

Microstructure and interfacial reactions between B₆O and (Ni, Co) couples

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Abstract

The search for suitable additives for boron suboxide (B₆O) materials which could improve densification, reduce sintering temperature and tailor the microstructure has been of great importance. In an earlier study it was shown that transition metal borides qualify as sintering aids for B₆O, but partial segregations of the boride secondary phases were found. In this work, efforts have been made to understand the chemical interaction between the B₆O and boride phase. A reaction couple of sintered B₆O, nickel and green compact B₆O were assembled and heat-treated at 1850 °C for 20 min. XRD and SEM examinations of the reaction zone show the formation of nickel boride, diffusing into the B₆O matrix and a substantial grain growth of B₆O at the interface.

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1. Introduction

In single crystalline form boron suboxide (B₆O) has hardness and fracture toughness that is comparable to that of cubic boron nitride (cBN) and a fracture toughness exceeding that of cBN [1]. However, while cBN requires ultra-high pressures to synthesize, B₆O can be made at atmospheric pressure, thus avoiding the great expense entailed in the use of high-pressure technologies [2–4]. Materials based on B₆O could be used in machining applications as an ultrahard material. However, contrary to the observations made for single crystal B₆O materials it was found that polycrystalline B₆O is very brittle and difficult to densify [5–7].

Attempts made to improve the fracture toughness by making polycrystalline B₆O composites with other hard materials such as diamond, boron carbide and cBN yielded high hardness values ($H_v \sim 46$ GPa) but fracture toughness did not exceed 1.8 MPa m^{1/2} [7,8]. Recently it was shown that B₆O materials with the addition of Al₂O₃ and rare earth oxides can be hot-pressed or densified by 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 500 g load) in comparison to pure B₆O materials (34 GPa) [2–3,9–12]. The investigation of the microstructure reveals that the material was densified predominantly by liquid phase sintering.

Thermodynamic considerations predicted that transition metals could be possible candidates as liquid phase sintering aids [11]. It was also noted that even if the additives are transition metal oxides or metals they will be converted during sintering of B₆O composites into borides.

In an earlier study [4], it was shown that adding transition metals to B₆O will produce materials containing boride secondary phases with acceptable properties but with segregations of the boride phases (Fig. 1). This raised an issue of the nature of these segregation processes. TEM investigation of CoB–B₆O samples had shown that the CoB phase is concentrated at triple junctions and that the grain boundaries between adjacent grains are not wetted. Therefore it is not clear whether transition metal borides can wet B₆O during the sintering process. This issue is of concern as wetting will strongly influence the densification and the microstructure formed.

Therefore, this paper aims to investigate the interaction between B₆O and transition metals and the wettability of B₆O by the formed liquid transition metal borides.

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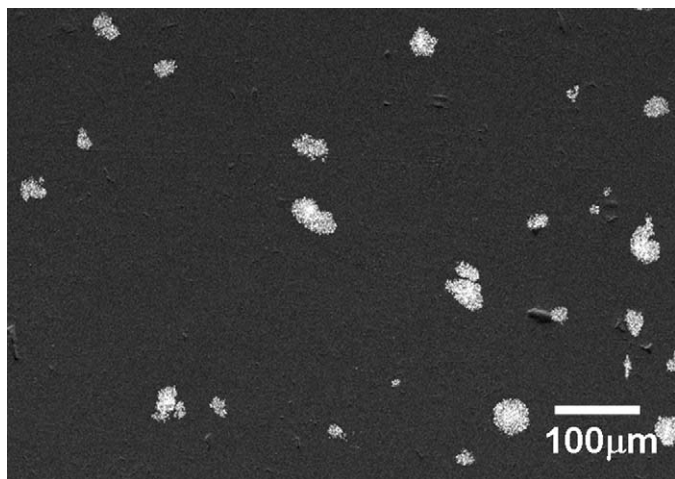


Fig. 1. SEM micrographs of the boride containing B_6O material showing segregation of the boride phase.

2. Experimental procedure

The starting B_6O powder was prepared by the reaction of B (amorphous) with B_2O_3 as described elsewhere [2–4]. The powder produced has a composition of B_6O_x with x within the range 0.8–0.9. This is a common feature in B_6O materials produced at ambient pressure [2,4,10]. The powder produced was jet milled up to a grain size of $2.5\ \mu\text{m}$ 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 $0.5\ \mu\text{m}$ measured using a Mastersizer 2000 (Malvern Instruments, Germany).

