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Oxidation resistance of B_6O-materials with different additives

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Abstract

The oxidation resistance of B_6O materials with and without Y_2O_3/Al_2O_3 additives and a typical cBN material were analysed in dry and wet air using TG measurements for up to 10 h and static experiments in a muffle furnace for up to 50 h. The results showed that the oxidation of the materials is sensitive to the composition of the atmosphere. In wet air with 17 vol.% H_2O a weight loss was measured for all materials. In dry air a parabolic increase of the mass and a formation of a glassy surface layer were observed for the B_6O materials whereas the cBN-material is characterized by the formation of a mostly crystalline layer.

The oxidation resistance is the lowest for the pure B_6O and the highest for the investigated cBN material.

Keywords: Boron suboxide; Microstructure-final; Thermal properties; Cutting tools

1. Introduction

B_6O-based materials are known as the hardest materials after diamond and cubic boron nitride with a hardness of 45 GPa measured on single crystals.[1–3] However, in contrast to the promising properties, B_6O materials have not yet been used commercially, because full densification requires high pressures (1–5 GPa).[4] The materials densified at high pressures have good hardness but a very low fracture toughness of 1–2 $MPam^{1/2}$. Unsuccessful efforts have been made to enhance the fracture toughness of B_6O by forming B_6O composites.[5–7]Hot pressing of B_6O powders resulted only in porous materials.[10] B_6O materials were prepared by hot pressing of mixtures of B and B_2O_3 at temperatures up to 2000 °C.[8,9] These materials had a high microhardness, but no other mechanical properties were determined.

Recently it was reported that B_6O can be hot pressed or densified by FAST/SPS with oxide additions. The resulting materials showed improved fracture toughness 3–4 $MPam^{1/2}$ with a slight reduction in hardness, as compared to pure B_6O materials.[11–16]

Microstructural investigations have shown that the oxide additives in B_6O materials form an amorphous grain boundary phase containing Y_2O_3 and Al_2O_3 beside B_2O_3. This amorphous oxide phase is concentrated in the triple junctions. Most of the grain boundaries are not wetted by the additives.[15] The same behaviour was found for the B_2O_3 in the pure B_6O.[12]

With a microhardness above 30 GPa and a HV5 hardness at 1000 °C which exceeds that of a commercial cBN cutting tools,[18] the B_6O-materials could be a potential candidate for cutting tools suitable for the machining of iron- or nickel-based materials. Apart from the wear resistance of these materials, also the chemical stability towards the machined material and the oxidation resistance play a decisive role for the use as cutting tools.

Recently the interaction between B_6O and compacted graphite cast iron was investigated.[19] It was shown that there exists only a minor interaction between these materials below 1100 °C. A comparable study of the oxidation resistance of high pressure densified B_6O and B_4C resulted in a much better oxidation resistance of B_6O.[17] It was shown that up to 1200 °C a high oxidation resistance exists caused by the formation of a B_2O_3 surface layer having a thickness of approximately 30 μm after 4 h exposure to an oxidising environment.

Therefore in this work we have analysed the oxidation behaviour B_6O-materials with and without oxide sintering additives in dry and wet atmosphere and compared it to a commercial cBN-materials containing 10 wt.% AlN as binder phase.

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2. Experimental

The starting B_6O-powder was produced in laboratory scale as described elsewhere.[14] The chemical composition of the B_6O powder was determined by ICP-OES. The following cation impurities were determined: Fe = 0.081 wt.%, Cr = 0.077 wt.%, Al = 0.047 wt.%, Mg = 0.12 wt.%. The mean grain size of the starting powder was 0.5 μm. The powders used beside B_6O were Al_2O_3 (AKP50) and Y_2O_3 (Grade C, HC STARCK, Germany). FAST/SPS was carried out on a HP D25 furnace (FCT, Germany) using graphite dies and graphite foils. Details of the preparation are given elsewhere.[13,15]

Two materials were used for the oxidation experiments:

- a pure B_6O-material with density of 2.47 g/cm^3, which corresponds to 97% of theoretical density.
- a B_6O-material containing approximately 2 wt.% Y_2O_3 and 2–2.3 wt.% Al_2O_3 additives with a density of 99.6% of theoretical density.

For comparison the oxidation resistance of a cBN material containing 90 vol.% cBN and 10 vol.% AlN based binder (AMB90) with a density of 3.33 g/cm^3 was investigated. The materials were cut in the necessary size and the surface was ground. The sample size used was approximately 3 mm × 3 mm × 10 mm.

