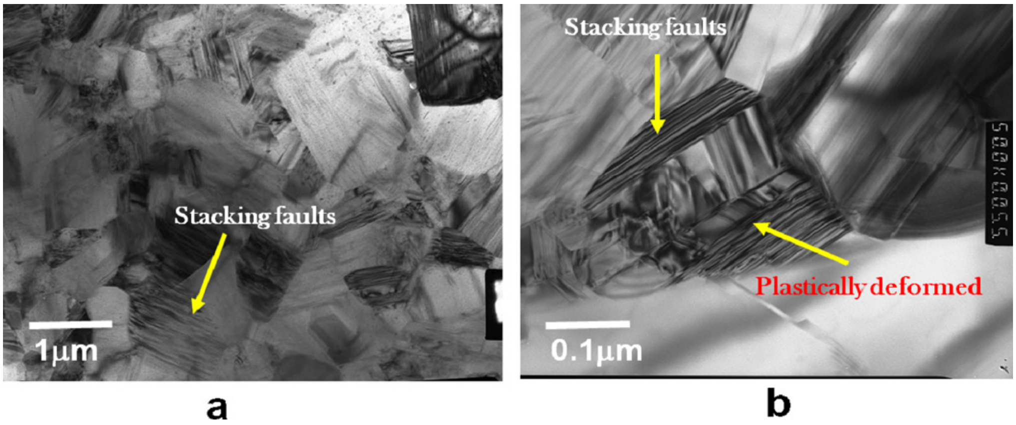

Fig. 1. TEM image of a B_6O sample hot pressed at 1900 °C showing (a) stacking faults and (b) plastically deformed grain.

hot pressed materials together with the amount of Cobalt content before and after sintering, Archimedes densities measured, open porosity, hardness and fracture toughness values obtained. The B_6O materials with cobalt sintering addition showed higher densification in comparison with the pure B_6O material despite the fact that the sintering temperature of these materials was 50 °C lower. The reason for the improved sintering is the formation of a stable boride liquid phase at temperatures above 1460 °C[23] wetting the B_6O and hindering the decomposition reaction which occurs in the pure B_6O material at the sintering temperature. Therefore, the addition of cobalt results in a more reproducible densification in comparison to pure B_6O materials.

Fig. 2a shows the dependence of the percentage theoretical density on the initial Co content in the B_6O powders sintered at

