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Liquid phase assisted densification of superhard B_6O materials

Mathias Herrmann [a,*], Jan Raethel [a], Axel Bales [a], Kerstin Sempf [a], Iakovos Sigalas [b], Mandy Hoehn [a]

[a] *Fraunhofer Institute for Ceramic Technologies and Systems, D01640 Dresden, Germany*
[b] *School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa*

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Abstract

B_6O-based materials are known as some of the hardest materials after diamond and cubic boron nitride with a hardness of 45 GPa measured on single crystals. Several attempts were made to produce B_6O materials by hot pressing, but without success. Based on thermodynamic considerations the possibility of the use of sintering additives was discussed and the developed concepts were validated by densification of the materials using FAST (field assisted sintering technique)/SPS methods and analysing the microstructure and properties of the resulting materials. Two groups of materials were found to be suitable for the densification: transition metals which form borides with B_6O, the elements of the first to fourth main groups of the periodic table and the rare earths (Sc, Y, and lanthanides) which are in equilibrium in the oxide form with B_6O and form a liquid phase during densification at 1700–1900 °C. Superhard dense B_6O materials were produced and their properties investigated.

Keywords: Sintering; Microstructure-final; Hardness; Borides

1. Introduction

B_6O-based materials are known as some of the hardest materials after diamond and cubic boron nitride with a hardness of 45 GPa measured on single crystals.[1] The structure of B_6O is quite similar to the structure of B_4C but B_6O is even harder than B_4C.[2] However, these materials have not been used in commercial applications so far because of the requirement to use high pressure (1–5 GPa) in order to achieve fully dense materials.[3] The resulting materials had good hardness but very low fracture toughness (1–2 MPa $m^{1/2}$).[3] B_6O consists of B_{12} icosahedral units connected by covalent bonds. Like B_4C, B_6O can be nonstoichiometric. It has the overall formula B_6O_{1-x} with x between 1 and 0.72. The high x values, i.e. the stoichiometric composition, were observed only in compounds made under high pressure synthesis.[4,5]

Efforts were 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,[6] boron carbide[7] and cBN.[8] 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 $m^{1/2}$.[6,8]

B_6O materials were prepared by hot pressing mixtures of B and B_2O_3 at temperatures up to 2000 °C.[9,10] These materials had high microhardness, but no other mechanical properties were determined. Hot pressing of B_6O powders in a wide temperature range described by Brodhag and Thévenot only resulted in porous materials with low hardness and poor mechanical properties.[11]

Recently we could show that B_6O materials with the addition of Al_2O_3 can be hot pressed at 1900 °C. The resulting materials have improved fracture toughness and only a slight reduction in hardness in comparison to pure B_6O materials.[12–14] Microstructural analysis showed that aluminium borate is formed at the grain boundaries beside micropores. The investigation of the microstructure reveals that the material was densified, at least predominantly, by liquid phase sintering. The densification of B_6O-materials at ambient pressure would make it possible to produce materials with properties similar to cBN-materials. The advantage of this method would be that no ultra high pressure is

* Corresponding author. Fax: +49 3512553600.
E-mail address: Mathias.Herrmann@ikts.fraunhofer.de (M. Herrmann).

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needed for the synthesis or the densification of these materials, as is the case for cBN materials.

The development of thermodynamic data for B_6O at high temperatures[13] has allowed predictions of the stability of the different phases in B_6O composites. On this basis several additives can be selected which could be suitable for the densification of B_6O. This search for additives is of great importance for the reduction of sintering temperature and the tailoring of the microstructure. For successful liquid phase sintering, beside the formation and stability of a liquid phase, a wetting of the B_6O by the main component is necessary. These data are difficult to predict and need experimental testing.

Based on thermodynamic calculations different groups of additive were determined and tested using FAST/SPS densification.

2. Experimental

The starting B_6O powder was produced on a laboratory scale as described in literature.[12] The chemical composition of the B_6O powder was determined using ICP OES. The compositions of the materials and the achieved properties are given in Table 1. The B_6O starting powder contains 0.25% Al and 0.32% Mg. Beside B_6O the following powders were used: Al_2O_3 (AKP50, Sumitomo, Japan), Y_2O_3 (Grade C, HC STARCK, Germany), TiB_2, TiH_2 (Grade C, HC STARCK, Germany), ZrO_2 (Thoso, Japan), HfO_2 (Treibacher, Austria); WO_3 was produced from WC (HC STARCK, Germany) by oxidation at 650 °C 10 h, TiO_2 (P25, DEGUSSA, Germany). TiH_2 was used as Ti source because it can be better milled than Ti powder due to its brittleness and its decomposition at temperatures less than 1000 °C.

