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Pressure infiltration of boron nitride preforms with molten aluminum

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Abstract

The infiltration of compacted cubic BN (cBN) with molten aluminum has been investigated as a potential route for a cheap and easy method of manufacturing cBN/metal composites. CBN compacts have been infiltrated with molten Al at a temperature between 670 and 800 °C and pressure of 15 MPa in vacuum. At these temperatures no pronounced interactions between hexagonal and cubic BN with Al was observed, allowing the complete infiltration of cBN with 12 μm mean grain size. After infiltration at 800 °C, the temperature was increased without pressure to convert aluminum into borides and AlN. The hardness of the resulting materials depends on the content of hexagonal, cubic BN and the rate of conversion of Al into borides and AlN. The infiltration height of less than 1 mm obtained from infiltrating the 3 μm cBN powder green compacts gave a hardness of 22.0 ± 0.6 GPa after heat treatment.

Keywords: A. Sintering; C. Hardness; E. Wear parts; Cubic boron nitride

1. Introduction

Sintering of cubic boron nitride (cBN) requires an ultra-high pressure and high temperature. The application of high pressure and high temperature facilitates mass transfer and hence bonding between phases in cBN-based composites. Composite structures prepared by mixing powders of boron nitride and metal aluminum followed by compressing into pellets and sintering at various high temperatures and high pressures (~5 GPa) have been reported (Rong and Fukunanga [1,2]). However, molten aluminum infiltration into a porous cubic boron nitride matrix has not been reported, but could be a possible way of production of cBN-composite materials. Infiltration requires that the pore structure be open and interconnected and that wetting does take place. The wetting angle in the Al-hBN system has been measured by Xue et al. [3] as a function of temperature (Fig. 1), showing that up to 950 °C the wetting angle is higher than 90 °C and only at higher temperatures wetting of cBN occurs by Al. There are no data available about wetting of cBN by Al but in a first approximation we assume that the wetting angles are similar. The infiltration of Al into BN will begin to take place spontaneously when the wetting angle becomes less than 90° at temperatures above 950 °C. However at higher temperatures the reaction between Al and cBN produces AlN and borides which makes infiltration more difficult. Thus there is a need to infiltrate at low temperatures before the onset of chemical reaction using an external pressure. The purpose of this work was to explore the possibility of infiltrating cBN with aluminum. Therefore infiltration experiments were done on preforms prepared from hBN and cBN-powders with different grain size.

2. Experimental procedure

The starting materials used were hexagonal Boron Nitride from H.C. Starck (average particle size 40 μm, lot no. 94253, 98.0%), cubic boron nitride from Element Six (Pty) Ltd. (average particle size 12, lot no. 1688326 and 3 μm, lot no. 1006406, 99.89% purity), high purity aluminum sheet from Goodfellow Metals (99.999% purity with thickness = 250 μm) and aluminum powder from Saarchem (99.9% purity with an

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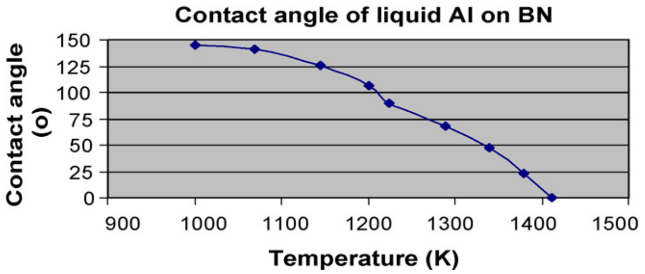

Fig. 1. The contact angle in the Al-hBN system (Rizzoli et al. [6]).

average particle size of 5 μm). The pure cBN powder was not possible to shape into preforms. Therefore two methods were used: partial hexagonalisation of the cBN powder and addition of 10 vol.% of Al powder. The preforms were produced by applying a pressure of 100 MPa. The pressed tablets had a diameter of 26 mm and a height of 3 mm.