Initially the oxidation resistance was tested in a laboratory furnace at 1000 °C up to 50 h which does not allow control of moisture. Thermogravimetric analysis (TG) in dry and wet air (dew point of 57 °C, 0.17 bar H_2O) was carried out using STA 449 C (Netzsch Gerätebau GmbH, Selb, Germany) with a special furnace for regulating the water vapour. In a first run the oxidation was tested up to 1 h at 1000 °C for all materials. In a second run isothermal oxidation up to 10 h was carried out for the B_6O material with oxide additives.

After oxidation the surface was examined with a field-emission scanning electron microscope (FESEM, Leo 982) with an EDS system attached to it. The phase composition was also determined by X-ray diffraction (XRD7, GE Inspection Technologies, Germany, $Cu_{K\alpha}$). Beside surface analysis, cross sections of some of the materials were prepared and investigated using electron microscopy.

Additionally, thermodynamic calculations were carried out using the FACTSAGE program (version 5.1) and the SGTE database.[20]

3. Results

The results of isothermal oxidation of the two investigated B_6O-materials are given in Fig. 1. The experiments were carried out in a muffle furnace. In these experiments no precise control of the moisture was possible. During these experiments the ambient conditions were approximately 30 °C and a humidity of 70%. Therefore it was thought that the moisture could have an influence on the results. To understand the influence of the moisture short term oxidation runs were carried out in a TG-system adapted for precise control of the atmosphere and for operating under high moisture. The results of the TG measurements are given in Figs. 2 and 3.

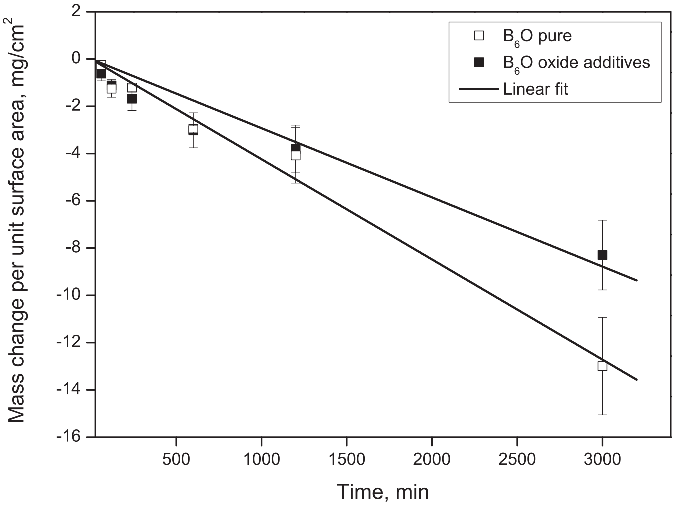

Fig. 1. Weight change of the B_6O-materials during isothermal oxidation at 1000 °C in a laboratory furnace.

During heating up at temperatures below 500 °C all runs show very similar behaviour independent on the atmosphere and the material. A small weight loss was observed, which is slightly higher for the pure B_6O-material. Above 500 °C mate-

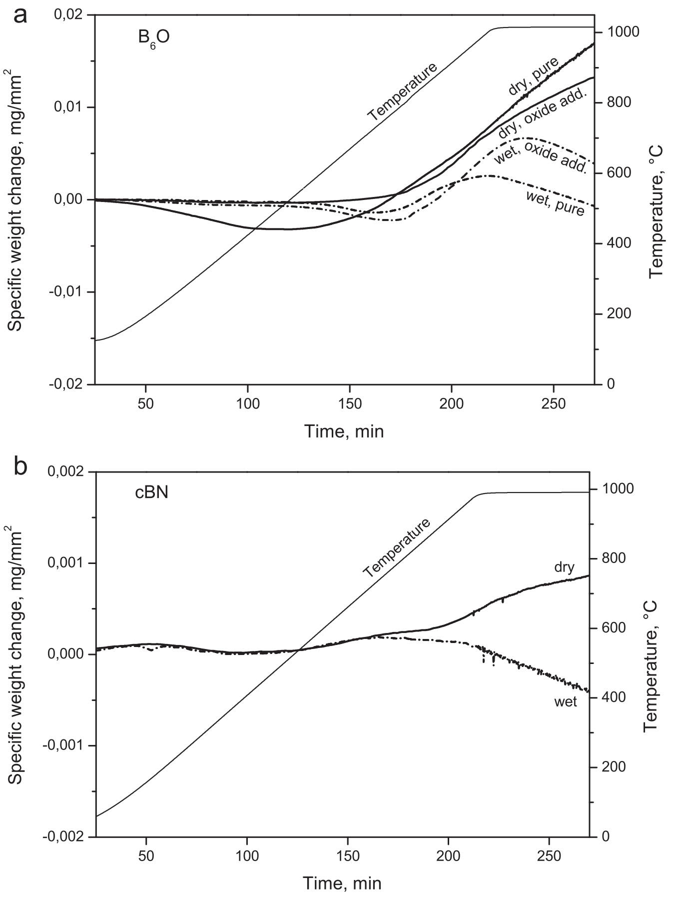

Fig. 2. Results of the TG investigation of the oxidation of the pure B_6O and with oxide additives (a) and cBN-materials (b) in dry and wet air.