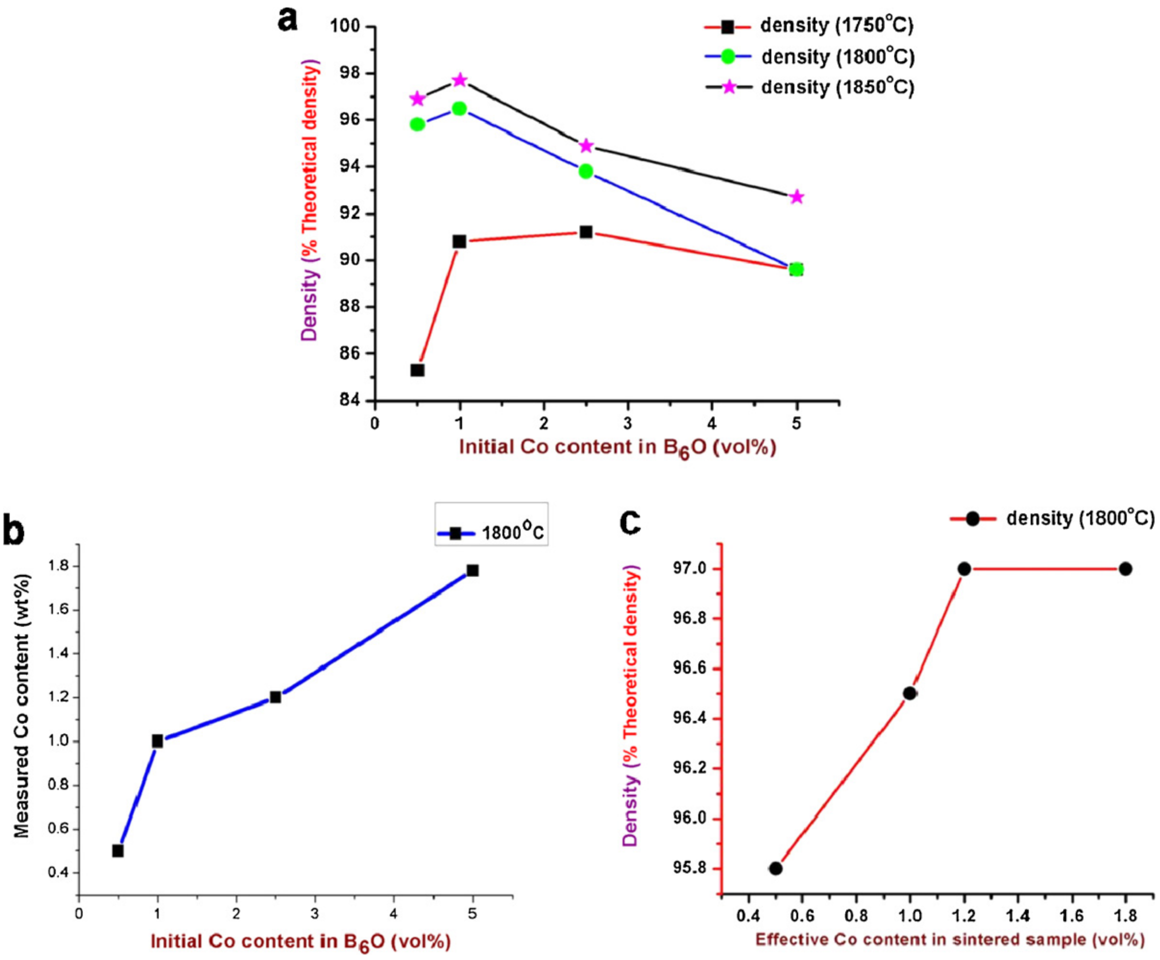

Fig. 2. (a) Density as a function of the initial cobalt content and sintering temperature. (b) Measured Co content against the initial Co content. (The original data for the first 2 points were used because no squeezing out was observed.) (c) Density of B_6O materials as a function of the effective cobalt content after hot pressing at 1800 °C.

Table 1
Compositions, density and mechanical properties of hot-pressed B6O materials.

Material	Starting Co content (vol%)	Co content after sintering (vol%)	Properties of sintered materials											
			1750 °C				1800 °C				1850 °C			
			Dens. (g/cm^3)	Open porosity (%)	H_{v1} (GPa)	K_{IC} (MPa m$^{0.5}$)	Dens. (g/cm^3)	Open porosity (%)	H_{v1} (GPa)	K_{IC} (MPa m$^{0.5}$)	Dens. (g/cm^3)	Open porosity (%)	H_{v1} (GPa)	K_{IC} (MPa m$^{0.5}$)
1. Pure B_6O[a]	–	–	–	–	–	–	–	–	–	–	2.46	3.7	30.2 ± 1.1	–
2. B_6O + 0.5Co	0.5	0.5	2.20	14.90	20.9 ± 2.1	4.4 ± 0.2	2.49	2.82	24.4 ± 1.1	4.3 ± 0.1	2.49	1.90	24.3 ± 0.8	3.6 ± 0.2
3. B_6O + 1Co	1	1	2.38	8.00	21.5 ± 1.7	4.6 ± 0.2	2.51	2.48	24.4 ± 1.7	3.7 ± 0.1	2.56	0.73	24.1 ± 1.7	3.5 ± 0.3
4. B_6O + 2.5Co	2.5	1.2	–	–	–	–	2.55	2.34	18.9 ± 1.3	4.8 ± 0.4	2.58	1.27	29.5 ± 1.8	3.5 ± 0.4
5. B_6O + 5Co	5	1.8	2.58	5.65	19.3 ± 0.4	6.0 ± 0.8	2.58	3.50	18.9 ± 1.3	4.8 ± 0.4	2.67	1.37	23.0 ± 1.2	4.3 ± 0.6

[a] Data for pure B_6O densified at 1900 °C.