For the preparation of partially hexagonalized cBN, small quantities of 12 mm cBN powder were heat treated under argon at 1350 °C for 720 min to convert 40% of the cBN to hBN and at 1300 °C for 2160 min to convert 10% of the cBN to hBN Rizzoli et al. [6]). The density of the preforms pressed from this powder was 64% of theoretical density (3.40 g/cm^3). A micronizing/turbular mixer was used to mix the cBN powder with 10 vol.% aluminum powder. Agate balls were used as mixing media for 1 h. For infiltration, a graphite die (with an outer diameter of 60 mm and inner diameter of 26 mm) and a 26 mm diameter punch were used. The Al discs were put in first, then the BN pellet followed by a tantalum washer, used to separate the cBN preform from the graphite punch and finally the graphite punch was placed on top. The loaded sample was then put into a cylindrical stainless steel chamber.

The tube furnace used during infiltration was a typical vertical tube furnace made by Thermopower Furnaces (TPF). This tube furnace allows the introduction of low uniaxial pressure (maximum 15 MPa for the die used) by applying a force from the top. The stainless steel chamber was used to contain the sample which was loaded inside the graphite die. This tube was then inserted inside the tube furnace and sealed at the top with a stainless steel lid. The furnace was evacuated to a pressure of 0.4 mbar and then flushed with argon gas. The chamber was evacuated again after 3 min and backfilled with argon before heating up to 300 °C at a rate of 5 °C/min in a furnace. At 300 °C the rotary pump was started again while heating to 800 °C at a rate of 5 °C/min and held at this temperature for 30–60 min. The furnace was then cooled at 10 °C/min to ambient conditions; however the cooling rate below 600 °C was slower than the programmed cooling rate. In the case of finer grains a hot press was also used to obtain an even higher pressure (up to 50 MPa). After infiltration, the samples were removed from the graphite die and were sectioned into eight pieces using a diamond saw. The sectioned pieces of a particular sample were then heat treated in a longitudinal Carbolite furnace at the following temperatures: 1100, 1200, 1250, 1300, 1400 and 1550 °C. The temperatures were normally kept for 60 min, except for one sample where the temperature was kept for 60 min at 1400 °C and for further 3 h at 700 °C. The purpose for this experiment was to enhance the formation of AlB_2 and to confirm that hBN phase does not form if it was not present in the initial stage. An extreme temperature of 1550 °C was used to investigate the conversion of cubic BN into the hexagonal polytype.

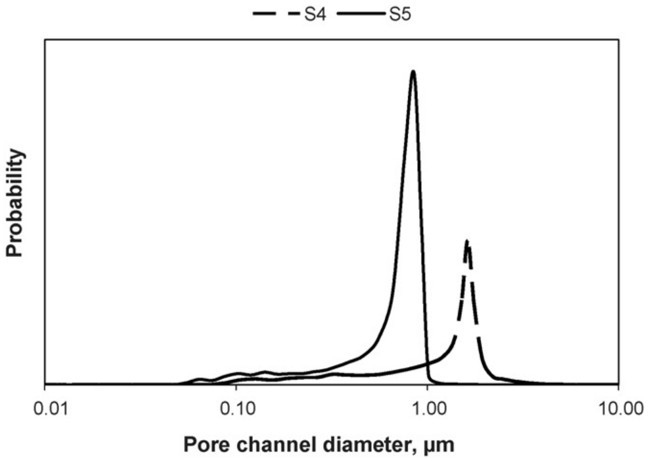

Fig. 2. Pore diameter distribution in green samples made of 3 μm (S5) and 12 μm cBN (S4).

Both reacted and unreacted composite samples were examined using a PW 1710 Philips powder diffractometer using Cu Kα radiation (2θ between 20° and 80° with a step size of 0.02° 2θ). The samples were also mounted, polished metallographically to 1 μm diamond finish and examined using scanning electron microscopy (SEM) and energy dispersive X-ray analysis. The results from the SEM and EDX analysis were used to identify free aluminum present and borides in the samples. The pore structures of the green samples were calculated using a PoreMaster-60 Quantachrome Instruments, Hg porosimeter (Fig. 2). The hardness was measured with a load of 10 kg.