The powder was mixed in an attrition mill with alumina milling balls (1–2 mm, Al_2O_3 99.6%). The solvent was ethanol. After milling the suspension was dried using a rotation evaporator. The wear of the alumina balls (0.65%) was included in the overall composition of the materials in Table 1.

FAST/SPS was carried out on a HP D 25 furnace (FCT Company, Germany) using graphite dies with an inner diameter of 30 mm and graphite foils. The graphite foils were coated with a BN suspension to prevent the interaction with the graphite. The densification was carried out in Ar. The temperature was measured with a standard pyrometer in the centre of the die.

The heating rate was 50 K/min. Since a non-conductive hBN coating was used, the densification is rather a fast hot pressing than a classical SPS process, which is characterised by a current going through the powder.

The densification was monitored by measuring the piston travel. This measurement was then converted into relative density change, normalizing the end position of the piston during the isothermal holding to the measured final density of the sample. The piston travel contains a contribution from thermal expansion of the whole setup. The comparison of curves with dense samples showed that there is a relevant deviation only during application of the load.

Cross sections of the materials produced were polished. The prepared cross sections were analysed using FESEM (Leo 982) with attached EDX system. The phase composition was determined using XRD (XRD7, GE Inspection, Cu Kα).

For microhardness testing an MHT-10 apparatus with Vickers indenter from Anton Paar was used. The indenter was placed in a lens barrel of an Olympus microscope. The test force can be varied between 0.05 and 400 Pont. For the measurement of the indentation an Olympus microscope with 500-times magnification was used. The microhardness value was calculated by using the AnalySIS software. 10 s dwell time was used for the indentation at the highest load. Five indentations were made for every material and every load.

3. Results and discussion

3.1. Thermodynamic calculations

Using the thermodynamic data given in[13] and using the SGTE database as well as the FACTSAGE programm[15] the different oxides were studied to determine their stability in comparison

Table 1
Properties of the densified B_6O materials (heating rate 50 K/min, holding time at maximum temperature 5 min).

Material	Additives (wt%)	Pressure (MPa)	T (°C)	H_V 0.4 (GPa)	Density (g/cm^3)	Phases[a]
1	2.62 Al_2O_3, 2.65 Y_2O_3	50	1850	31.2 ± 0.6	2.56	B_6O
1	2.62 Al_2O_3, 2.65 Y_2O_3	80	1800	33.0 ± 0.7	2.60	B_6O
2(E)[b]	0	50	1900	34.2 ± 0.6	2.50	B_6O
2(E)[b]	0	50	1850		2.36	B_6O
5	2 Al_2O_3, 2 Y_2O_3	50	1850		2.53	B_6O
5-ZrO_2	2 Al_2O_3, 2 ZrO_2	50	1900	36.9 ± 0.6	2.57	B_6O, ZrB_2
5b-ZrO_2	2 Al_2O_3, 2 Y_2O_3, 2 ZrO_2	50	1850		2.60	B_6O, ZrB_2
5b-HfO_2	2 Al_2O_3, 2 Y_2O_3, 2 HfO_2	50	1850		2.52	B_6O, HfB_2
5b-WO_3	2 Al_2O_3, 2 Y_2O_3, 4 WO_3	50	1850		2.61	B_6O, W_2B_5
5-TiH_2	2 Al_2O_3, 4 TiH_2	50	1850	33.6 ± 0.6	2.51	B_6O, TiB_2
5-TiB_2	2 Al_2O_3 2 Y_2O_3 10 TiB_2	50	1850		2.64	B_6O, TiB_2
		50	1900	36.8 ± 0.6	2.68	
B + TiO_2	B + TiO_2	50	1850		2.79	B_6O, TiB_2

[a] Determined by XRD, an amorphous grain boundary is present.
[b] Pure B_6O without additives.

