Journal of the European Ceramic Society **18** (1998) 1037–1043

PII: S0955-2219(98)00031-4
0955-2219/98/$19.00 + 0.00

Formation of Boron Nitride Thin Films on β-Si_3N_4 Whiskers and α-SiC Platelets by Dip-Coating

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(Received 17 March 1997; accepted 2 February 1998)

Abstract

Thin films of boron nitride have been deposited on the surface of β-Si_3N_4 *whiskers and* α-*SiC platelets by dip-coating in aqueous and methanolic boric acid solutions, respectively followed by drying at room temperature, heating in nitrogen flow, and finally nitriding in an ammonia flow at 1000°C. X-ray photoelectron spectroscopy (XPS), infrared (IR) spectroscopy and scanning electron microscopy (SEM) studies proved the formation of boron nitride surface coating. The XPS studies indicated that the methanolic boric acid solution was a more effective precursor as compared to the aqueous solution. Transformation of* H_3BO_3 *to BN was much more efficient on the surface of SiC platelets than on that of* Si_3N_4 *whiskers. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Silicon nitride based ceramic composites are potential materials for high temperature applications. However, they are brittle and have low fracture toughness which hinders their broad application. The concepts of whisker pull-out, bridging and crack deflection are very often applied to improve the toughness of ceramic matrix composites (CMC).[1–4] Depending on the nature of the whisker/platelet and matrix, strong whisker/matrix interaction can be expected.[5] This type of interaction could lead to strong bonding between matrix and whisker resulting in brittle CMCs. Extent of the chemico–physical interaction between the toughening element and the matrix is an important parameter in determining the microcracking of the matrix and the whisker/matrix debonding, and thereby the toughness of composites. Whisker/matrix interfacial properties can be weakened by using a whisker coating. The coating must withstand the processing of the composite, and it should be chemically stable. Boron nitride has unique chemical and physical properties such as low density, high melting point, chemical inertness, high thermal conductivity and very high hardness in a wide range of temperature (this is valid only for the cubic BN). Therefore, it is widely used, both as a bulk material and as thin films in electronic and ceramic applications.[6,7] Boron nitride coatings have been used in SiC fiber reinforced SiC,[8] Si_3N_4 whisker reinforced Si_3N_4[9] and in some other oxide matrix composites. Usually the BN coatings have been obtained by chemical vapor deposition (CVD) using either B_2H_6–NH_3 or BCl_3–NH_3.[7] Most commonly the BCl_3–NH_3 system is in use. In spite of the fact that CVD has some advantages over other coating processes, it is associated with several disadvantages, as well. A critical disadvantage is the formation of a large amount of NH_4Cl as byproduct during the deposition reaction which may block the reactor outlet. In addition, the precursors used in CVD processes are toxic, corrosive and expensive.

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In this paper an alternative method of BN deposition on the surface of Si_3N_4 whiskers and SiC platelets and characterization of these coatings is described. The particular method involves a dip-coating in boric acid solutions followed by nitridation in ammonia.

2 Experimental

2.1 Materials

Silicon nitride whiskers used in this study were supplied by Institute of Structural Macrokinetics, Chernogolovka, Russia. The aspect ratio of the whiskers is 4·7. Other characteristics of the whiskers were presented elsewhere.[10] Silicon carbide platelets were supplied by C-Axis Technology (AZ, USA) in three different grades: superfine (SF), fine (F) and medium (M). In this work the SF grade platelets were studied. The average size of the platelets is 11 μm, they have an aspect ratio of 8–10 and are crystalline. For further details of the platelets a previous paper[11] is referred. AR grade boric acid was supplied by Lachema, Brno.

2.2 Synthesis

Saturated solutions of boric acid at room temperature were prepared by dissolving 6·35 g of H_3BO_3 in water corresponding to concentration of 0·1 M or 20·20 g of H_3BO_3 in methanol corresponding to concentration of 0·33 M. To these solutions 3 g of silicon nitride whiskers or silicon carbide platelets were added. The mixture was gently stirred by a glass rod in order to disintegrate the agglomerates, if any. The suspensions were filtered on a Watchman 40 filter paper and then dried at room temperature for 5 h. The dried samples were placed in the rotating specimen cell and put into the CVD apparatus. The apparatus was evacuated to $1{\cdot}3\times10^{-1}$ Pa and the nitrogen flow was started. The temperature was raised at a rate of 20°C min^{-1} to 1000°C, while the nitrogen was replaced by an ammonia flow. The nitridation was carried out at a rotation speed of 20 rpm of the tube for different time dwells. A nitrogen flow was maintained during cooling to room temperature. The samples were then carefully removed from the reactor and stored in an evacuated desiccator for characterization.