3. Results

Infiltration of a hBN (average particle size 40 μm) tablet with Al was used as preliminary study. This was successfully achieved at 800 °C and 12 MPa. All infiltration results are summarized with some relevant properties in Table 1. The infiltration of preforms S2–S3 prepared from partially hexagonalized cBN powder with the initial mean grain size of 12 μm has been equally successful under the same conditions used for the hBN preforms. Sample S2 that initially contains 40 vol.% hBN and 60 vol.% cBN was found to be 98% of the theoretical density. The open porosity of the infiltrated sample has been measured to be 0.15%. Preforms prepared from cubic boron nitride powder (12 μm) pressed with 10 vol.% Al additions (S4) has also been fully infiltrated with Al (Table 1). The infiltration of the preforms prepared from the 3 μm cBN powder (S5) could be infiltrated up to a thickness of about 0.6 mm (Table 1). An increase of the applied pressure up to 50 MPa did not improve infiltration of the preform prepared from the fine grained cBN-powder.

Table 1
Infiltrated samples with some relevant properties

Sample name	Starting powder	Green density (g/cm^3)	Al infiltrant (%)	Density after infiltration (g/cm^3)	% of theoretical density	Phase content
S1	Hbn	1.85	19	2.19	98	Al, hBN
S2	40% hBN/60% cBN[a]	1.91	36	2.82	98	Al, hBN, cBN
S3	10% hBN/90% cBN[a]	1.87	40	2.69	97	Al, hBN, cBN
S4	10% Al/90% cBN[a]	1.97	42	2.83	97	Al, cBN
S5	10% Al/90% cBN[b]	–	40	–	–	Al, cBN

[a] Mean grain size 12 μm.
[b] Mean grain size 3 μm.

Table 2
Heat treatment results of the samples

Sample name	Annealing temperature (°C)	Density after heat treatment (g/cm^3)	Open porosity (%)	Phases present
S1	1300	2.17	0.34	AlN, hBN
S2	1200	2.83	0.11	Al, AlN, hBN, AlCu, cBN
S2-13	1300	2.85	0.14	AlN, hBN, AlCu, cBN
S2	1400	2.77	0.10	AlN, hBN, AlCu, cBN
S3	1300	2.72	1.2	AlN, hBN, cBN, Al
S4	1100	2.87	0.35	Al, AlN, cBN
S4	1200	2.90	0.24	Al, AlN, Al_2O_3, cBN
S4-13	1300	2.85	0.24	AlN, Al_2O_3, cBN
S4-15	1550	–	–	AlN, hBN, cBN
S4-14-7	1400 then 700 for 3 h	2.89	0.21	AlN, hBN, cBN, AlB_2
S5-13	1300	–	–	AlN, Al_2O_3, cBN

The results of the heat treatment at different temperatures of all samples are summarized in Table 2. The samples annealed at 1100–1200 °C contain still unreacted Al independently of the kind of the starting powder. The heat treatment at 1300 °C results in samples in which all Al reacts with BN. The SEM images in Figs. 3 and 4 show the microstructure of the samples prepared from hBN preforms and from cBN after infiltration and heat treatment. The images show that the samples are completely infiltrated. They reveal also the different microstructure formed from hBN and cBN preforms.

The XRD measurements of the samples S2 and S3 (which were prepared using different amounts of hBN in the starting material) reveal the presence of some hBN after infiltration and after heat treatment at different temperatures. It was observed (S2) that the intensities of the hBN peaks decrease from 1100 to 1200 °C. This is expected since hBN reacts with Al. However after heat treatment at 1300 °C, the intensity of the hBN peak is higher in comparison to the samples heat treated at 1200 °C and it was found to be even higher at 1400 °C. This may suggest that some of the cBN transforms to hBN at higher temperatures or the difference in the reaction rate of cBN and hBN is reduced.

There is no hBN present in sample S4 after heat treatment to a maximum of 1400 °C. However, the sample heat treated at 1550 °C for 60 min (S4-15) showed the presence of the hBN phase. This is expected since the cBN-hBN conversion normally takes place under these conditions.