to B_6O. A first approximation of the thermodynamic function of B_6O was obtained by McMillan.[5] The estimated value for ΔH_{298} was −622.2 kJ/mol. This is 20% less than the measured values ($\Delta H_f^{\theta}(B_6O, 298.15\,K) = -527 \pm 32\,kJ\,mol^{-1}$),[20] i.e. the measured data reveal a lower stability of B_6O than the estimated data of McMillan.[5] Calculations in this paper are based therefore on the measured values.[20]

The interaction of B_6O with the different compounds could be described by two reactions:

(1) The oxidation of B_6O and the formation of metals or borides. According to the reaction

$$MO_x + (0.125x + 0.1875z)B_6O \Leftrightarrow \frac{(1.125x + 0.1875z)}{3}B_2O_3(\text{liquid}) + MB_z \quad (1)$$

If the Gibbs free energy of this reaction is positive, then the oxide is stable in contact with B_6O. It would also indicate that borides could react with B_2O_3 and form B_6O giving the possibility to control the amount of B_2O_3 in the starting powder.

(2) It is important for the densification that MO_x can react with residual or added B in the starting powder and to form B_6O. This can also be an indication of the ability of the oxide to increase the oxygen content (x value) of the B_6O_{1-x} phase. This reaction can be formulated as follows:

$$MO_x + (z + 6x)B \Leftrightarrow xB_6O + MB_z \quad (2)$$

Borides which are stable with B_6O must have a negative Gibbs free energy of reaction (2).

The Gibbs free energy of both reactions at 1700 °C, i.e. the desired sintering temperature is given in Fig. 1.

The formation of mixed compounds or liquids is not taken into account by the given thermodynamic data, because such data are not available for most of the oxides used in this study. The solubility of the different components in the liquid or the formation of mixed oxides or borates will slightly shift the boundary between the stable oxides and borides. This has to be taken into account. However, the ΔG values of the reactions of the transition metal oxides with B_6O are quite negative, so that the equilibrium solubility of the oxides in the liquid/glass phase formed would be very small. Indeed no Ti, W, and Zr could be observed in the oxide triple junctions using EDX analysis (see Section 3.2).

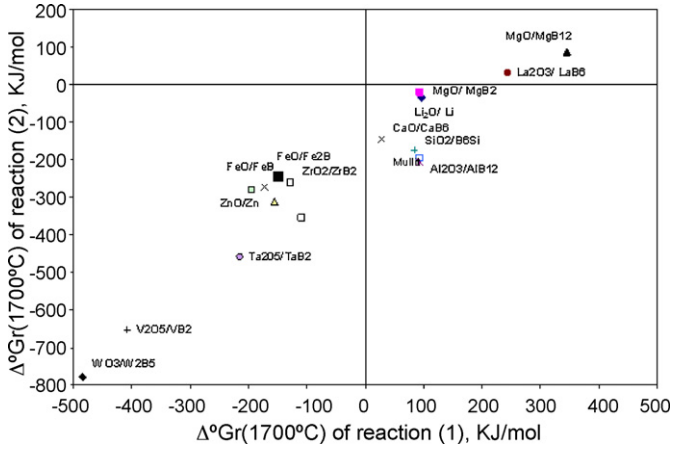

Fig. 1. Gibbs free energy of the interaction of different oxides with B and B_2O_3 (The composition of the starting oxides and of the resulting boride/metal are marked at the points.).

The data show that all chosen transition metal oxides of the IV to the VIII group react with B_6O to form borides. All these oxides also oxidize B to B_6O (the ΔG of reaction (2) is negative). This means that all the transition elements of these groups will form B_6O/boride composites independently of the starting powders (oxides + B or B_6O; B_6O + metals or borides). Recent investigations of the interaction of Pd with B_6O revealed the formation of Pd_2B.[16] Thus, the formation of borides is also likely for the Pt-group elements.

A starting powder mixture of B_6O and the transition metal oxides will result in the formation of some additional B_2O_3. The addition of the oxides or the metals, therefore, can be used to control the overall oxygen content in the material. It has to be mentioned that B_2O_3 has a high vapour pressure which could result in some decomposition of the materials.

All investigated oxides of the first to the fourth main group of the periodic table as well as the rare earths are in equilibrium with B_6O and can form an oxide secondary phase which forms a liquid during sintering interacting with some remaining B_2O_3. This was previously shown in the case of Al_2O_3 addition.[13,14]

The Gibbs free energy of the reaction of the oxide with B (reaction (2)) is for some of the oxides negative, while for others it is positive. This would not restrict their use as sintering additives, but if boron is present in the starting powder or is produced by decomposition, then Si-, Al- . . .oxides will react with boron to form B_6O and borides. In the case of MgO additions the Mg rich borides can be formed. The ΔG values of reaction (2) for La, Mg, and Li oxides are very close to 0. Therefore, the formation of stable mixed oxides or borides can shift the ΔG.