1750 °C, 1800 °C and 1850 °C, respectively. As a general trend, the densification of the B_6O materials produced increases with the sintering temperature from 1750 °C to 1850 °C due to the closure of pores at higher temperatures. Also, it was expected that densification of the hot pressed B_6O materials should increase with increase in the initial Co addition, since more liquid would be available during sintering. On the contrary, this expected trend was obtained up to 1 vol% Co addition. Although, for higher cobalt addition the measured density of the B_6O materials increases (Table 1), comparing with theoretical density, the relative density decreases (Fig. 2a). This is caused by the fact that, liquid was found to squeeze out for materials with more than 1 vol% Co addition during hot pressing. Hence, further investigation of B_6O materials with more than 1 vol% Co was carried out using inductively coupled plasma optical emission spectrometry (ICP/OES) analysis to determine the actual amount of cobalt retained in the materials hot pressed at 1800 °C. The result of this analysis was compared with the initial cobalt added to the B_6O powder (Fig. 2b). The maximum effective Co content in the sintered materials was determined to be 1.8 vol%, with more than 60% of the initial cobalt squeezed out during the densification. Fig. 2c shows the dependence of the percentage theoretical density on the effective Co content in the B_6O materials sintered at 1800 °C. The graph showed that the expected trend of improved densification with increase in the amount of cobalt addition can be established. But for Co content higher than 1.2 vol% no more increase in the density was observed. The calculated relative density can contain some systematic errors, which can result in a shift to higher values in the real materials.

SEM images of B_6O materials doped with cobalt are shown in Fig. 3. The dark area represents B_6O phase and the white area represents the boride secondary phase. The homogeneous distribution of the boride phase is similar for both near the surface and at the centre of the samples. Pores which could be inherent in the matrix due to the decomposition reactions at the sintering temperature as well as pull-outs of the softer binder phase during polishing were seen as dark spots in the samples. The images reveal porosities less than 3% in the materials with Co content higher than 1vol%. These systematic errors are connected with the amount of B_2O_3 in the sample and the uncertainties in the stoichiometry of the B_6O which can result in the variation of the B_6O density between 2.5 and 2.6 g/cm^3. TEM investigation of B_6O material containing 5 vol% cobalt (Fig. 4) reveals that during cooling the liquid boride crystallizes as CoB phase in triple junctions as shown by diffraction of the electron beam and surrounds well facetted B_6O grains formed by solution precipitation process. Most of the grain boundaries between B_6O grains were not wetted by the CoB.

3.2. *Mechanical properties and microstructure of B_6O materials*

The Vickers hardness of the hot pressed B_6O material without additives yielded a value of 30.2 ± 1.0 GPa using a load of 1 kg. This value is comparable with the data in the literature

