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Comparative study of reactive and non-reactive sintering route for producing B_6O–TiB_2 materials

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Abstract

Boron suboxide (B_6O) based materials containing TiB_2 additions were produced in this study via two routes (non-reactive and reactive sintering) and were consolidated using a hot press, which was operated between the temperatures of 1800–1900 °C and at an applied pressure of 50 MPa for 20 min dwelling time. Relationships between the formed phases, microstructures and mechanical properties of the sintered materials were established. The density was higher in the reactive sintered materials with finer microstructure than in the non-reactive sintered counterpart. Generally, the mechanical properties of the B_6O–TiB_2 materials were enhanced when compared to the pure B_6O material.

Keywords: C. Mechanical properties; Densification; Microstructure; Boron suboxide

1. Introduction

Extensive effort has been directed towards designing and developing materials with a combination of properties approaching, or even surpassing, those of diamond. Boron-rich solids provide good candidates [1–5], giving rise to a large family of materials with unique crystal structures and a range of interesting physical and chemical properties; these are related to their short interatomic bond lengths and their strongly covalent character. Boron-rich phases with structure based on α-rhombohedral B (α-rh B) include boron carbide and boron suboxide (nominally B_6O). These materials combine high hardness with low density and high chemical inertness, making them useful as abrasives and for other wear applications under severe conditions [1–5].

B_6O powders can be produced at ambient pressure at 1300 °C, under argon, by reducing B_2O_3 with B, or by oxidation of boron with zinc oxide or other oxidants [6–10]. 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 [6–10]. Application of high pressure during the synthesis of B_6O can significantly increase the crystallinity, oxygen stoichiometry, and crystal size of the products [6–8].

In addition, it is very difficult to sinter B_6O powders to full density, even across wide temperature ranges as described by Brodhag and Thevenot [11], but a careful selection of additives, combined with controlled sintering conditions could result in dense B_6O materials. Previous hot pressing studies [12–15] 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. These materials were hot pressed either under vacuum or argon at temperatures in the range of 1600–2200 °C. Although an

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average Knoop hardness (100 g load) between 30–38 GPa was measured, the fracture toughness values were low (≤2 MPa $m^{0.5}$) or sometimes not reported [12–15]. 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. (1998) [3] also did not produce fully dense material. The density of that material was reported to be above 95% of theoretical. Therefore, the use of ultra-high pressures does not guarantee completely dense materials.

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 [9], boron carbide [7], and c-BN [8]. Even though high hardness values were recorded for the composites (HV∼46 GPa), the fracture toughness values did not exceed 1.8 MPa $m^{1/2}$ [7–9]. It was shown [16] that B_6O materials with the addition of Al_2O_3 and rare earth oxides can be densified by the hot pressing or SPS/FAST technique at 1800–1900 °C. The resulting sintered materials had improved fracture toughness (3–5 MPa $m^{1/2}$) and only a slight reduction in Vickers microhardness (31 GPa under 5 kg load) in comparison to pure B_6O-materials (34 GPa under 1 kg load) [16–21]. The microstructure revealed that the material was densified predominantly by liquid phase sintering. Additionally, it was shown that transition metals can be used as sintering additives too. Independently of the starting nature of the additives, whether oxides or metals, during sintering they form borides [22].

TiB_2 has shown potential for use as cutting tools, armour materials, and even as cathode material for refining aluminium using a Hall–Heroult cell [23]. This is essentially because it possesses the combination of high hardness, good elastic modulus, good electrical conductivity and resistance to corrosion in molten metal environments [23]. Srivatsan et al. [24] studied the influence of TiB_2 content on microstructure and hardness of a TiB_2–B_4C composite, and found that the densification of B_4C was low (around 70%) when sintered below 2200 °C. However, the authors stated that increase in TiB_2 addition, increased the density of the composite at a sintering temperature of 1700 °C (although the value was not reported). For an addition of 25 vol% TiB_2, this phase also contributes to 15% increase in microhardness. Similarly, the addition of 50 vol% TiB_2 in SiC improved the fracture toughness of the SiC ceramic by 50% [25].