On the basis of the calculations conducted in this work, an improved densification through liquid phase sintering can be expected using stable oxides like CaO, Y_2O_3, Sc_2O_3, or other rare earths, or Al_2O_3, SiO_2, and MgO, alone or in combination with each other. The use of alkaline oxides as sintering additives is restricted by their high vapour pressure.

The transition metal oxides used in this study can form only transient oxide liquid due to the interaction with the B_6O resulting in the formation of borides and some B_2O_3 which forms a liquid, but has a high vapour pressure. The in situ formation of hard borides, e.g. TiB_2, offers the possibility to adapt the chemical composition or to use the metal oxide and B as a combined sintering additive.

To validate the thermodynamic findings different compositions of B_6O with Y_2O_3/Al_2O_3, TiH_2, TiB_2, ZrO_2, HfO_2 and, WO_3 additions were tested as sintering additives. The phase composition and some properties of the resulting materials were determined.

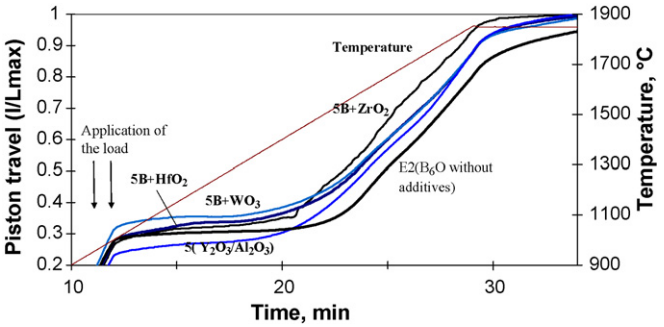

Fig. 2. Densification curves of the samples with different transition metal oxide additives in comparison to the pure B_6O powder and the material with Y_2O_3/Al_2O_3 additives.

3.2. Densification and microstructure of the composites

The materials, densities, phase compositions and properties are given in Table 1. The densification curves are given in Figs. 2 and 3. The data showed that the addition of Y_2O_3/Al_2O_3 strongly increases the degree of densification. Complete densification is achieved at 1850 °C for the compositions with the additives, whereas the pure B_6O powders can only be densified to 95% of theoretical density at this temperature. The same density as for the pure material can be reached for materials with additives at temperatures which are 50–100 °C lower. Fast densification starts at 1350–1370 °C for the material with the Y_2O_3/Al_2O_3 additives whereas the densification of the pure material starts only at 1450 °C (Fig. 2).

Some B_2O_3 is present on the surface of the B_6O powder as a result of the powder processing operation (approximately 1–1.5 wt%). This phase forms a liquid at temperatures above 480 °C and allows the densification to occur at lower temperatures. At temperatures above 1700–1800 °C B_2O_3 vigorously evaporates, and therefore the densification is retarded.[6] The added stable oxides Y_2O_3/Al_2O_3 react with the B_2O_3 and form a stable oxide rich liquid phase[10] during sintering which helps to reduce the densification temperature. The additives increase the amount of liquid and hinder the decomposition reactions during sintering in comparison to pure B_6O materials. Therefore, the addition of Y_2O_3/Al_2O_3 (stable oxides) results in a more reproducible densification in comparison to pure B_6O materials.

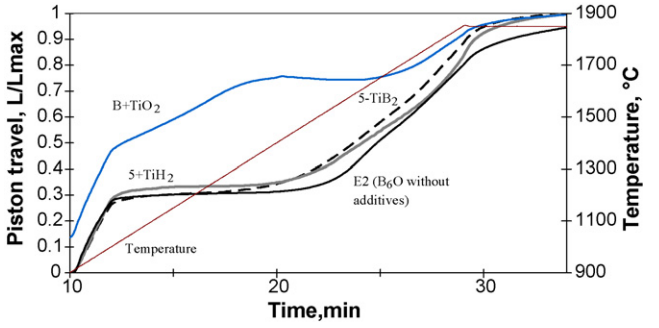

Fig. 3. Densification curves of the samples with different titanium containing additives in comparison to the pure B_6O powder and the material with Y_2O_3/Al_2O_3 additives.