2.3 Description of the apparatus

Scheme of the rotary CVD apparatus is presented in Fig. 1. The samples were loaded to the quartz specimen cell with an internal diameter of 20 mm. The specimen cell is placed in a quartz tube having an internal diameter 28 mm. The quartz tube is attached to a variable speed motor. Both ends of the tube are sealed. The tube itself is rotating in a vertical furnace of 80 cm length. A thermocouple is inserted in the glass tube from the gas inlet side to measure the temperature of specimen cell. The reactor is evacuated by a rotary pump attached at the gas outlet side. Ammonia gas was passed through two drying columns containing KOH and Na metal, respectively, before entering to the reactor through a mass flow meter.

2.4 Characterization

The surface morphology of original and coated whiskers/platelets was studied by scanning electron microscopy (SEM) in an equipment of Jeol JSM-35 type. Infrared (IR) spectroscopic investigation in a Perkin–Elmer 983 G spectrometer were aimed at finding the bonding character of boron and nitrogen. X-ray electron spectroscopic (XPS) studies were carried out by a Kratos XSAM 800 spectrometer operating in fixed analyzer transmission (FAT, pass energy 80 eV) and fixed retarding ratio (FRR, retarding ratio 20) modes using a Mg K_α (1253·6 eV) excitation.

3 Results

3.1 IR studies

IR spectra of pure and dip-coated Si_3N_4 whiskers are shown in Fig. 2. Pure BN has two characteristic bands: a strong band at 1373 cm^{-1} attributed to B–N stretching vibrations and a weaker band at 816 cm^{-1} attributed to B–N–B bending vibrations.[12,13] Strong absorption bands in the 1110–800 cm^{-1} region together with bands at 582 and 447 cm^{-1} reported for pure Si_3N_4[14] are present in the spectra of both dip-coated whiskers (Figs 2(b) and 3(c)). The positions and intensities of Si_3N_4 bands are almost the same, but the difference is observed near 1380 cm^{-1}, where BN absorption is expected. Only a slight inflection reflects very low content of BN for aqueous solution, while well-pronounced band at 1382 cm^{-1} indicate higher amount of BN bonds for methanolic solution and consequently formation of a thicker film as compared to aqueous case.

No substantial differences in the IR spectra of BN films formed on SiC platelets (not shown) indicate that this method is not sensitive enough to monitor the surface changes of Sic.

3.2 SEM studies

SEM micrographs of the original and dip-coated silicon nitride whiskers reveal that the original whisker has smooth surface which is free of any macro-defects (Fig. 3(a)). The surface of dip-coated whiskers subjected to nitridation is rougher, nevertheless there is no surface cracking or spalling (Figs 3(b) and (c)). Surface of the original silicon

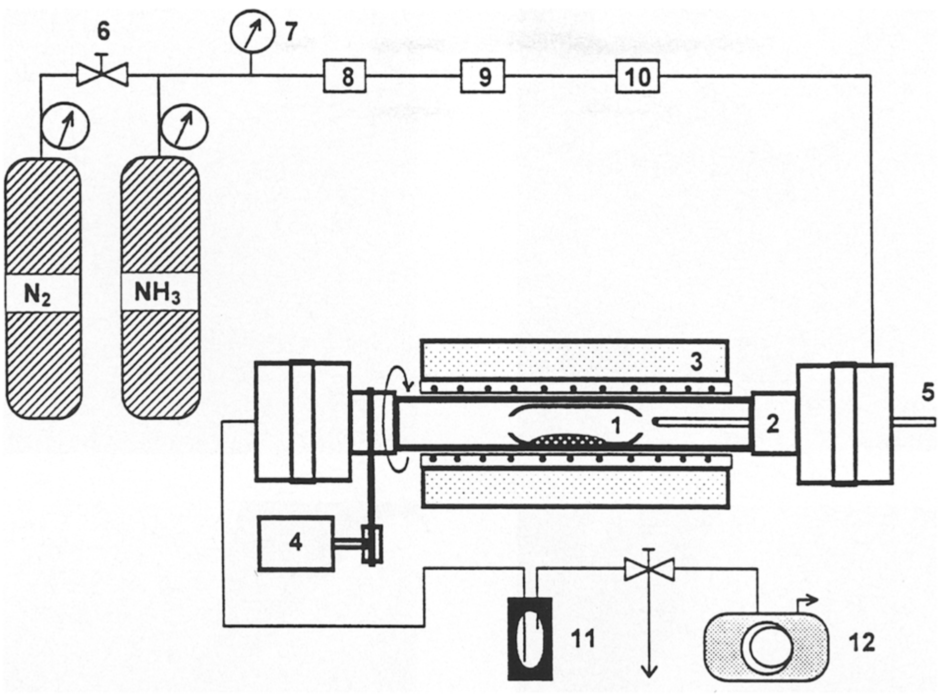

Fig. 1. Schematic diagram of rotary specimen bed CVD apparatus: 1. specimen cell; 2. rotary reactor; 3. resistance furnace; 4. motor driver; 5. thermocouple; 6. regulating valve; 7. manometer; 8. drying column (KOH); 9. drying column (Na); 10. mass flow meter; 11. trap; 12. rotary pump.