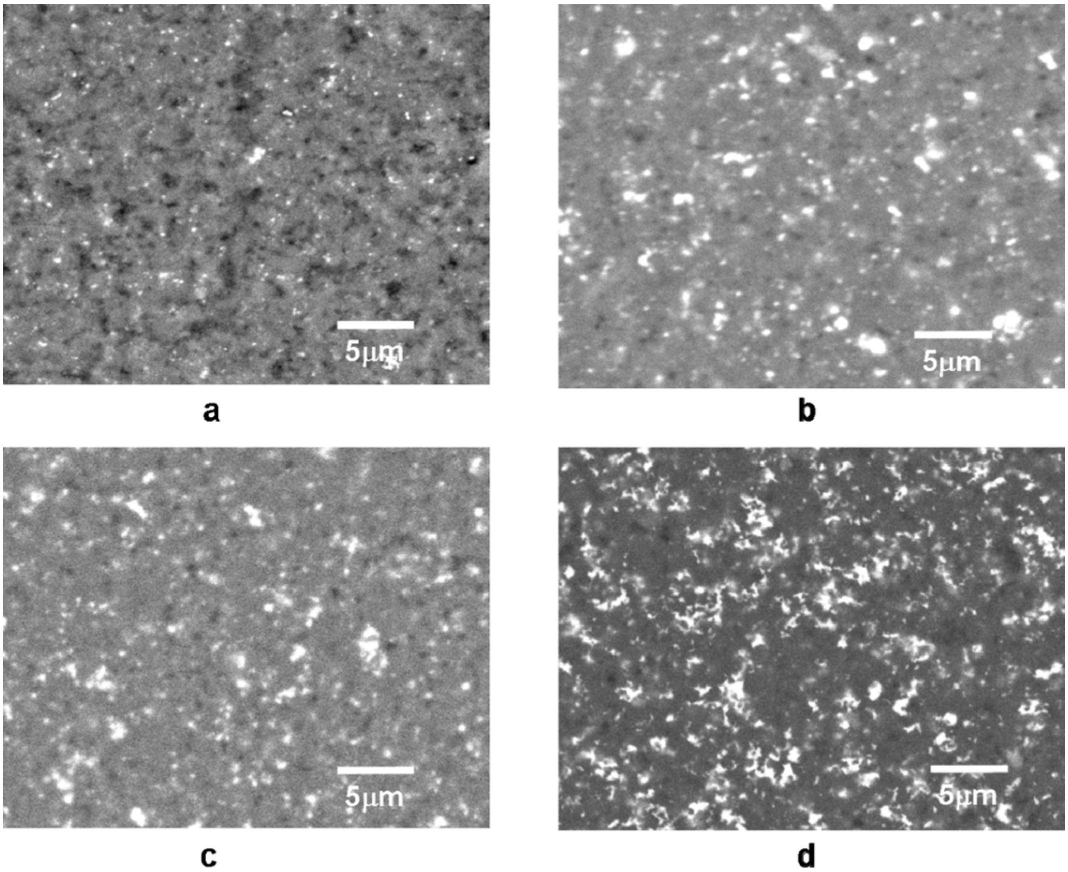

Fig. 3. SEM–BSE images of B_6O materials doped with (a) 0.5 vol%, (b) 1 vol%, (c) 2.5 vol% and (d) 5 vol% cobalt addition hot pressed at 1850 °C for 20 min.

31–33 GPa (200 g load)[21] at high pressure materials, 34.8 GPa by Shabalala et al.[5], 38 GPa (100 g load) by Holcombe and Ottis[24] considering the higher load used in this investigation. The fracture toughness of the sintered pure B_6O sample could not be measured due to the chipping of the B_6O crystals during indentation. It was concluded that the sample had low fracture toughness and it is brittle. Recently, the fracture toughness of FAST densified pure B_6O was measured using the single edge V-notch beam test (SEVNB) the fracture toughness was 1.5–2 MPa m$^{0.5}$, confirming the low fracture toughness of pure B_6O was too brittle to maintain integrity during indentation.[25]

Fig. 5a shows the dependence of the hardness and percentage porosity of sintered B_6O materials on the initial cobalt content in B_6O powder and sintering temperatures. From the graph, increase in temperature from 1750 °C to 1850 °C decreases the porosity in the sintered materials, while the hardness increases due to the improvement in densification at higher temperatures. Also increase in the initial cobalt content in the starting powder

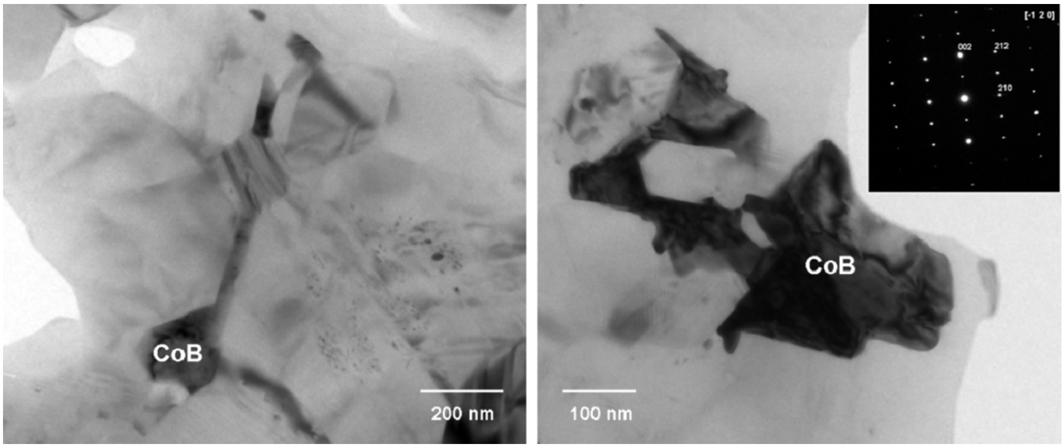

Fig. 4. TEM micrographs of B_6O material with 5 vol% Co addition, densified at 1850 °C for 20 min, showing the diffraction pattern observed from the CoB phase revealing the formation of CoB.