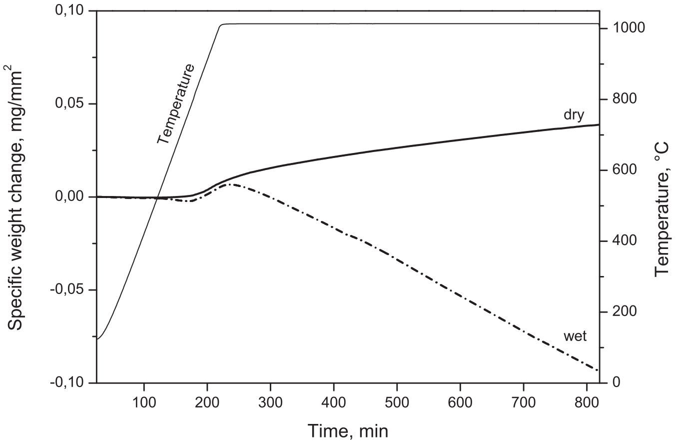

Fig. 3. Results of the TG investigation of the oxidation of B_6O with oxide additives in dry and wet air for 10 h.

rials in dry air are characterized by a small increase in mass, while the mass loss of samples oxidised in wet air continued to higher temperatures before it changes to a slight mass increase above 750 °C (Fig. 3). At higher temperatures (especially in the isothermal period) the samples behave differently in the different atmospheres. In the wet atmosphere a general weight loss was observed for all materials. For the pure B_6O-material and the cBN-material this weight loss starts nearly immediately after reaching the target temperature of 1000 °C at the beginning of the isothermal period. In contrast the decrease in mass for the B_6O-material with oxide additives is slightly delayed and starts about 20 min after reaching the beginning of the isothermal segment. In the dry atmosphere a weight gain was observed for all materials, which is higher for the pure B_6O-material in comparison to the B_6O-material with oxide additives. For the cBN-materials the weight gain and the weight loss are generally smaller in comparison to the B_6O-materials.

The XRD investigations of the B_6O-materials showed only H_3BO_3 formed as additional crystalline phase after 1 h oxidation and after 10 h oxidation in the material with additives. Additionally Al_5BO_9 and yttrium aluminium borate could be detected. H_3BO_3 is not stable at 1000 °C therefore the H_3BO_3 found by XRD must be formed during cooling or after the experiment (even if the samples were stored in a desiccator with drying agent). Therefore, the morphology of the surface layers observed by SEM does not exactly represent the state at high temperatures. This is necessary to bear in mind when discussing the results.

SEM investigations of the materials oxidized in wet air show facetted platy crystals, arranged in rosettes, which contain alumina, yttria and boron oxide (EDX measurements) and needles containing mostly yttria and boron oxide and a small amount of alumina (Fig. 4a–c). These phases were not observed by XRD after 1 h oxidation but were visible after 10 h oxidation.

In dry air such crystals are not formed (Fig. 5a–d). The SEM-micrographs of the 1 h in dry air oxidised B_6O material with oxide additives showed the formation of ball like inclusions (Fig. 5c and d). The EDX analysis of these inclusions reveals that they are rich in yttria and alumina whereas the surrounding surface layer consists of nearly only boron and oxygen (hydrogen cannot be detected). After the 10 h oxidation stage these ball like inclusions disappear. In minor amount the same inclusions were also found during oxidation in wet air after 10 h in areas where fewer crystals had formed.