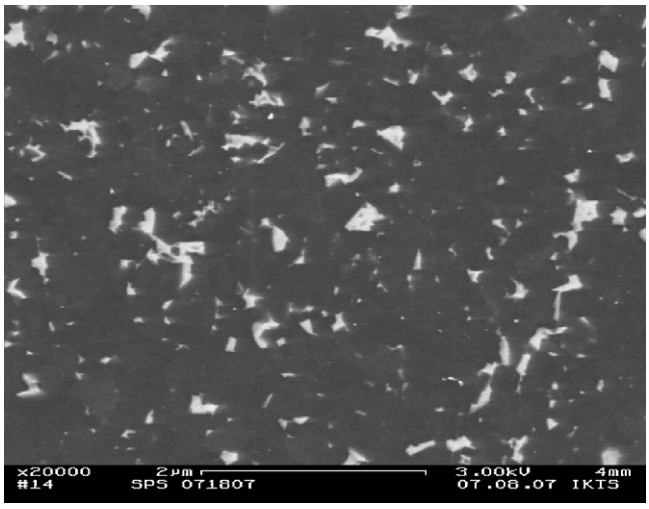

Fig. 4. SEM image of the microstructure of material 1.

The microstructures of the materials containing additives of Y_2O_3/Al_2O_3 also reveal the presence of such a liquid, because no crystalline grain boundary phases are found. SEM micrographs in Fig. 4 shows a homogeneous distribution of the Y_2O_3/Al_2O_3 additives (white phase) in the triple junctions.

The grain size of the material cannot be determined, but from the SEM micrographs it can be concluded that the grain size is less than 1 μm. Therefore, no grain growth occurs. This is most likely due to the very short sintering times employed (Fig. 4).

The addition of transition metal oxides also improves the densification in comparison to the pure B_6O powder. The increase in densification is not as pronounced as in the case of Y_2O_3/Al_2O_3.

At low temperatures the added transition metal oxides (ZrO_2, TiO_2, WO_3) form a liquid with the B_2O_3 present on the surface of the B_6O powder. The solubility of TiO_2 or WO_3 at 1200 °C is 10–25 mol% (corresponding to 12–50 wt%, respectively).[17] Additionally, non-dissolved oxides can also remain in the resulting material. These remaining oxides can provide some lubricity because they can be densified at these temperatures.

The oxides are thermodynamically not stable (see Section 3.1) and quantitatively transform into borides and B_2O_3 (reaction (1)). The B_2O_3 decomposes, at least partially, at high temperatures.

The borides formed have a high melting point and can only be sintered without additives at high temperatures.[18] Therefore, they cannot significantly accelerate the sintering in comparison to pure B_6O. At high temperatures, the remaining Al_2O_3 and MgO (from the wear of the milling media and from the starting powder, respectively) only form a liquid with the B_2O_3 improving the densification. Al, B, O and some Mg were found in the triple junctions examined by SEM/EDS (Fig. 6). The grain boundary pockets are partially removed by polishing indicating their lower chemical stability.

The grain boundary phase containing Y_2O_3/Al_2O_3 is chemically much more stable than the boron rich grain boundary phase, which was observed in the materials containing the transition metal oxides and some Al_2O_3. The lower stability results in the partial removal of the grain boundary phases during polishing.

This becomes visible in Fig. 6b and is not visible in Fig. 4. From the investigations of borate glasses[19] it is known that the transition temperature of the amorphous grain boundary also increases up to 800 °C with Y_2O_3/Al_2O_3 addition. This has a positive effect on the high temperature stability.

The conversion process of the transition metal oxides into borides takes place at temperatures below 1500–1600 °C. The completion of the reaction results in some retardation of the sintering at intermediate temperature. This is also clearly seen in the reaction sintering of B and TiO_2 (Fig. 3).

This mixture densifies much faster in the temperature region between 1000 and 1600 °C than the other composites with TiH_2 or TiB_2 additions. This is related to the reaction of TiO_2 with B:

$$TiO_2 + 14B \rightarrow 2B_6O + TiB_2. \quad (3)$$

A run interrupted at 1600 °C showed that TiB_2 and a very disturbed or nanocrystalline B_6O are formed at these temperatures. However, the densification is only completed at temperatures higher than 1650 °C (Fig. 3).