Therefore, it was suggested that TiB_2 could be a useful additive for enhancing the properties of B_6O materials for structural and wear applications [19]. These investigations showed that B_6O material with 10 wt% TiB_2 and 4 wt% oxide additives densified by Field Assisted Sintering Technology/Spark Plasma sintering (FAST/SPS) was nearly 100% dense and had microhardness of 37 GPa ($HV_{0.4}$) [19]. Additionally, it was also shown that the application of a reactive sintering route based on mixtures of TiH_2–B_6O or B–TiO_2 is an alternative and cost-effective method for the preparation of B_6O–TiB_2 composites. However, except for the hardness of 34 GPa for the B_6O–TiH_2 reactive route, no further properties were reported [19]. Thiele et al. [26] recently densified B_6O–TiB_2 composites through a non-reactive, as well as a reactive, preparation route using FAST/SPS at temperatures in the range of 1850–1900 °C. They obtained high hardness values in the ranges of 29–36 GPa ($HV_{0.4}$) and 22–28 GPa (HV_5) for the reactive compositions in comparison to 27–31 GPa ($HV_{0.4}$) and 15–24 GPa (HV_5) for the non-reactive preparation procedure, respectively. It was reported that the macrohardness HV_5 of these materials reduces by only about 25–33% from room temperature to 1000 °C. This exceeds the hardness of commercial c-BN tools at 1000 °C.

Therefore, this paper aims at comparing the densification, microstructure and properties of B_6O–TiB_2 materials produce via reactive and non-reactive routes and densified by a hot pressing technique.

2. Experimental procedure

The starting B_6O-powder was prepared by the reaction of B with B_2O_3 as described elsewhere [10,16,18]. The powder produced was jet milled 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 changed from semi-transparent dirty yellow to colourless with the removal of contaminant from the steel balls, followed by washing in ethanol to remove the remaining H_3BO_3. After washing, impurities of 0.09 wt% Fe and 0.01 wt% Cr were found (ICP-OES SPECTRO CIRUS CCD, Spectro analytical Instruments (Pty) Ltd, South Africa).

For materials made by the non-reactive route, the B_6O powder was mixed with 20 vol% TiB_2 (Grade F, ABCR, GmbH, Germany) in an attrition mill using steel balls of 2.5 mm diameter and a milling speed of 200 rpm for 30 h, with 200 ml isopropanol per 100 g powder were used as the milling media. The mean grain size after milling was ∼0.5 μm.

For materials made by the reactive route, stoichiometric amounts of amorphous boron (Grade I, H.C. Starck, Germany) and TiO_2 (P25, Degussa, Germany) (i.e., 65.45 wt% B powder and 34.55 wt% TiO_2) were mixed in an attrition mill using the same milling parameters as for the non-reactive route. The composition was chosen according to the reaction:

$$TiO_2 + 14B \rightarrow TiB_2 + 2B_6O \quad (1)$$

The starting compositions used for making the materials in this study are given in Table 1. In both cases, the admixed powders were cleaned using the same procedure described for

Table 1
Composition of the additives (wt%) and the TiB_2 in the sintered materials.

Sample	Additive content (wt%)				TiB_2 in sintered material (vol%)
	B	B_6O	TiB_2	TiO_2	
Pure B_6O	–	100	–	–	–
B_6O+TiB_2	–	69.39	30.61	–	20.00
B+TiO_2	65.45	–	–	34.55	19.58

Table 2
Compositions, density and mechanical properties of hot-pressed B_6O materials.

Material	Method	TiB_2 content in sintered material (vol%)	Properties of sintered materials									
			1800 °C				1850 °C				1900 °C			
			Dens. g/cm³	Open porosity (%)	HV_5 (GPa)	K_{IC} (MPa $m^{0.5}$)	Dens. g/cm³	Open porosity (%)	HV_5 (GPa)	K_{IC} (MPa $m^{0.5}$)	Dens. g/cm³	Open porosity (%)	HV_5 (GPa)	K_{IC} (MPa $m^{0.5}$)
Pure B_6O*	–	–	–	–	–	–	–	–	–	–	2.46	3.7	30.2 ± 1.1	–
B_6O+TiB_2	Non-reactive	20.00	2.79	2.8	19.8 ± 1.8	4.3 ± 0.4	2.79	2.7	19.0 ± 1.3	4.8 ± 0.2	2.80	2.7	22.5 ± 3.7	4.4 ± 0.4
B+TiO_2	Reactive	19.58	2.80	2.3	22.0 ± 1.8	4.0 ± 0.2	2.84	0.5	25.2 ± 3.2	4.0 ± 0.8	2.84	1.1	23.2 ± 1.1	4.5 ± 0.3

the pure B_6O powder and there was less than 0.1% contaminant remaining.