The milled B_6O powder was repeatedly washed in 1 M HCl in order to remove contamination from the steel balls, followed by washing in ethanol to remove remaining H_3BO_3 . After the washing process 0.09 wt% Fe and 0.01 wt% Cr were found as the impurities present (ICP-OES SPECTRO CIRUS CCD, Spectro Analytical Instrument (Pty) Ltd., South Africa).

Pure B_6O materials were hot-pressed (HP20 Thermal Technology) in hBN-lined-graphite dies in argon at $1900\ ^\circ\text{C}$ and a pressure of 50 MPa for 20 min to produce the densified part. Additionally, green compacts of both B_6O and nickel powders (grade C, Alfa Aesar) were made at pressure of 45 MPa using a hydraulic press. A sandwich of Ni compact between both green and densified B_6O samples (Fig. 2) were arranged inside the hBN crucible and heat-treated at $1850\ ^\circ\text{C}$ for 20 min with the pressure of 10 MPa.

After the heat treatment, cross-sections of the reaction couples were polished using diamond slurry and were characterized

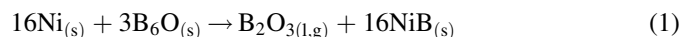
using X-ray diffraction (PW1830; Philips; Cu $K\alpha$ radiation, 2θ range: $10\text{--}80^\circ$, step size 0.02°). Microstructure observations were carried out using scanning electron microscopy (Philips, XL30 SERIES) with attached EDX system.

Furthermore, B_6O was separately mixed with 1 vol% of Co and Ni using a precipitation method, which involves the precipitation of $\text{Co}(\text{OH})_2$ or $\text{Ni}(\text{OH})_2$ on the surface of B_6O using the reaction of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and alkaline solutions. The metallic oxide was then reduced in an H_2/Ar atmosphere at $800\ ^\circ\text{C}$. The powders were sintered at $1850\ ^\circ\text{C}$ at 50 MPa pressure and 20 min isothermal sintering time. After sintering the materials were ground to clean their surface from the hBN lining. The density of the samples was determined using Archimedes principle. Cross-sections of the materials were polished and were characterized in terms of the phases present and their morphology. Vickers hardness (H_v) and fracture toughness (K_{IC}) were measured using indentation techniques under loads of 1 kg for pure B_6O sintered sample and 5 kg for B_6O materials with additives. 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 [13], with the calibration constant $\xi = 0.016$ and elastic constant $E = 470\ \text{GPa}$ [14].

3. Results and discussion

3.1. Reaction couple $B_6O\text{--}Ni\text{--}B_6O$

The phase analysis of the reaction zone shows the complete transformation of the metallic nickel into nickel boride, which agrees with the chemical reaction given in Eq. (1):



Due to the elevated temperature involved, a large percentage of B_2O_3 escapes due to high vapour pressure [3], while some amount may remain as B_2O_3 in triple junctions as found in pure B_6O materials [9], or can be partially incorporated into the B_6O lattice increasing the stoichiometry (increasing x in B_6O_x). The Ni–B phase diagram [15] reveals that nickel boride would be liquid at temperatures higher than $1590\ ^\circ\text{C}$. Therefore it would be expected that at temperature used in the experiment the boride is liquid and would infiltrate the B_6O .

The microstructure of the reaction zone of the couple is given in Fig. 3. The diffusion of the liquid into both the green and densified compact is visible. A higher magnification shows that the NiB diffuses into the densified B_6O part in a homogeneous manner up to $100\ \mu\text{m}$ in the 20 min of isothermal dwell time.

An EDX scan across the reaction zone shown in Fig. 4, illustrate that the dense B_6O material $100\ \mu\text{m}$ below the surface is free of any other elements other than boron and oxygen. The dotted line in the figure marks maximum depth of diffusion of nickel boride into the densified B_6O part within the dwelling time used.

The results reveal that the liquid boride infiltrates the dense B_6O material with a relative high speed. This is a strong indication that the B_6O is wetted by the melt. Therefore the

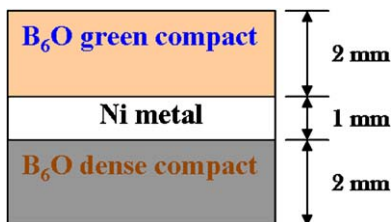


Fig. 2. $B_6O\text{--}Ni\text{--}B_6O$ couple arrangement.