The phase composition (B_6O and TiB_2) was found to be independent of the starting mixture (TiH_2 or $TiB_2 + B_6O$ or TiO_2 and B). As in the case of the phase composition of the other samples investigated in this work, this confirms the predictions of the thermodynamic calculations.

The addition of 10 wt% of TiB_2 to the composition of the $B_6O + Y_2O_3/Al_2O_3$ does not change the densification behaviour significantly (cf. curves in Figs. 2 and 3).

The microstructure of material 5-TiB_2 is shown in Fig. 5. It is possible by EDX analysis to see that the TiB_2 grains are in the range of 1–2 μm and that the oxide grain boundary contains Y_2O_3/Al_2O_3 and some B_2O_3.

The microstructure of the materials with TiH_2 additions are given in Fig. 6. The material is dense and the formation of borides is visible. The particle size of the precipitated borides is less than 1 μm. During sample preparation the oxide grain boundary is more extensively removed by polishing than the hard B_6O and borides. This more intensive polishing behaviour was observed only for the materials without Y_2O_3 additions and with additions

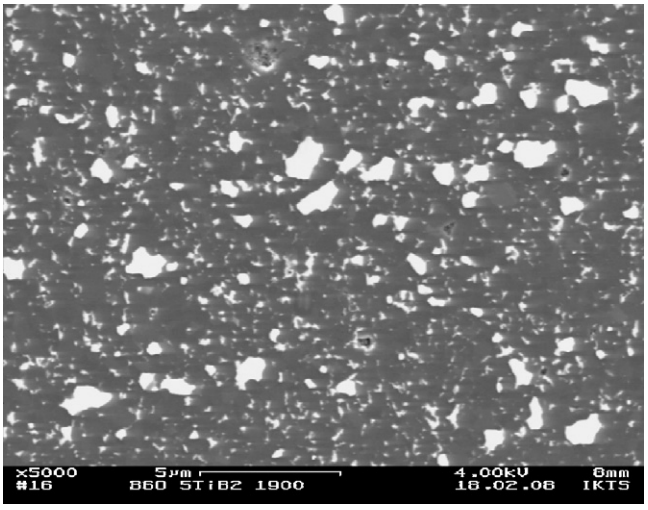

Fig. 5. SEM image of the microstructure of sample 5-TiB_2.

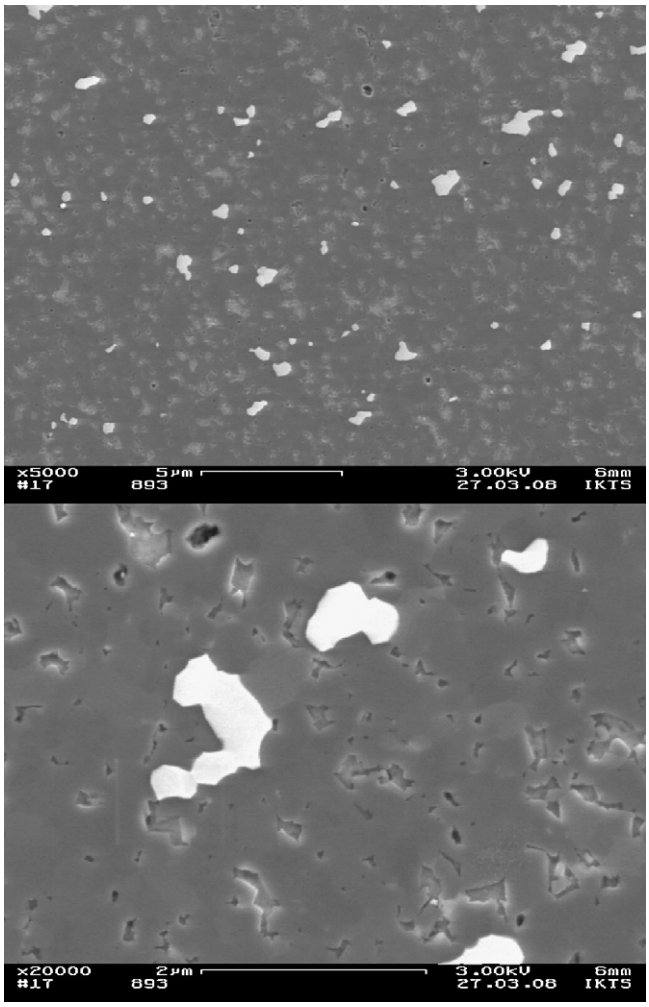

Fig. 6. SEM micrograph of sample 5-TiH_2 showing the TiB_2 precipitates (white phase) and the oxide grain boundary partially polished out.