Pure B_6O powder was then 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 admixed powders (reactive and non-reactive) were sintered at temperatures between 1800 °C and 1900 °C and 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 1800 °C had shown only a density of less than 90% of theoretical [18].

After sintering, all the samples were ground to clean their surfaces from the hBN lining. The density of the samples was determined using Archimede's principle. Cross-sections of the materials were polished using a diamond slurry with different particle sizes from 9 to 1 μm. They were characterised using X-ray diffraction (PW1830; Philips; Cu Kα radiation, 40 KV, 20 mA, 2θ range: 10–80°, step size 0.02°). Microstructure observations were carried out using scanning electron microscopy (Philips, XL30 SERIES) with an attached EDX system. TEM specimens were prepared by grinding 3 mm diameter cylindrical samples, using a mixture of water and diamond powder with a Gatan polisher to a thickness of 100 μm. The samples were then dimpled from both sides until approximately 30 μm in thickness in the centre, and ion milled using a PIPS argon ion mill at 5 keV and 4° until electron transparency was achieved. TEM analysis utilising the techniques of electron diffraction (ED) and energy dispersive spectrometry (EDS) were performed using a Philips CM20 TEM operated at 200 kV.

The Vickers hardness and fracture toughness were measured using indentation techniques under a load of 1 kg (for pure B_6O sintered sample) and 5 kg (for B_6O materials). The average of five measurements was used to determine the properties of the samples. The fracture toughness was determined via the direct crack measurement method using Anstis's equation [27], with the calibration constant $\xi = 0.016$ and elastic constant $E = 470$ GPa [28].

3. Results and discussion

3.1. Densification and microstructure of B_6O materials

Table 2 summarises the density and porosity of the materials obtained. The B_6O material densified without additives at 1900 °C had a density 96.5% of theoretical, which agrees with the value obtained by Kayhan and Inal [29].

The B_6O–TiB_2 composites reached a density higher than 95% at 1800 °C. Further increase in sintering temperature only slightly increased the density, whereas the densities of the reactively sintered samples were even higher. SEM investigations of the cross sections (Fig. 1) reveal only minor porosity, therefore it was assumed that an even higher relative density was achieved, based on the uncertainties in the calculation of the theoretical density. Due to the fact that B_6O is a non-stoichiometric compound whose density changes slightly with oxygen content, a value 2.55 g/cm³ was used corresponding to $B_6O_{0.9}$. The presence of B_2O_3 in the sample, found on the