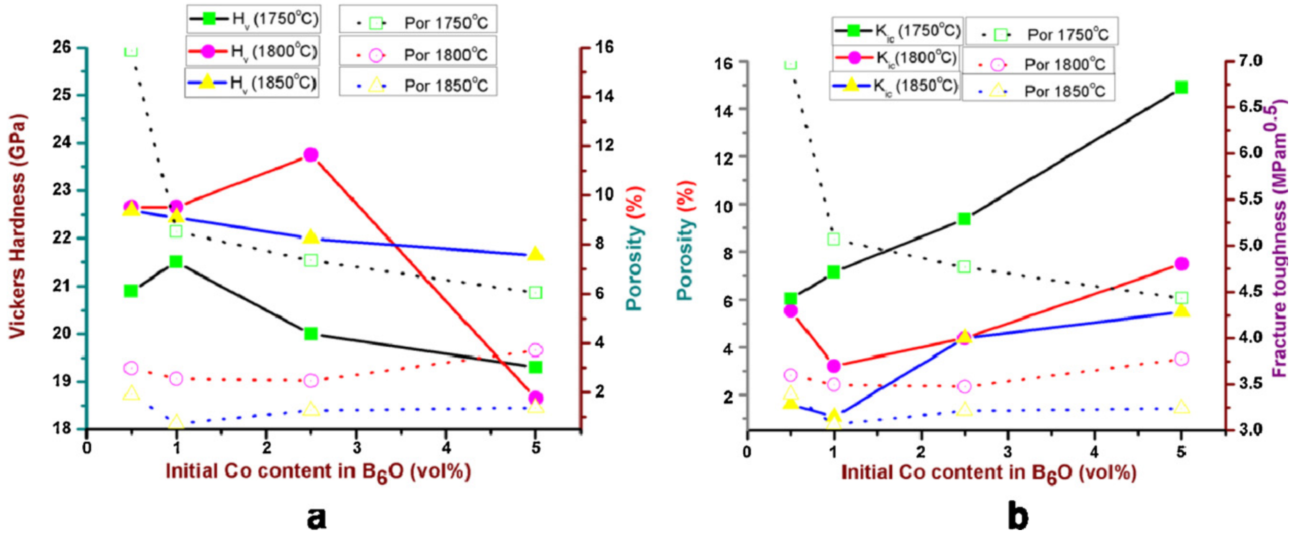

Fig. 5. (a) H_{V1} and porosity (b) Porosity & K_{IC} of B_6O materials as a function of initial cobalt content in the starting mixture.

decreases the hardness due to the increase in the softer second phase present in the hard B_6O matrix. Conversely, the fracture toughness measured shows an opposite behaviour to hardness in terms of dependency on percentage porosities and initial cobalt content in the starting B_6O powder (Fig. 5b) i.e. fracture toughness increases with the percentage porosity in the samples, since the pores within B_6O materials tend to act as crack arrest point which can result to an overestimation of the K_{IC} by the used method. Also, increase in cobalt content increases the fracture toughness through the addition of a softer phase into the hard B_6O matrix. Therefore, B_6O material with 5vol% cobalt addition and hot pressed at 1750 °C showed the highest values for fracture toughness but a very low hardness, since it combines less hard phase and the highest porosity. It must be noted that the real concentration of cobalt content in the sintered materials is much less for materials with high cobalt addition due to the squeezing out effect, nevertheless the trend for properties are the same (Fig. 6a and b).

Generally, the hardness of the Co-doped B_6O materials was slightly lower to that of the pure dense B_6O material. This is mostly caused by the lower hardness of the CoB phase. In this study, the addition of cobalt additive produced materials with improved fracture toughness comparable to that of the pure B_6O.

Fig. 7 shows SEM image of the crack propagation on the polished surface of B_6O-cobalt containing sintered material. The image reveals some crack deflection around the second phase, which was as a result of stresses formed due to the difference in coefficients of thermal expansion CTE ($\alpha_{B6O} = 5.5 \times 10^{-6}/°C^{-1}$ and $\alpha_{CoB} = 7.24 \times 10^{-6}/°C^{-1}$)[7,26] resulting in changed fracture modes of the material during cooling. However, the extend of this crack deflection is too low to explain the strong increase in the fracture toughness of this material, it therefore serves as a basis for further investigation into the mechanisms which enhance the improvement in the fracture toughness of these class of materials.