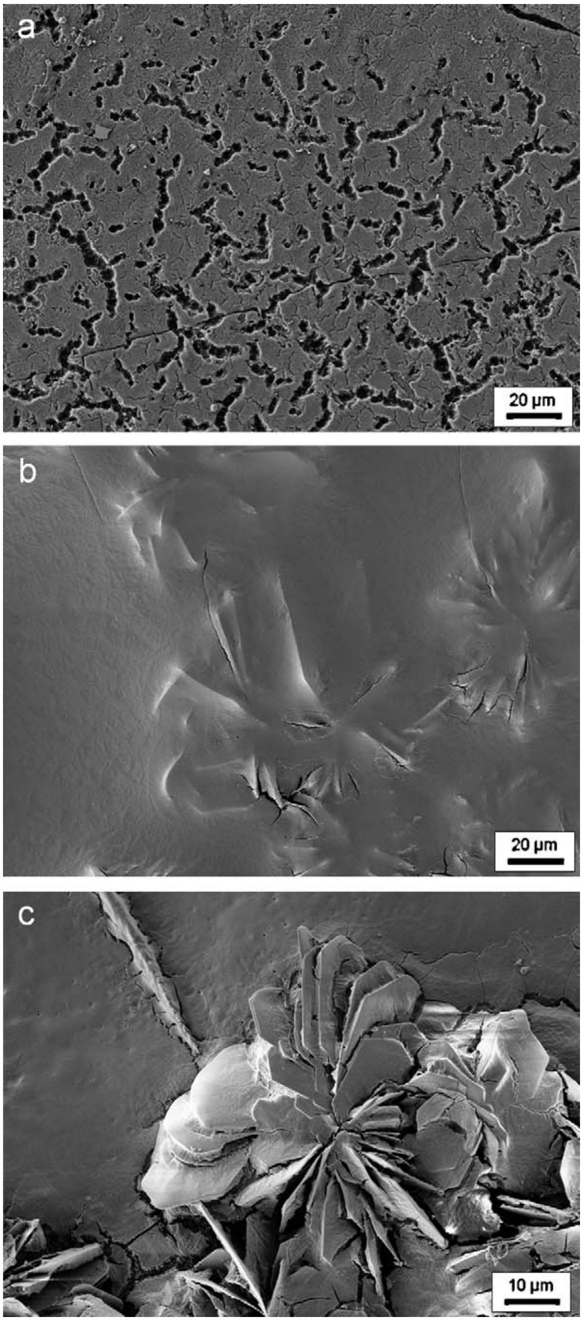

Fig. 4. SEM micrographs of the surface of oxidised in wet air pure B_6O material (a) and the B_6O material with oxide additives (b and c).

The SEM-figures of the different oxide layers on the B_6O materials reveal cracks which are most probably produced by the thermal mismatch of the surface layer and the substrate (Figs. 4 and 5). The layers look porous especially after the oxidation in dry air. The layer observed for the materials with oxide additives under wet conditions reveal more a glassy like layer with the crystalline inclusions mentioned before (Fig. 4b and c).