The micrograph of the polished surface for the sample S4-14-7 (Fig. 4) reveal that the material has two major phases: the dark cBN phase and a white AlN/alumina boride binder phase. The white phase is composed mainly of aluminum nitride. However, the borides detected by XRD are also present in this phase. The EDX was used to identify the phases. Fig. 5 shows the Vickers hardness measured samples prepared using 12 μm cBN powder and with 3 μm cBN powder. The Vickers hardness measured on the S2-13 sample was found to be only about 6 GPa. The reason of the relatively low hardness is the hBN phase found in the sample and the weak bonding of the cBN samples. The hardness of the samples S4 heat treated at different temperatures result in increased hardness. The

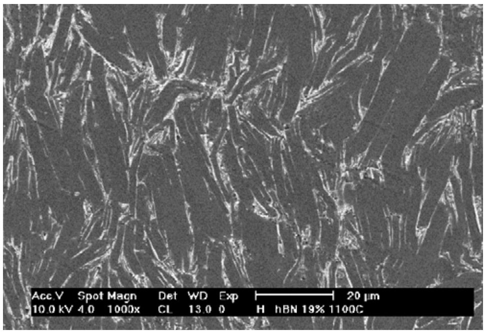

Fig. 3. SEM micrograph of the S1 sample after heat treatment at 1300 °C for 1 h.

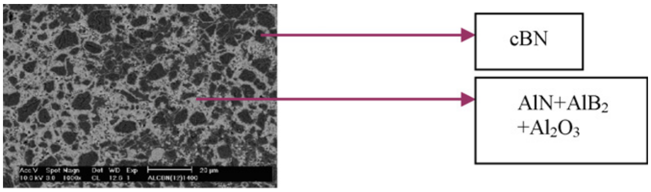

Fig. 4. SEM micrograph of the S4-14-7 sample.

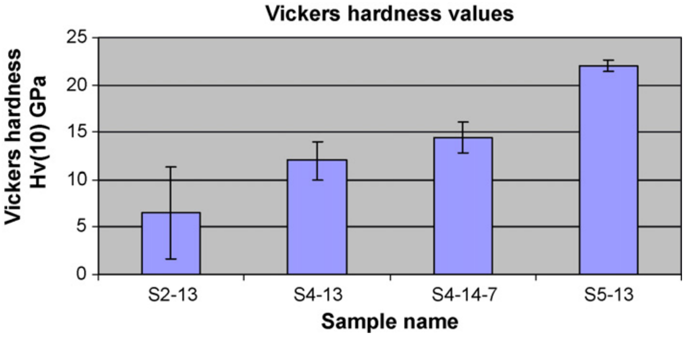

Fig. 5. The Vickers hardness measured on the Al infiltrated cBN samples. Sample S5-13 contains 3 μm cBN instead of 12 μm.

hardness is influenced by the heat treatment schedule. The Vickers hardness measured on the thin S5-13 sample found to be 22.0 ± 0.6 GPa. The higher hardness could be expected since a finer powder was used.

4. Discussion

The results showed that the hBN samples could be successfully infiltrated at a temperature of 800 °C and pressure of 12 MPa. The SEM microstructure of the sample shows that the Al phase is homogeneously distributed in the hBN matrix. The material is characterized by large platelet like hBN grains, which have a preferred orientation due to the pressing of the preform.

The infiltration of the preforms prepared from the 12 μm powder was equally successful under the same conditions used for the infiltration of hBN. This was independent on whether the preform was prepared by the partially hexagonalized cBN powder or from pure cBN with 10 vol.% Al binder. The pressure used during infiltration was much higher than predicted from the wetting angle data for hBN (Fig. 1). Using the Washburn equation (German [4]) and the measured pore channel diameter distribution (Fig. 2) the pressure necessary for infiltration of 90% of pores in that preform by molten Al would be 4.22 MPa. The preform prepared from the 3 μm cBN-powder exhibits a much lower mean pore channel diameter (Fig. 2). The pressure for infiltration of 90% of pores of that preform can be calculated to be 23.3 MPa. In this case the infiltration of the material would be expected to occur under the pressure of 50 MPa. Nevertheless only an infiltration height of 0.6 mm was obtained. The low infiltration could be connected to some surface reaction of the BN with Al reducing pore channel diameters; however such reactions were not observed by XRD. On the other hand, on the surface of the BN there exists some B_2O_3, which amount for the low grained material is larger than that of the coarse grained material. The oxide could strongly diminish the wetting and infiltration as was shown recently (Sithebe et al. [5]).