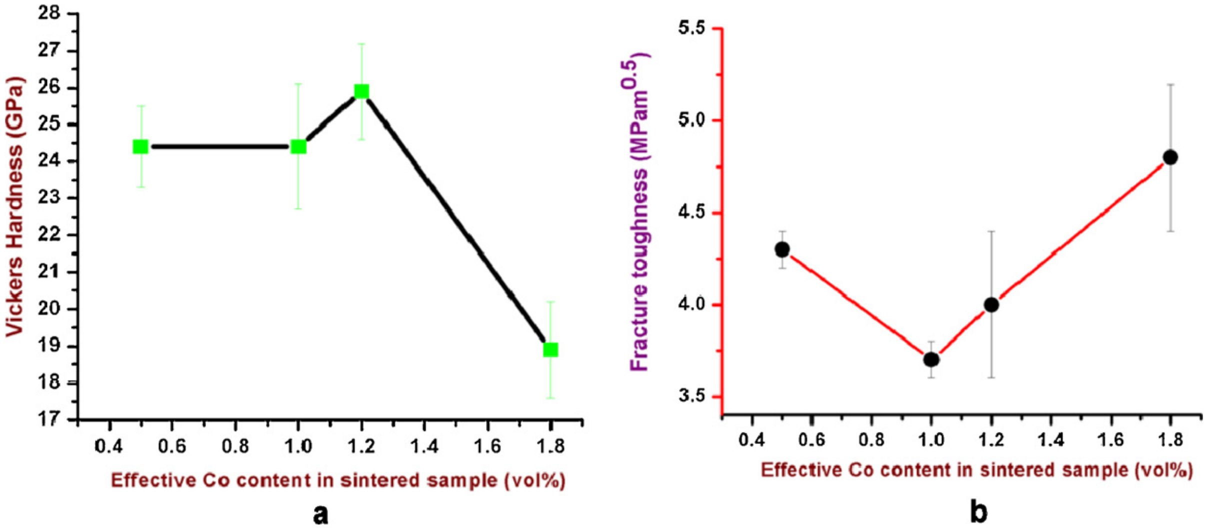

Fig. 6. (a) H_{v1} and (b) K_{IC} as a function of the effective cobalt content in the sintered B_6O materials at 1800 °C.

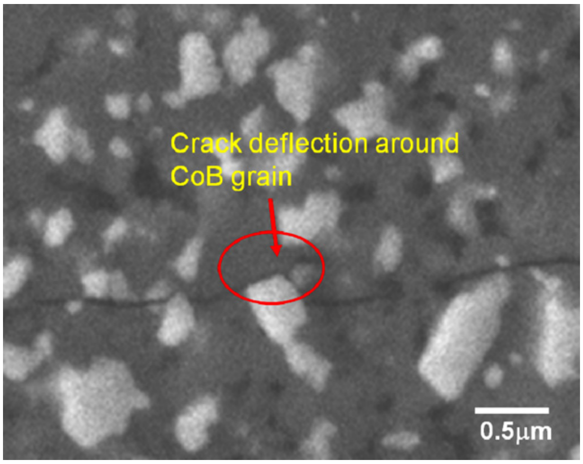

Fig. 7. SEM micrographs of the polished surface (with propagating cracks) of B_6O sintered material doped with 5 vol% cobalt.

4. Conclusion

B_6O materials doped with (0.5–5) vol% cobalt were hot pressed at temperatures between 1750 °C and 1850 °C to a density higher than 97% of theoretical. However, the desired broad variation of the cobalt content was not achieved due to the squeezing out of CoB during sintering. Consequently, the prepared samples only contained additives in a relative narrow range between 0.5 and about 2 vol%. In all compositions CoB was observed as a secondary phase. This is in agreement with the thermodynamic calculations.[14] Materials with increased fracture toughness [from 1 to 1.5 MPa $m^{0.5}$ for pure B_6O to ∼3–6 MPa $m^{0.5}$ with boride additives (Indentation-Method)] with only slightly reduced hardness can be prepared. The mechanisms of the significant improvement in the fracture toughness in comparison to the pure B_6O material are still not completely clear and need further investigations.

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