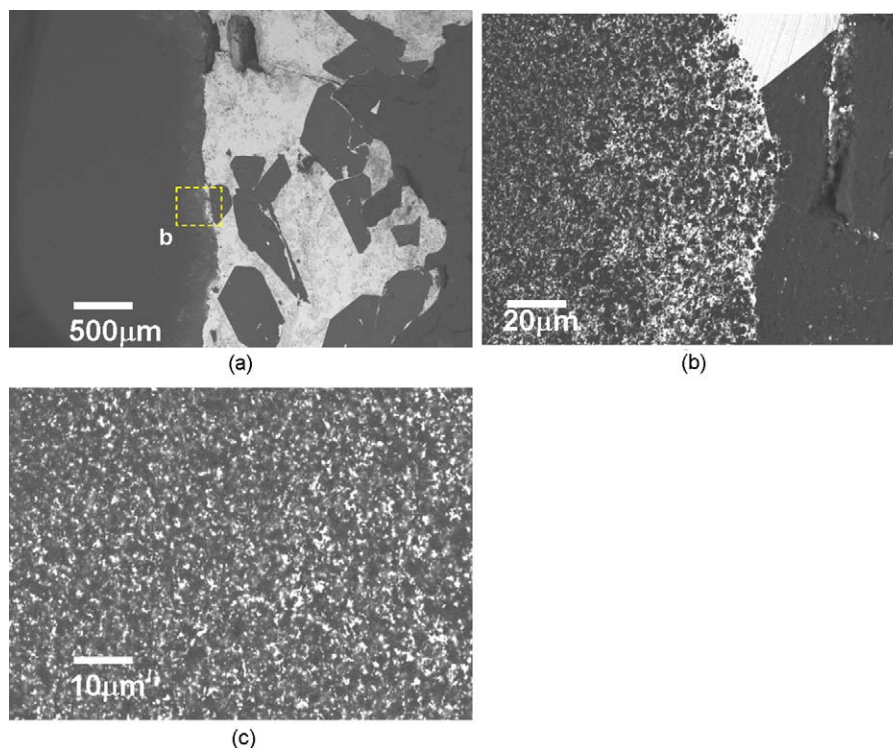


Fig. 3. SEM micrograph of the B_6O –Ni– B_6O reaction zone: (a) overview, (b) boundary of the melt with dense B_6O (area b in figure a) and (c) detailed micrograph of the infiltrated dense B_6O material.

observed segregations after sintering must be connected with an insufficient mixing of the additives. It has to be pointed out that all B_6O materials with boride additives investigated by TEM (Cr, Ti, Co, Zr containing materials) [16,17] so far showed that the boride phase is concentrated in the triple junctions and the grain boundaries between adjacent grains do not contain the transition metals. This gives an indication that the wetting must be strongly temperature dependant.

At the interface between the Ni and the B_6O materials up to 100 μm large B rich grains are formed. The EDS analysis (Fig. 4) reveals that these grains have only a very low oxygen concentration. Therefore these grains are most probably B which could not be detected by XRD measurement. The existence of wettability and solubility prove that the sintering of B_6O with transition metal borides like Ni, Fe and Co is a classical liquid phase sintering. This sintering mechanism allows a reduction of the sintering temperature by more than 50 $^{\circ}C$ even if the amount of additives is only 1 vol%

3.2. Sintering of coated B_6O powder

The B_6O material hot-pressed without additives at temperature of 1900 $^{\circ}C$ resulted in a material having 96.5% of the theoretical density. Phase analysis of the sintered pure B_6O sample reveals only B_6O . The Vickers hardness of this sample was 30.2 GPa measured using 1 kg load. Higher load caused extensive fracturing. Hence, the fracture toughness of this material could not be determined by this method. This agrees with the result presented by other researchers using ultra-high pressures [6–8].

The B_6O powders coated separately with Co and Ni were hot-pressed at 1850 $^{\circ}C$. Densities of more than 97.5% theoretical density were obtained. The theoretical densities were calculated on the basis of the rule of mixtures of the phases formed (the density of $B_6O_{0.86}$ (2.55 g/cm³) was used as the density of boron suboxide). The B_6O materials with the Co and Ni sintering additives showed higher densification in comparison with the pure B_6O material despite the fact that the sintering temperature of these materials was 50 $^{\circ}C$ lower.

The reason for the improved sintering is the formation of a stable boride containing liquid phase at temperatures above 1590 $^{\circ}C$ wetting the B_6O . During cooling the boride liquid crystallizes as NiB phase as shown by XRD. This means that the boride is in equilibrium with B_6O at sintering temperature.