The lowest temperature at which Al reacted completely with BN after 1 h was found to be 1300 °C. The amount of AlN phase increases with increasing temperature, however nearly no increase was observed above 1300 °C confirming this conclusion.

Sample S2 was heat treated for 1 h at temperatures between 1000 and 1400 °C. During heat treatment at temperatures between 1000 and 1300 °C, the amount of hBN phase decreases due to its reaction with aluminum. However at a temperature of 1400 °C the content of hBN phase increases again. The results showed that differences in the reactivity of hBN and cBN with aluminum are small; therefore higher amount of hBN in the starting preform will not be consumed preferentially during the reaction with the aluminum. Therefore the use of metallic binder phases for shaping of preforms are more suitable than the use of the hBN-binder.

Sample S4 was prepared without any hBN in the starting powder. The Al reacted with cBN and no hBN was observed at temperatures up to 1400 °C. The reaction between Al and cBN produced AlN and AlB_{12} at temperatures higher than 1000 °C. The AlB_{12} phase could not be detected with the X-ray diffraction however AlB_2 which forms at lower temperatures decomposes at higher temperatures to form both Al and AlB_{12} (Rizzoli et al. [6]).

The hardness of the materials obtained in this work strongly depends in one hand on the remaining cBN content in the samples, and on the other hand on the amount of remaining hBN. Therefore all samples containing hBN (S1, S2 and S3) exhibit low hardness (Fig. 5). Also the hardness of the materials which do not contain hBN (S4) showed much lower hardness than commercially ultrahigh pressure produced cBN materials like AMB 90, made by Element Six (31 GPa). This is due to the low cBN content left after the reaction and the low hardness of the AlB_{12}, AlN binder phases. The amount of residual cBN is determined by the porosity of the preform. But even 60 vol.% cBN in the preform do not result in 60 vol.% cBN, due to the reaction of Al with cBN (1 vol.% Al reacts approximately with 0.5 vol.% cBN).

5. Conclusions

cBN preforms were fully infiltrated with molten aluminum when the cBN used had a grain size of 12 μm. The density of the samples was found to be greater or equal to 98% of the theoretical density. The infiltration was limited in extend for cBN grain sizes of 3 μm. This is probably due to the oxide content of the powder and due to reactions closing the pores. At infiltration temperature of 800 °C no reaction between cBN/hBN and Al was observed by XRD. At temperatures above or 1100 °C the reaction takes place. The conversion of Al into AlN and AlB_{12} can be done without transformation of cBN into hBN.

References

[1] X.Z. Rong, O. Fukunaga, Sintering of cubic boron nitride with added aluminum at high pressure and high temperatures, Trans. Mater. Res. Soc. Jpn. 14B (1994) 1455–1458.

[2] X.Z. Rong, T. Tsurumi, T. Yano, O. Fukunaga, High-pressure sintering of cBN-TiN-Al composite for cutting tool application, Diamond Related Mater. 11 (2002) 280–286.

[3] M. Xue, J.T. Wang, F.M. Zhao, Penetration and adhesion behaviour of boron nitride by liquid aluminum, J. Mater. Sci. Lett. 11 (1992) 199–201.

[4] R.H. German, Sintering Theory and Practice, John Wiley and Sons Inc., New York, 1996, pp. 568.

[5] H.S.L. Sithebe, D. McLachlan, I. Sigalas, M. Herrmann, Sintering cBN ceramics with Al binder, Advances in Science and Technology 45 (2006) 1364–1370.

[6] C. Rizzoli, P.S. Salamakha, O.L. Sologub, G. Bocelli, X-ray investigation of the Al-B-N ternary system: isothermal section at 1500 °C: crystal structure of the $Al_{0.185}B_6CN_{0.256}$ compound, J. Alloys Compd. 343 (2002) 135–141.