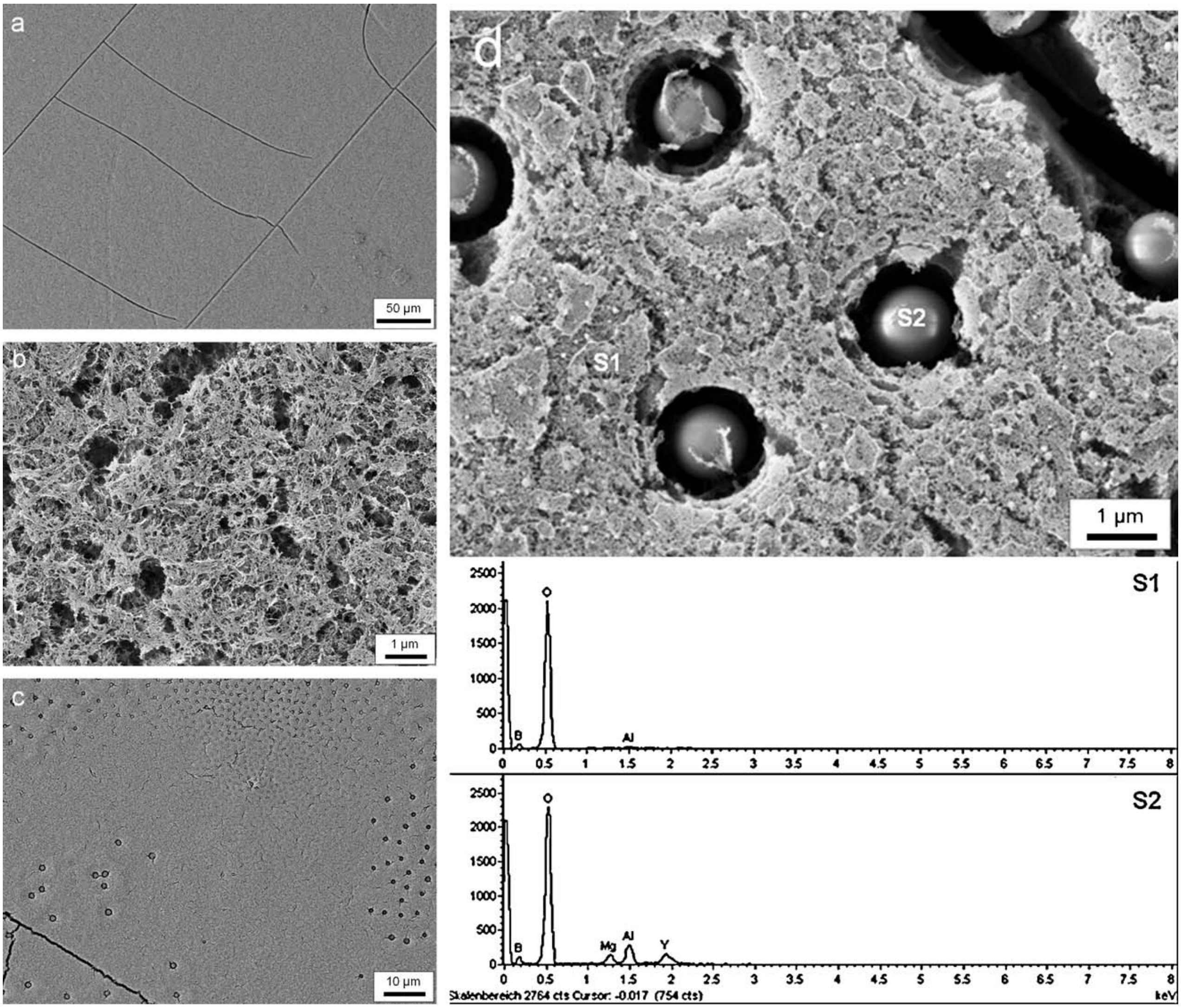

Fig. 5. SEM micrographs of the surface of B_6O oxidised in dry air. Pure B_6O materials (a and b), B_6O material with oxide additives (c and d).

Cross sections of the B_6O-material with additives after 10 h oxidation in dry and wet air are shown in Fig. 6a and b, respectively. The micrographs reveal a thickness of the oxide layer of less than 10 µm for the sample oxidised in dry air. The layer consists of boron and oxygen and minor amounts of Al, Y, Mg and very few impurities. The microstructure below the oxide layer was not altered. In the case of the oxidized in wet air material the oxidation is stronger. The surface layer consists of two sub layers – the outer B_2O_3 glassy phase containing layer in which the different crystals are embedded and beneath of this layer an up to 10 µm thick area enriched with the sintering additives. Some of the large platy crystals seen on the surface started to growth in this layer.

The XRD and SEM analysis of the cBN-material reveals that aluminium borate was newly formed during the oxidation on the cBN–AlN composite. SEM micrographs of the surface of this material showed mostly needle like crystals (Fig. 7). From the literature it is known that Al_5BO_9 can grow in the form of needles in a borate glass.[21]

Table 1 contains the summarized data of the isothermal oxidation period. In Table 1 are given the calculated rate constants for the linear time law $\Delta m = \mathrm{Kt} + \Delta m_0$ and for the square root time law $\Delta m^2 = \mathrm{Kt} + b$. Beside the rate constant also the R^2 values of the fits are given. In some cases a fit of both laws was possible with nearly the same accuracy. In these cases both values were given. Additionally the weight changes after 1 h are shown. These data shows more obvious the differences in the oxidation behaviour independent of the oxidation-time law.

4. Discussion

At low temperatures all samples exhibit a small weight loss. This is connected to desorption of moisture and the evaporation of the HBO_2 during heating. The thermodynamic calculations showed (Fig. 8a and b), that the acid completely decomposes above 300 °C. In the B_6O samples which are oxidised in a wet atmosphere this weight loss persists part up to 750 °C. This could be caused by the fact that the thin surface layers consisting

Table 1
Results of the analysis of the isothermal period at 1000 °C.

Sample	Condition	Linear[b] constant; mg/(cm^2 min)	Square root[b] constant; mg^2/(cm^4 min)	R^2	ΔM_{max}; after 1 h, mg/cm^2	Theoretical mass[c] gain, ΔM_{th}%	ΔM_{max}; corrected[d], mg/cm^2
AMB90	Dry	0.65×10^{-3}[a]	9×10^{-5}[a]	0.96/0.99	0.086	37.6	0.23
	Moisture	-0.84×10^{-3}	–	0.91	−0.043		
CVD hBN	Dry Oxygen		3.3×10^{-5}[e]				
B_6O pure	Dry		4.6×10^{-2}	0.99	1.88	158.2	1.18
	Moisture	-7.0×10^{-3}		0.996	−0.17		
	Furnace	-4.3×10^{-5}		0.98			
B_6O with oxide additives	Dry		2.4×10^{-2}	0.999	1.4	151.3	0.93
	Moisture	-18×10^{-3}		0.999	0.2		
	Furnace	-2.3×10^{-5}		0.99			

[a] Not equivocal.