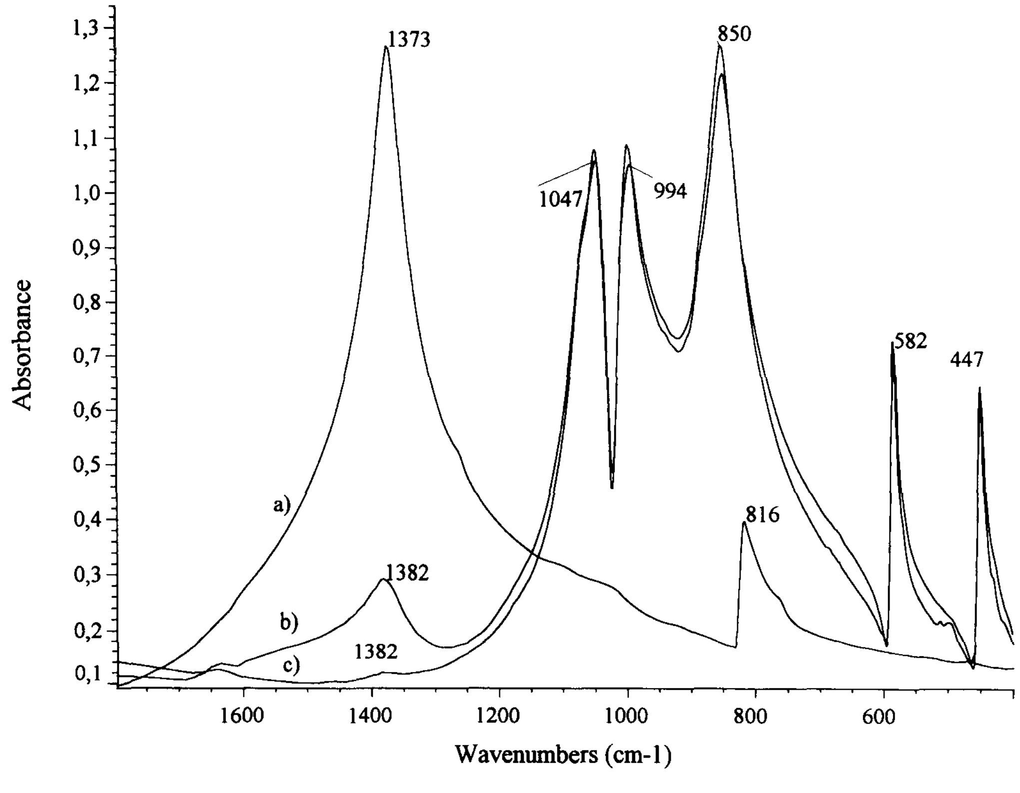

Fig. 2. IR spectra of (a) BN and (b) Si_3N_4 whiskers dip-coated in methanol (b) or (c) water boric acid solution and nitrided in ammonia.

carbide platelet is not smooth contrary to the whiskers. Small droplets can be observed throughout the surface (Fig. 4(a)). Coating in the aqueous boric acid solution followed by nitridation resulted in a rough surface coverage (Fig. 4(b)). Surface of platelets coated in methanolic boric acid solution contains a lot of droplets, most probably formed during the dip-coating itself.

3.3 XPS studies

The surface chemistry of silicon nitride whiskers and silicon carbide platelets were characterised both before and after coating by XPS. The XPS results are given in Tables 1–7. Surface chemical compositions and bonding characteristics of the different samples are discussed below.