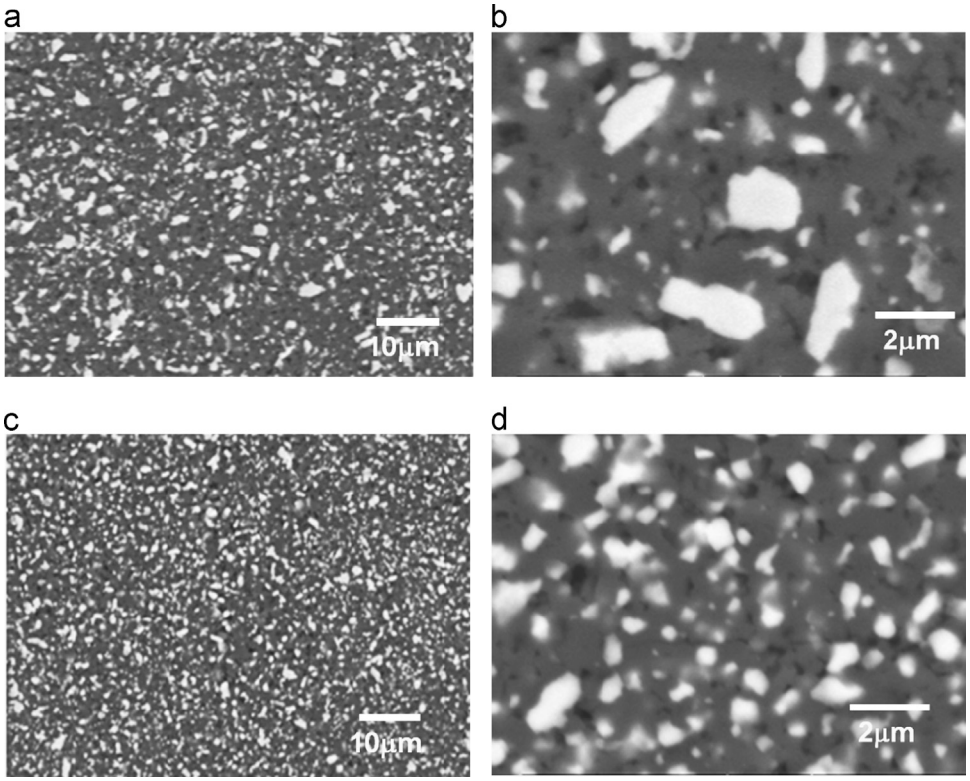

Fig. 1. SEM-BSE micrographs of (a and b) B_6O–TiB_2 via non-reactive routes and (c and d) B–TiO_2 materials via reactive routes, sintered at 1900 °C.

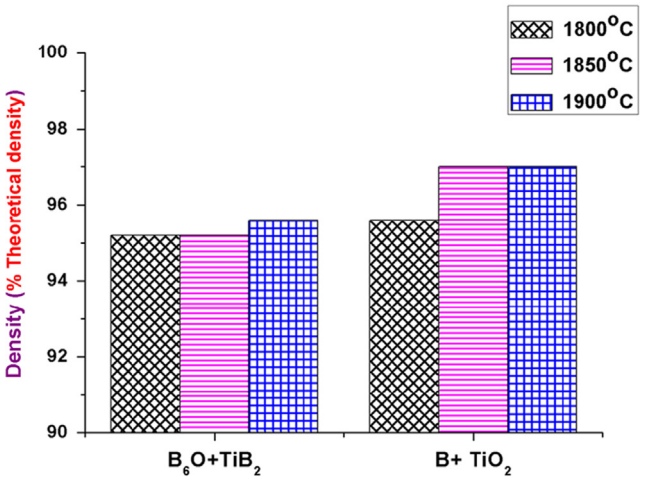

Fig. 2. Density of sintered B_6O–TiB_2 and B–TiO_2 materials.

surface of the starting B_6O and B powders also contributed to the uncertainty. The density was calculated under the assumption that all B_2O_3 had evaporated during the sintering process. Therefore, the values of the relative density given in Fig. 2 are the lower limit. The values of open porosity of the B_6O–TiB_2 materials were lower than those obtained for pure B_6O, implying that the addition of TiB_2 phase slightly suppresses that phenomenon. The open porosity is usually concentrated in the near surface area and forms due to local decomposition during sintering [18]. Therefore the reduced open porosity can be taken as evidence of the improved stability under sintering conditions, and hence improved densification of the boron suboxide material.

The same phase compositions (B_6O and TiB_2) were present after sintering, independently of the compositions of the starting mixture, either for B_6O+TiB_2 or B+TiO_2. This agrees with the predictions based on thermodynamic data [19]. The addition of TiB_2 only slightly improved the densification, because boride is also solid at the sintering temperatures, thereby limiting mass transport. However, a small amount of B_2O_3 on the surface of the B_6O powder could allow the formation of liquid phase at low temperature which drives the densification. Fig. 2 shows the percentage of theoretical density of the B_6O–TiB_2 materials sintered via the reactive and non-reactive routes. A slight improvement of the densification without any change of the properties can be achieved via the reactive sintering route. The B+TiO_2 system experienced rapid densification during the formation of TiB_2 by an exothermic reaction at around 800 °C [26]. Formation of B_6O at this temperature was not observed by XRD, therefore it is suggested that it formed as an amorphous phase at this temperature as a result of Eq. 1. The formation of well crystallised B_6O occurs only at approximately 1400 °C, while fully dense materials were produced only at 1800–1900 °C (same temperature as for the non-reactive system) [26]. The advantage of the reactive sintering method is that the densification is more intensive at lower temperatures and therefore reduces the interaction with the dies and the furnace atmosphere [19,26].

The microstructures of the materials sintered at 1900 °C for non-reactive and reactive routes are given in Fig. 1. Both materials were characterised by homogeneously dispersed