[b] Linear time dependence – $\Delta m = Kt + \Delta m_o$; square root time dependence $\Delta m^2 = Kt + b$.

[c] Theoretical mass change according to reactions (1)–(3).

[d] Corresponds to 100 $\Delta M_{max}/\Delta M_{th}$.

[e] Data of Jacobson.[24]

of B_2O_3 (and the additives) formed during grinding and storage are attacked by the moisture and at least partially removed. This is confirmed by thermodynamic calculations showing high vapour pressure of boron containing species in wet atmosphere (Fig. 8b). On the other hand the vapour pressure for boron containing species is several orders of magnitude lower in dry atmosphere. Therefore an evaporation of the B_2O_3 surface layer could not take place.

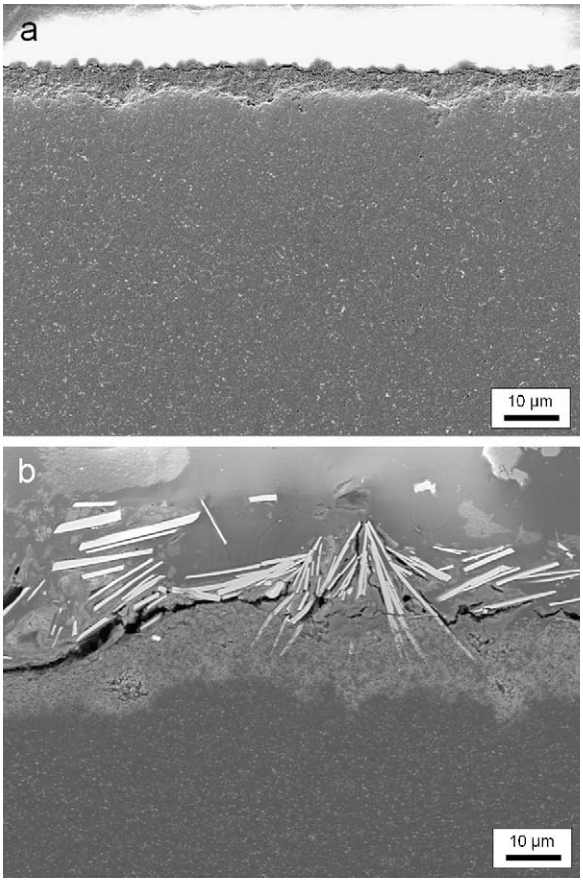

Fig. 6. SEM micrographs of the cross section of the B_6O-material with oxide additives oxidised in dry air (a) and wet air (b).

Further increase of the temperature results in a weight gain for all samples independently on the atmosphere. This indicates that the oxidation of B_6O or cBN is the main process and the evaporation due to the water vapour is less pronounced in this temperature interval.

In dry air and at high temperatures the oxidation of all materials is connected to an increase in weight. The weight gain during oxidation of B_6O, as depicted by Eq. (1) below

$$B_6O + 4O_2 \Rightarrow 3B_2O_3 \quad \Delta m = 158.2\% \tag{1}$$

is approximately 4 times higher than the oxidation of cBN

$$2BN + 1.5O_2 \Rightarrow B_2O_3 + N_2 \quad \Delta m = 39.2\% \tag{2}$$

The oxidation of the AlN-binder of cBN results in an even smaller weight gain:

$$2AlN + 1.5O_2 \Rightarrow Al_2O_3 + N_2 \quad \Delta m = 24.4\% \tag{3}$$

Therefore the same mass change of the different materials is not caused by the same extend of the reaction.

The theoretical mass gains of the materials using Eqs. (1)–(3) are given in Table 1 (assuming the same rate of oxidation of BN and AlN).

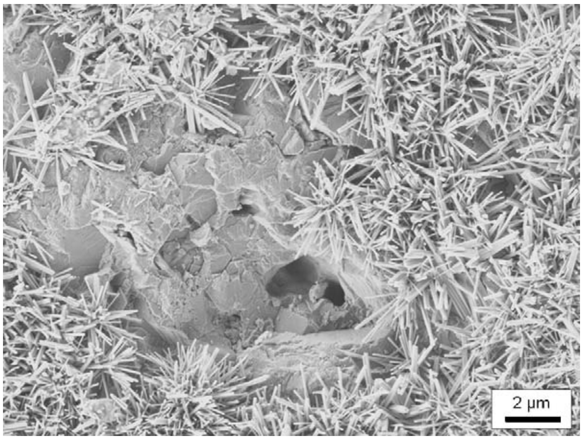

Fig. 7. SEM micrographs of the surface of the c-BN material with oxide additives oxidised in wet air.