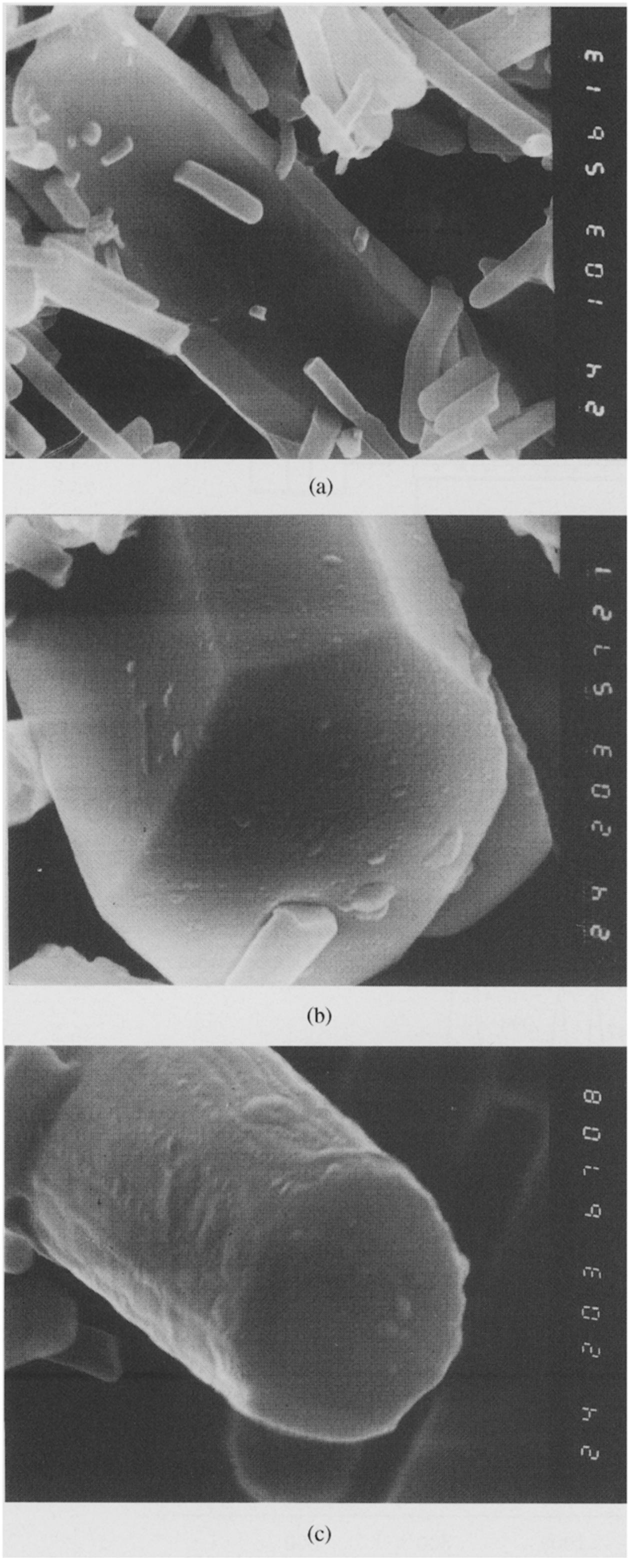
(a)
(b)
(c)

Fig. 3. Surface morphology of (a) the original, (b) dip-coated and (c) in ammonia nitrided Si_3N_4 whiskers.

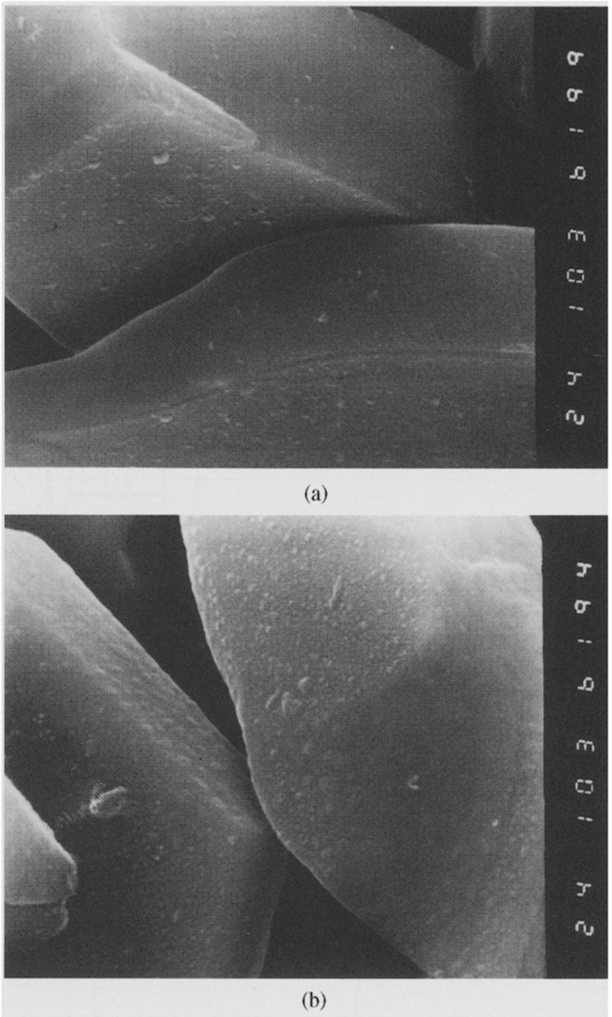
(a)
(b)

Fig. 4. Surface morphology of (a) the original and (b) dip-coated and nitrided SiC platelets.