of other oxides or TiH_2 which interact with B_6O forming B_2O_3. It has to be mentioned that even the addition of an oxide free metal (TiH_2) results in an increased content of B_2O_3 due to reaction

$$8Ti + 3B_6O \rightarrow 8TiB_2 + B_2O_3 \quad (4)$$

These interactions result in an increase of B_2O_3 in the grain boundary phase. Higher B containing glasses are softer and chemically less stable.[11] Therefore, they will be more sensitive to polishing than the more stable Y_2O_3–Al_2O_3–B_2O_3 glasses generated in the case of sample 1 and 5-TiB_2.

The kind of the transition metal additive (Ti, Zr, Ta, W,. . .), i.e. oxide, metal or boride has no influence on the phase formed. It has an influence only on the oxygen content of the material. Perhaps the addition of these oxides increases the oxygen content in the B_6O_{1-x}. During sintering a small shift of the lattice parameter was observed which perhaps is caused by this process. On the other hand the increase in the oxygen content can result in the formation of B_2O_3 which forms with other oxides (Al_2O_3, MgO) a weak grain boundary phase or evaporates during sintering. This effect can be minimised by simultaneous addition of a transition metal or

Table 2
Schematic presentation of the influence of the additives on the phase composition and oxygen balance in the materials.

Nr.	Addition	Phases formed during densification	Effect on composition
1	M (metal) M = Ta, W, Mo, Fe, Cr, Ni. . .	Boride	Increase of oxygen activity reducing x in B_6O_{1-x} or producing B_2O_3, which may partially evaporate
2	MO_x (metal oxide) M = Ta, W, Mo, Fe, Cr, Ni, Co	Boride	As in Nr. 1, but stronger shift to the oxygen rich compounds
3	MB_x (metal boride) M = Ta, W, Mo, Fe, Cr, Ni, Co	Boride	No or minor change on the ratio of B_2O_3/B_6O or the stechiometry of B_6O_{1-x}
4	$M^{II}O_x$ (metal oxide) M^{II} = Al, Y, Sc, Mg, Si	Borates or borate glasses, or oxides	No change in the oxygen balance, formation of an chemical stable less B_2O_3 rich oxide grain boundary phase

its metal oxide and elemental boron as shown in the material B-TiO_2.

In contrast to the above, the addition of stable oxides like Al_2O_3, MgO, Y_2O_3, Sc_2O_3 or their mixtures results in the stabilisation of the B_2O_3 already present in the starting powder. Also this would minimize the reduction of the oxygen content in the B_6O phase. These processes are summarized in Table 2.

4. Conclusions

Based on thermodynamic considerations the use of sintering additives for boron suboxide was discussed. Two groups of materials were considered suitable for the densification:

- Oxides or metals of the transition metals of the fourth to the eighth group of the periodic table, which form borides with B_6O.
- Oxides of the first to fourth main group of the periodic table and the rare earth (Sc, Y, La, and lanthanides) which, in their oxide form, are in equilibrium with B_6O and form a liquid phase during densification at 1700–1900 °C.

The effectiveness of the additives was proven by means of densification experiments using the FAST/SPS method. Completely dense materials were produced with hardness (H_V 0.4) higher than 33 GPa.

The addition of ZrO_2, TiO_2, WO_3 and HfO_2 results in the formation of the corresponding borides. Beside the boride an amorphous grain boundary phase was formed, which includes MgO, Al_2O_3 and Y_2O_3 if such additives were introduced. The addition of Y_2O_3/Al_2O_3 results in dense materials with a minor oxide grain boundary phase indicating the stability of these oxides in contact with B_6O.

It could also be shown that B_6O/TiB_2 composites can be produced by reaction sintering of TiO_2 and B.

The results show that it is possible to produce dense superhard B_6O materials without high pressure. The improved densification of the materials in comparison to pure B_6O is connected with the formation of a liquid phase during densification. The correlation of preparation, microstructure and properties of this new class of superhard materials needs further investigation.

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