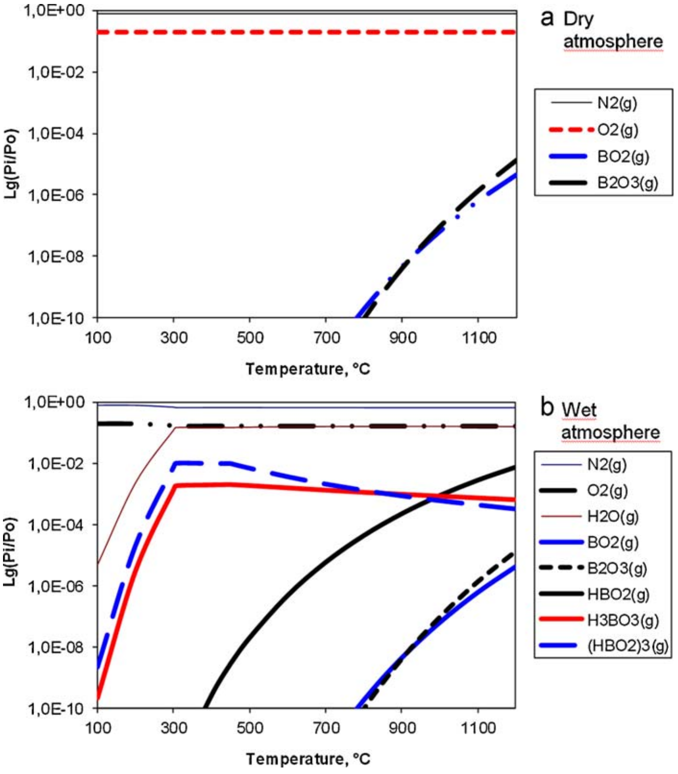

Fig. 8. Results of the thermodynamic calculations of the gas phase above B_2O_3 in dry (a) and wet air (b).

By normalising the mass gain by the theoretical mass gain (last column in Table 1) it becomes obvious that the oxidation of the B_6O materials in dry air is about 4–5 times stronger than that of the cBN material.

The additive containing B_6O-material has a weight gain which is about 25% less than that of pure B_6O materials. The isothermal weight gain can be described by the law

$$\Delta m^2 - \Delta m_o^2 = Kt \tag{4}$$

which corresponds to the model of the formation of a protective surface layer. This is also in agreement with the microstructural observation showing the formation of a 5–10 μm thick layer after 10 h oxidation. Even if they are very porous and not protecting, at high temperatures they would be a borate glassy layer containing the sintering additives or only B_2O_3. During cooling and storage such B_2O_3 rich glasses are not stable and react with moisture forming boric acid. An additional evidence for the glass formation is the ball like precipitates after 2 h oxidation of the material containing sintering additives. At high temperatures or during cooling the composition of the formed boride glass will be in the immiscibility region of the glass. The separation in the glass will result in such segregations. The segregations are known for example for $B_2O_3/Al_2O_3/SiO_2$ glasses in the B_2O_3 rich area[22] and will form only in a certain ratio of $Y_2O_3/Al_2O_3/B_2O_3$. Therefore for longer oxidation experiments the additives may also be diluted.

In wet atmospheres pure B_6O and the cBN-materials showed a weight loss during the isothermal oxidation time. The B_6O-material with the Y_2O_3/Al_2O_3 sintering additives showed increasing weight in the first 20 min of the isothermal oxidation. After the initial period a linear weight loss was observed all the time as it was observed also in the isothermal 50 h oxidation. This is an evidence of the paralinear kinetics under these conditions.[24]