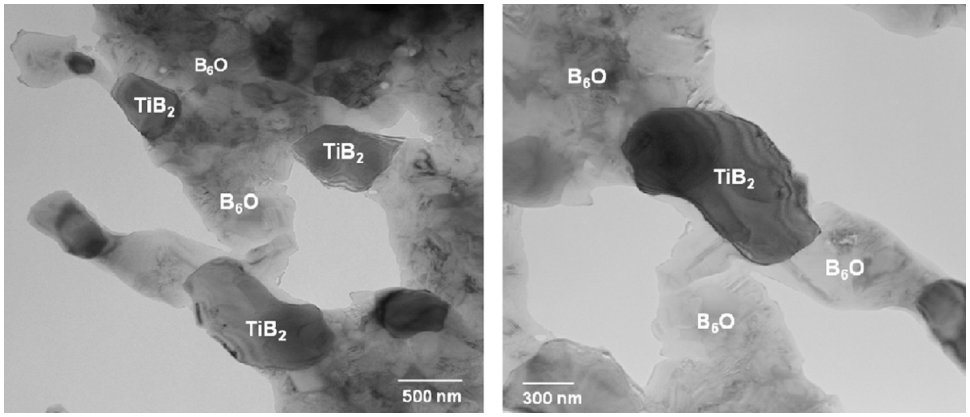

Fig. 3. TEM micrographs of B_6O material with 20 vol% TiB_2 addition densified at 1900 °C for 20 min at different magnifications.

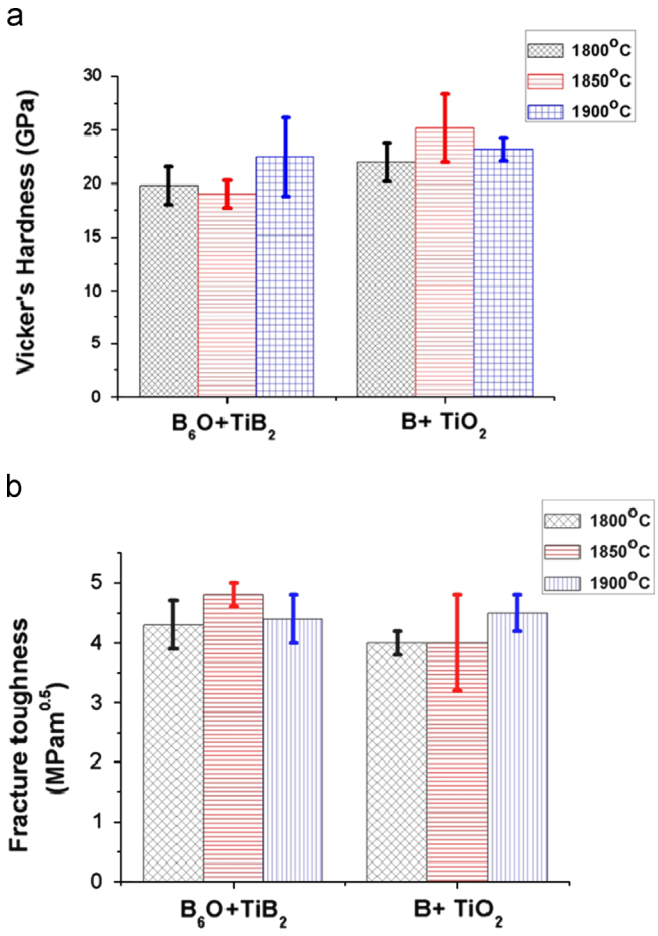

Fig. 4. Comparison between the properties of non-reactive B_6O-20 vol%TiB_2 and reactive B–TiO_2 materials (a) Hv_5 and (b) K_{IC}.

TiB_2 particles in a matrix of B_6O. For the reactively sintered materials, the grain size of the precipitated boride was less than 1 μm, while for the non-reactive sintered materials the average grain size of the boride was about 2 μm with visible pores when compared with reactively sintered materials. The observed pores are partly due to the decomposition reactions at the sintering temperature in the matrix and the pulling out of TiB_2 grains during mechanical preparation of the cross section.

TEM micrographs in Fig. 3 reveal that the mean TiB_2 grain size for the non-reactively sintered sample is in the range of 1–2 μm, indicating that no grain growth occurred; this might be attributed to the sintering time employed.

3.2. Mechanical properties and microstructure of B_6O materials

The Vickers hardness of the hot pressed B_6O materials without additives was 30.2 ± 1.0 GPa using a load of 1 kg. This value is comparable with the data in the literature, i.e. 31–33 GPa (200 g load) by Itoh et al. [3] for high pressure sintered materials, 34.8 GPa by Shabalala et al. [10], 38 GPa (100 g load) by Holcombe et al. [30], 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, and was concluded that the sample had low fracture toughness. Recently, the fracture toughness of FAST densified pure B_6O was measured using the single edge V-notch beam test (SEVNB), as 1.5–2 MPa. $m^{0.5}$ [31], confirming that the fracture toughness of pure B_6O is too low to maintain integrity during indentation.