SEM images of these materials are shown in Fig. 5. The dark area represents B_6O and the white area represents the boride secondary phase. The distribution of the boride phase is similar for both near the surface and at the centre of the samples. The homogeneous distribution of the boride phase in these materials reveals that the reason for segregation in the earlier study was poor mixing of the powder in the planetary mill rather than the wettability of B_6O by the boride secondary phase present during sintering. The same microstructure was observed in the Ni and Co doped B_6O materials. Also the melting point of the formed borides CoB (T_m = 1460 $^{\circ}C$) and NiB (T_m = 1590 $^{\circ}C$) are similar. Therefore the same sintering mechanism can be assumed in both systems.

The Vickers hardness and fracture toughness of the sintered B_6O material (ball milled and coated powders) are compared in Table 1. The hardness of the composites is slightly lower to that

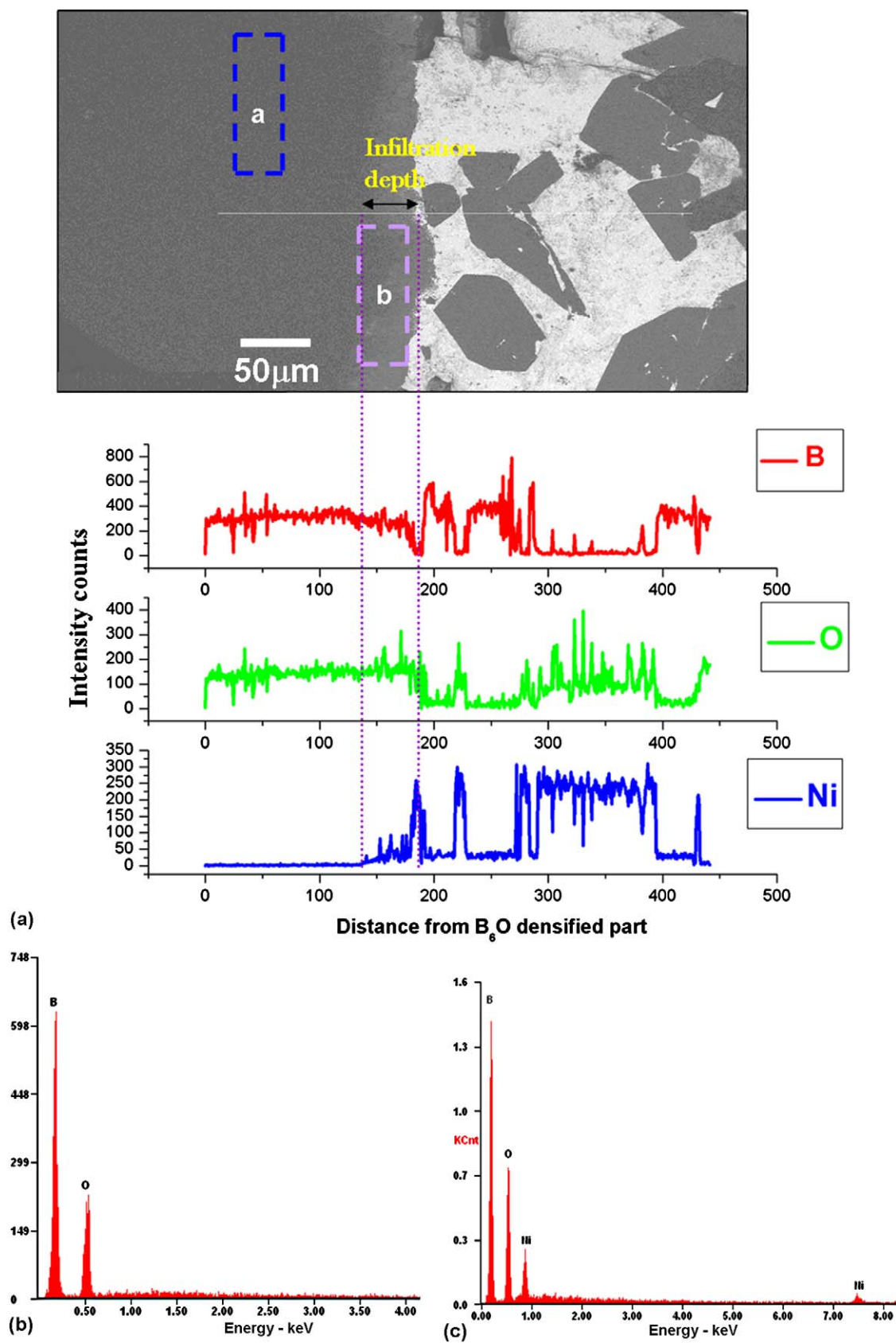


Fig. 4. (a) A line scan across the B₆O–Ni–B₆O reaction zone, (b and c) EDS analysis of area a and b in figure (a).