The thermodynamic calculations showed that the gas phase over B_2O_3 strongly depends on the moisture content (Fig. 8). In the dry atmospheres only very low partial pressures of B containing species are observed (1×10^{-7} atm). In the wet atmosphere at 1000 °C the partial pressure of HBO_2, H_3BO_3 $(HBO_2)_3$ are all nearly 1×10^{-3} atm. Therefore in the dry atmosphere the oxide layer is stable whereas in the wet atmosphere the evaporation of the layer as HBO_2, H_3BO_3 $(HBO2)_3$ is the main reason for the observed weight loss. The determined linear time dependence in the experiments also agrees with this mechanism. Nevertheless an oxide layer was found on the surface of the B_6O materials. This implies that the oxidation of the pure surface is faster than the evaporation by the reaction with the moisture. This also explains the fact that at the beginning of the isothermal oxidation of B_6O with oxide additives a weight gain was observed. Assuming that the oxidation is determined by the diffusion of oxygen through the formed oxide layer, the oxide layer at the beginning was still too thin to be protective. Therefore the oxidation of the B_6O can be regarded as faster than the evaporation. With increasing layer thickness the diffusion of the oxygen slows down and therefore also reduces the oxidation. After the initial period a steady state is reached resulting in the linear time law. The oxide additives are enriched in the layer and will reduce the evaporation rate in comparison to the pure B_6O-material. The enrichment is clearly seen in the cross section after 10 h oxidation (Fig. 6b and c). Such enrichment is not expected for the oxidation in dry air. This is confirmed by the oxidation layer formed in the case of dry air oxidation (Fig. 6a).

The oxidation rate and mechanism can be determined by the 10 h TG runs. The constants are given in Table 1. The constants derived from the other two materials (1 h TG runs) are less reliable due to the short experiment time.

The 1 h oxidation of the cBN material was not enough to determine the time dependence of the weight gain. With nearly the same R^2 values the square root time dependence and the linear time dependence can be fitted (99.8 for the square root dependence; 96.2 for linear growth). Also the analysis of the surface layer (Fig. 7) shows no real evidence of a formation of a protecting layer. The higher Al_2O_3 content formed on the surface in cBN-material in comparison to the B_6O materials resulting in a stronger formation of crystalline aluminium borate phases (needle like grain growth). This can have an influence on the oxidation resistance. In the literature [24,25] dense CVD hBN and a wurtzite like –BN materials were investigated showing that up to 1000 °C the materials only oxidize slowly. For dense CVD h-BN a paralinear oxidation behaviour was observed due to moisture in the air. In oxygen with a dew point <-60 °C a parabolic rate constant was observed, which was similar to that observed here (Table 1). A similar behaviour was observed for wurtzite like –BN materials showing parabolic oxidation behaviour in the temperature interval 900–1100 °C and weight loss at 1300 °C (paralinear kinetics).[25]

All results showed that the oxidation resistance of the cBN-material is better than for the B_6O-materials investigated. Nevertheless the oxide additives can improve the oxidation resistance due to stabilization of the glassy surface layer by the oxides.

Another reason for the higher oxidation resistance of the cBN material beside a higher additive content, could be the much larger grain size of the cBN grains (10 μm) in comparison to the B_6O materials having grain sizes of 0.2–2 μm.

The lowest weight loss constants were observed for the materials oxidized in the muffle furnace. Satisfactory linear time dependence can be fitted if the first point (1 h) is not taken into account (Table 1). This is connected with the lower water partial pressure. It is still enough to result in an oxidation regime, where the evaporation of the boric acid determines the process. Also the data derived from this run reveals a clearly higher oxidation resistance for the material with the oxide additives.

For a more detailed comparison we have used the observed weight changes divided by the theoretical weight change determined by the reactions (1)–(3) (Table 1). The results showed that the oxidation resistance of cBN is up to 4–5 times higher than that of the B_6O-materials, and the oxidation resistance of the material with oxide additives is 20% higher than that of the pure B_6O.

Moisture can intensify the oxidation. This is known from SiC-, Si_3N_4 –ceramics were faster oxidation in wet atmospheres takes place.[23] Also in the B_6O-materials after 10 h oxidation the formed surface layer is thicker in the case of wet oxidation.

5. Conclusion

The investigation of the oxidation of B_6O-materials with and without additives has shown that during oxidation at 1000 °C a glassy surface layers is formed.

These glassy layers act as diffusion barrier. Therefore a square root time dependence of the weight change was observed.

The formed B_2O_3 rich layers are moisture sensitive and form boric acid during cooling and storage.

In wet atmospheres the reaction of the boron oxide layer with the moisture and the evaporation as boric acid is a rate controlling step. Linear time laws are determined. The materials with oxide additives showed a higher oxidation resistance because the formed glassy phase is more stable and in wet air the formation of different crystalline phases were observed. An improvement of the oxidation behaviour of the B_6O-materials seems possible by tailoring the kind and content of the additives. The cBN-materials showed a higher oxidation resistance than the investigated B_6O-materials. The full understanding of the differences in the oxidation behaviour needs further investigation.

Acknowledgment

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