In Fig. 4, the hardnesses of the B_6O–TiB_2 materials prepared by both reactive and non-reactive routes were slightly lower than for pure B_6O. This might be due to the weak interface between the B_6O and TiB_2 phases, causing a more extensive pull out of TiB_2 grains during processing. However, fracture toughness of the materials improved substantially with the addition of TiB_2 in comparison to that of the pure B_6O. Material sintered at 1850 °C by the reactive sintering route had higher hardness than the non-reactive route material. The increase is due to the microstructure of this class of materials having less porosity and reduced grain size. However, the fracture toughness of the B_6O–TiB_2 materials made by both methods was the same when the standard error of measurement was taken into account.

SEM images of the crack paths of the polished reactive sintered B_6O–TiB_2 materials are shown in Fig. 5. The advancing crack bowed around the TiB_2 particles expending some of its energy in changing the crack planes, thereby increasing the fracture toughness of the materials. However,

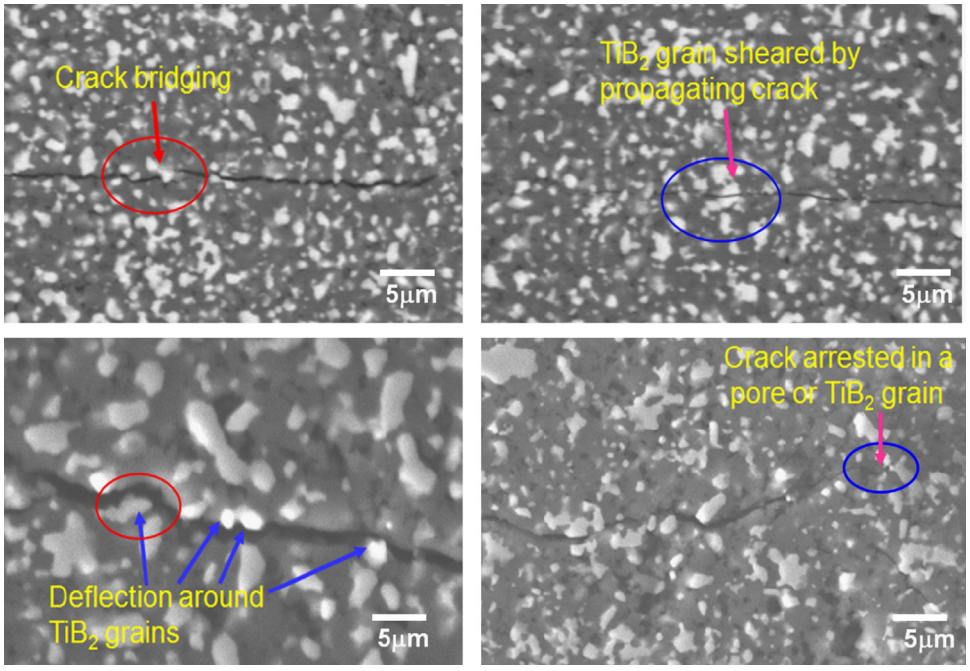

Fig. 5. SEM-BSE micrographs of the polished surfaces (with propagating cracks) of reactive sintered B_6O sintered materials showing different toughening mechanisms (B_6O phase-grey, TiB_2 phase-white).

sometimes the crack went through the TiB_2 grains. A more detailed analysis showed that this normally took place if several TiB_2 grains had grown together. The crack paths revealed that different fracture mechanisms such as crack deflection due to bimetallic stresses, or due to crack arrest in the secondary phase and at pores can be proposed for the different B_6O–TiB_2 materials produced. However, the extent of these fracture modes is too low to explain the pronounced increase in the fracture toughness of this material. It therefore serves as a basis for further investigation into the mechanisms which enhance the fracture toughness of this class of materials.

4. Conclusion

Investigations concerning the reactive synthesis of B_6O by B–TiO_2 mixtures and non-reactive sintering were carried out. Fully densified B_6O–TiB_2 materials were produced by both methods using hot pressing at temperatures in the range of 1800–1900 °C. The reactive synthesis resulted in more pronounced densification at lower temperatures, improving reliability of the process and providing a cost effective way of producing the material. A much finer microstructure was observed for the reactive sintered materials, resulting in higher hardness values than the non-reactive sintered materials.

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