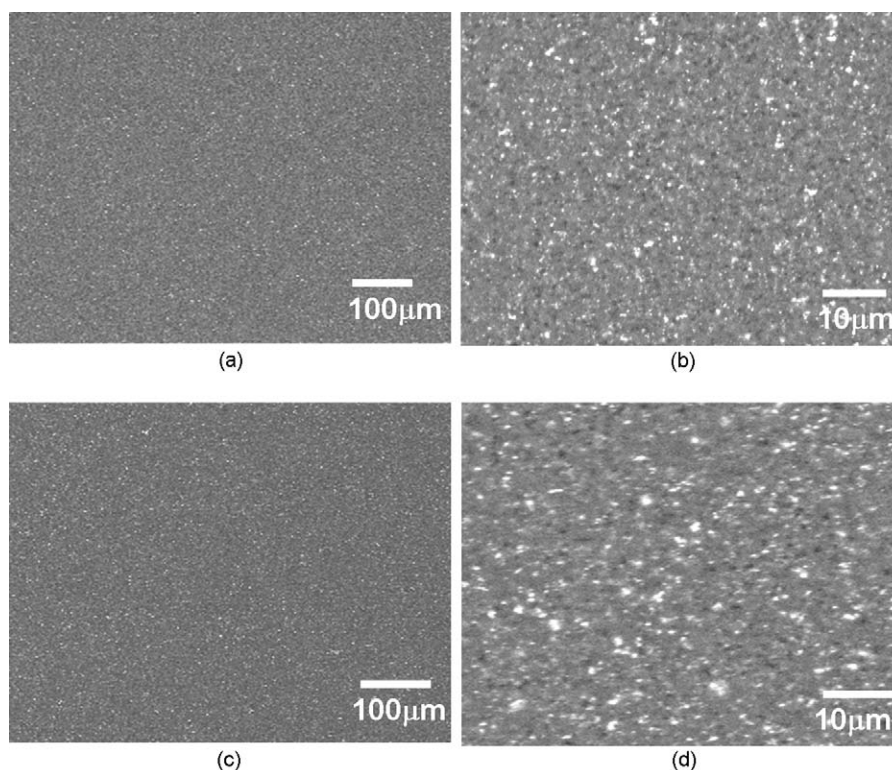


Fig. 5. SEM micrographs of the polished surfaces of (a and b) $B_6O + Ni$ (c and d) $B_6O + Co$.

Table 1
Compositions, density and mechanical properties of hot-pressed B_6O materials.

Sintered material	Additive content (wt%)	Density (g/cm^3)	Open porosity (%)	H_{v5} (GPa)	K_{IC} ($MPa m^{0.5}$)
B_6O	–	2.46	3.7	30.2 ± 1.0^a	–
$B_6O + Co^b$	1.33	2.53	1.2	33.9 ± 2.2	3.2 ± 0.5
$B_6O + Co^c$	3.41	2.56	0.7	28.6 ± 1.1	3.9 ± 0.4
$B_6O + Ni^b$	3.70	2.53	2.0	30.7 ± 1.1	3.4 ± 0.6
$B_6O + Ni^c$	3.41	2.56	0.6	27.6 ± 0.5	3.8 ± 0.4

^a H_{v1} .

^b Admixed powder with segregation.

^c Coated powder.

of the pure B_6O materials. This is mostly caused by the lower hardness of the CoB and NiB phases. The data also revealed that the materials with segregated boride phase have higher hardness than the well-distributed samples. This might be due to the higher probability of making indentations on the B_6O rich regions in the material. The segregation therefore causes inhomogeneous properties across the material.

The produced B_6O materials with secondary boride phases showed improved fracture toughness comparable to that of the materials with mixed oxide additions [3,14].

4. Conclusion

A reaction couple consisting of B_6O and Ni heat-treated at $1850^\circ C$ for 20 min showed the formation of the boride phase at the interface and diffusion of the liquid boride into the B_6O compact. This is evidence of good wetting between the boride and the B_6O phase. The observed grain growth reveals an

intensive solution precipitation mechanism. The analysis of the processes and the microstructure reveal that in this kind of materials liquid phase sintering takes place resulting in a hard material with an improved toughness in comparison to pure B_6O .

Acknowledgements

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