Table 1. The data of XPS measurements for BN

Orbital	*Measured position (eV)*	*Raw area*	*Comp. (at%)*
O1s	532·8	729	1·1
O1s	531·4	267	0·4
N1s	398·1	24 236	41·1
N1s	399·0	1206	2·1
C1s	284·7	6108	13·6
C1s	287·0	386	0·9
C1s	283·2	230	0·5
B1s	190·4	10 696	38·0
B1s	191·7	647	2·3

3.3.1 Reference materials

3.3.1.1 BN. The sample is essentially with a small amount of surface oxygen and carbon contamination (Table 1). The chemical state of B corresponds to BN. Small amount of B is probably in the form of B–(O,N).

3.3.1.2 As received silicon nitride whiskers. There is a large oxygen content and a considerable carbon contamination (Table 2). The basic part of Si is in Si_3N_4 chemical state; part Si corresponds to sub-nitride (SiN_x, $x < 1{\cdot}3$) and silicon oxynitride. The Auger parameter ($\alpha = 101{\cdot}6 + 1612{\cdot}5 = 1714{\cdot}1$ eV) also indicates Si_3N_4 state.

3.3.1.3 As received silicon carbide platelets. The sample is partly oxidised with a relative large amount of carbon in excess (Table 3). The main components of Si and C corresponds to the SiC chemical state. Small amounts both Si and C are oxidised. The excess of C can be either in elemental or hydrocarbon form. The Auger parameter ($\alpha = 100{\cdot}0 + 1615{\cdot}1 = 1715{\cdot}1$ eV) indicates SiC state.

Table 2. The data of XPS measurements for β-Si_3N_4 whiskers

Orbital	*Measured position (eV)*	*Raw area*	*Comp. (at%)*
Si2p1	101·6	9988	20·8
Si2p	100·3	1725	3·6
Si2p	103·1	2037	4·3
Si2p	284·6	4764	15·2
C1s	286·4	593	1·9
C1s	283·3	538	1·7
C1s	288·7	258	0·8
O1s	532·3	9410	20·4
O1s	530·7	1058	2·3
O1s	533·4	562	1·2
N1s	397·4	10 110	24·5
N1s	398·9	574	1·4
N1s	396·0	788	1·9

Table 3. The data of XPS measurements for α-SiC platelets

Orbital	*Measure position (eV)*	*Raw area*	*Comp. (at%)*
O1s	532·2	4632	13·5
C1s	282·3	5811	24·8
C1s	284·7	6273	26·9
C1s	285·8	783	3·4
C1s	288·4	275	1·2
Si2p	100·0	9482	26·5
Si2p	101·6	1349	3·8

Table 4. The data of XPS measurements for BN–H_2O–β-Si_3N_4

Orbital	*Measured position (eV)*	*Raw area*	*Comp. (at %)*
Si2p1	101·6	6148	12·8
Si2p	102·6	3083	6·5
Si2p	103·7	1254	2·6
Si2p	100·3	494	1·0
C1s	284·7	3892	12·4
C1s	286·2	575	1·8
C1s	283·2	407	1·3
O1s	532·5	8406	18·3
O1s	530·9	836	1·8
O1s	533·8	1177	2·6
N1s	398·0	10 302	25·0
N1s	399·6	384	0·9
N1s	396·6	1266	3·1
B1s	190·3	1284	6·5
B1s	191·6	455	2·3
B1s	193·2	177	0·9

Table 5. The data of XPS measurements for BN–MeOH–β-Si_3N_4

Orbital	*Measured position (eV)*	*Raw area*	*Comp. (at%)*
Si2p	99·7	150	0·4
Si2p	101·4	816	2·0
Si2p	102·5	1010	2·5
Si2p	103·9	282	0·7
C1s	283·0	624	2·3
C1s	284·7	3794	14·1
C1s	286·1	882	3·3
O1s	532·5	2753	7·0
O1s	530·9	701	1·8
O1s	533·9	754	1·9
N1s	398·1	11 234	31·9
N1s	399·4	535	1·5
N1s	396·4	1061	3·0
B1s	190·4	4174	24·8
B1s	191·7	466	2·8

Table 6. The data of XPS measurements for BN–H_2O–SiC platelets

Orbital	*Measured position (eV)*	*Raw area*	*Comp. (at%)*
Si2p	99·8	3427	8·0
Si2p	100·8	1556	3·6
Si2p	102·2	1266	3·0
Si2p	98·5	179	0·4
C1s	282·3	2969	10·6
C1s	284·7	4972	17·8
C1s	286·1	664	2·4
O1s	532·4	3943	9·6
O1s	531·1	741	1·8
O1s	533·7	524	1·3
N1s	398·0	7853	21·4
N1s	399·7	352	1·0
B1s	190·5	2855	16·3
B1s	192·1	451	2·6
B1s	193·1	56	0·3

Table 7. The data of XPS measurements for BN–MeOH–SiC platelets

Orbital	*Measured position (eV)*	*Raw area*	*Comp. (at%)*
Si2p	99·5	256	0·6
Si2p	101·2	354	0·8
Si2p	102·6	630	1·4
Si2p	103·9	155	0·4
C1s	282·6	403	1·4
C1s	284·6	3945	13·7
C1s	286·0	446	1·6
O1s	532·5	3439	8·1
O1s	531·1	831	2·0
O1s	533·9	468	1·1
N1s	398·1	11 932	31·5
N1s	399·7	442	1·2
N1s	396·6	959	2·5
B1s	190·4	5053	28·0
B1s	191·6	1047	5·8

3.3.2 Dip-coated samples

3.3.2.1 Silicon nitride whiskers dip-coated in aqueous boric acid solution and nitrided. The B1s peak of the particular XPS spectrum could be deconvoluted to three components. Major part of boron is present as BN, Table 4 and Fig. 5. There is much less B–(N, 0) and even less B_2O_3. The surface silicon is mainly coupled to Si_3N_4 ($\alpha = 1714{\cdot}2$ eV). SiO_2 and lower valance $Si(N,C)_x$ states were also detected. The surface oxygen concentration is relatively high which refers to a remarkable surface oxidation, and probably hydrolysis as well. The carbon contamination is not higher than usual. The surface B/Si ratio is 0·38. The Si as an reference element was chosen because its amounts can be consider as constant for all measured β-Si_3N_4 whiskers samples.

3.3.2.2 Silicon nitride whiskers dip-coated in methanolic boric acid solution and nitrided. The dominant B-containing surface species is BN, Table 5 and Fig. 6. However, a small amount of B-(N,O) can also be observed. The silicon is mainly in Si–(O,N) bond. There is less surface Si_3N_4. Some

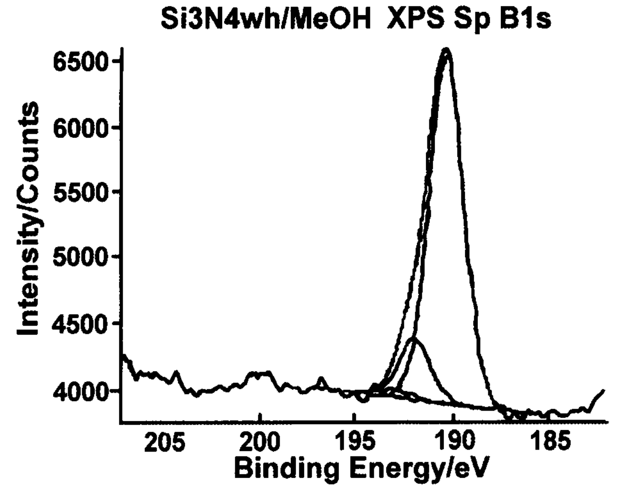

Fig. 5. Decomposition of the B1s peak of the XPS spectrum of BN coated Si_3N_4 whiskers by dip-coating in aqueous boric acid solution and nitrided.

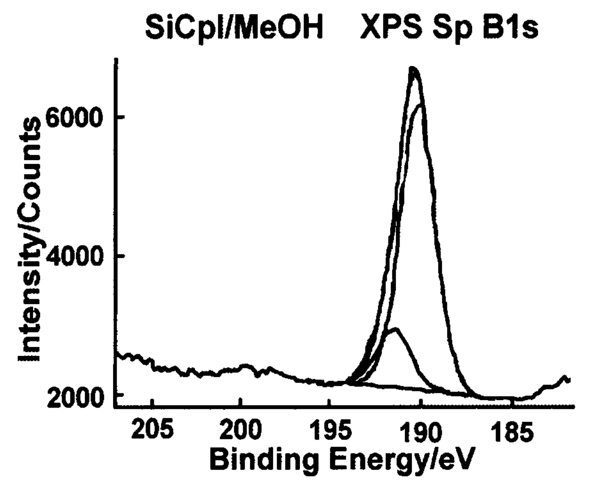

Fig. 7. Decomposition of the B1s peak of the XPS spectrum of BN coated SiC platelets by dip-coating in aqueous boric acid solution and nitrided.

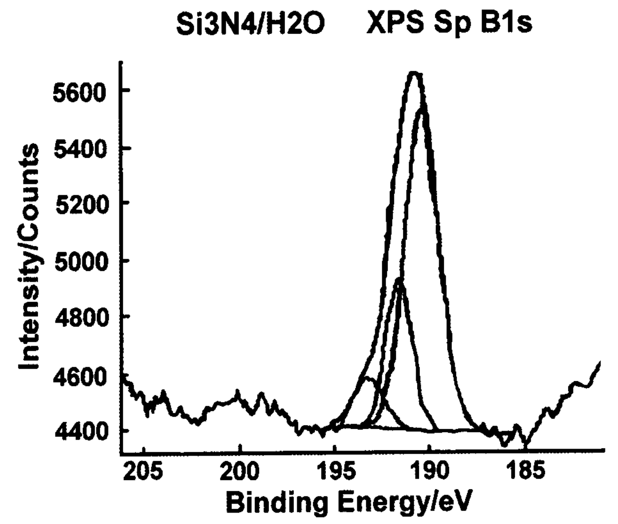

Fig. 6. Decomposition of the B1s peak of the XPS spectrum of BN coated Si_3N_4 whiskers by dip-coating in methanolic boric acid solution and nitrided.

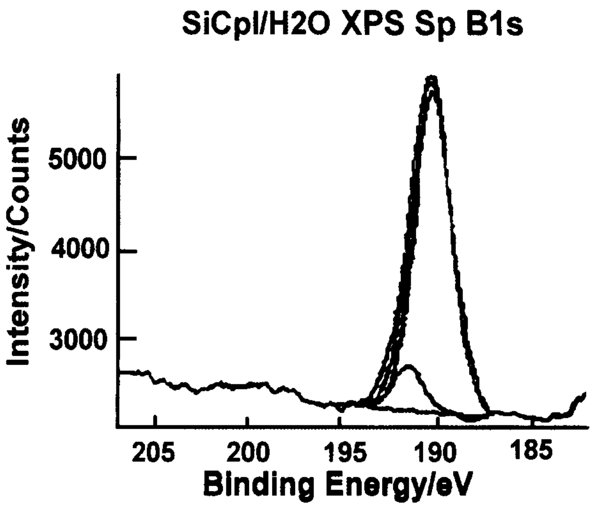

Fig. 8. Decomposition of the B1s peak of the XPS spectrum of BN coated SiC platelets by dip-coating in methanolic boric acid solution and nitrided.

SiO_2 and Si of lower valence state were also detected. The surface of this sample is less oxidised than that of sample dip-coated in the aqueous solution. However, the surface carbon contamination is pretty similar in the two cases. The B/Si ratio is 5·0 in the particular sample which indicates a thicker coating in the methanol case as compared to the aqueous case.

3.3.2.3 Silicon carbide platelets dip-coated in aqueous boric acid solution and nitrided. The surface boron is mainly connected to BN, Table 6 and Fig. 7. The majority of silicon is in SiC ($\alpha = 1714{\cdot}9$ eV). A smaller portion of it may be present as Si–(C, N), Si–(O, N) or as elemental silicon. There is some carbide-type carbon (282·3 eV) which can be clearly distinguished from the CH_x-type or from the elemental carbon. The surface of this sample is less oxidised than that of the corresponding silicon nitride. There is a surface B/Si ratio of 1·3 which is higher than that of Si_3N_4 coated in similar conditions. The Si as an reference element was chosen because its amounts can be consider as constant for all measured SiC platelets samples.

3.3.2.4 Silicon carbide platelets dip-coated in methanolic boric acid solution. The majority of surface boron is in the BN state (Table 7 and Fig. 8). The silicon is mostly Si–(O, N)-type. Less than one third of surface silicon is connected to SiC ($\alpha = 1715{\cdot}0$ eV). There are small amounts of surface Si–(C, N) and SiO_2 species. Surface of particular samples is less contaminated by oxygen as compared to SiC dip-coated in aqueous boric acid solution. The carbide-type carbon (282·6 eV) was detected in a small amount only. The surface B/Si ratio is equal to 10·7. If the ratio of B/Si is consider as an measure of the weight fraction of BN surface layer either on β-Si_3N_4 whiskers or SiC platelets, the methanolic-boric acid solution proved to be a much more effective precursor than the aqueous boric acid solution in terms of BN film deposition.

4 Discussion

The IR, SEM and XPS studies revealed that dip-coating followed by nitridation resulted in the formation of BN films on the surface of silicon nitride whiskers and silicon carbide platelets. This coating technique is very simple. Formation of boron nitride could be described by the following equations.

$$2\,H_3BO_3 \rightarrow B_2O_3 + 3\,H_2O \qquad (1)$$

$$B_2O_3 + 2\,NH_3 \rightarrow 2\,BN + 3\,H_2O \qquad (2)$$

Boric acid is transformed to borate at 237°C. Increase of the temperature to 1000°C leads to the formation of a vitreous borate layer on the surface of silicon nitride whiskers and silicon carbide platelets. This surface layer can be slowly nitrided. Most probably nitridation starts on the uppermost surface and then it proceeds to the interior of the vitreous layer. Hence, it is recommended to ensure a nitridation time of at least 45 min.

XPS results indicate the presence of residual elemental carbon on the surface of original SiC platelets. This free carbon probably changes the chemistry of nitridation. Instead of reaction (2) as above, a faster reaction i.e. carbothermal nitridation takes place:

$$B_2O_3 + 3C + 2NH_3 \rightarrow 2BN + 3CO + 3H_2 \qquad (3)$$

Si–N species were detected on the surface of BN-coated SiC platelets by XPS. It refers to a partial surface nitridation during the heat treatment in ammonia. A similar phenomenon was observed in the dip-coating of silicon carbide fibers by boron nitride previously.[15] The amount of deposited BN and thus thickness of the BN film can be probably changed by the concentration of the boric acid solution: the B/Si ratio increased in the case of saturated methanolic solution as compared to more diluted ones.

5 Conclusion

Formation of BN films on the surface of thoughening elements by dip-coating in boric acid solutions followed by nitridation is a much simpler technique than the usual CVD process. Coating prepared in this way do not substantially changes the surface roughness of whisker/platelet and does not cause spalling or cracking of surface BN thin layer. The ratio B/Si and thus thickness of the coating can be adjusted by the concentration of boric acid solution. The XPS studies confirmed that the surface of SiC platelets may be partially nitrided in the given conditions. The methanolic-boric acid solution proved to be a more effective precursor than the aqueous boric acid solution in terms of BN film deposition.

Acknowledgements

This work was partly financed by Slovak Grant Agency under the contract nos 2 1169 96 and 2 1130 96.

References

1. Fabers, K. T. and Evans, A. G., Crack deflection processes–I. Theory. *Acta. Metall.*, 1983, **31**(4), 565–576.
2. Fabers, K. T. and Evans, A. G., Crack deflection processes–II. Experiment. *Acta. Metall.*, 1983, **31**(4), 577–584.
3. Dusza, J. and Šajgalik, P., Fracture toughness and strength testing of ceramic composities. In *Hand Book of Advanced Material Testing*, ed. N. P. Cheremisinoff and P. N. Cheremisinoff. Marcel Dekker, New York, 1995, pp. 399–436.
4. Rice, R. W., Mechanisms of toughening in ceramic matrix composites. *Ceram. Eng. Sci. Proc.*, 1981, **2**(7–8), 661–701.
5. Luthra, K. L., Chemical interactions in high temperature ceramic composites. *J. Am. Ceram. Soc.*, 1988, **71**(12), 1114–20.
6. Arya, S. P. S. and D'Amico, A., Preparation properties and application of boron nitride thin films. *Thin Solid Films*, 1988, **157**, 267–282.
7. Paine, R. T. and Narula, C. K., Synthetic routes to boron nitride. *Chem. Rev.*, 1990, **90**, 73–91.
8. Dugne, O., Prouhet, S., Guette, A., Naslain, R. and Sevely, J., Interface characterization by transmission electron microscopy and auger electron spectroscopy in tough SiC fiber (nicalon)-SiC matrix composite with a boron nitride interphase. Dev. Sci. Technol. Compos. Mater., in Proc. 3rd Eur. Conf. Compos. Mater., Bordeaux, March, 1989, pp. 129–135.
9. Neergaard, L. J. and Homeny, J., Mechanical properties of beta-silicon nitride whisker/silicon nitride matrix composites. *Ceram. Eng. Sci. Proc.*, 1989, **10**(9–10), 1049–1062.
10. Dusza, J., Šajgalik, P., Bastl, Z., Kavečanský, V. and Ďurišin, J., Properties of β-silicon nitride whiskers. *J. Mater. Sci. Lett.*, 1982, **11**, 208–211.
11. Brail, D, Tremblay, S. P. and Fiset, M., Silicon carbide platelet-reinforced silicon nitride composites. *J. Mater. Sci.*, 1993, **28**, 5486–5494.
12. Sugiyama, K. and Itoh, H., *Chemical Vapor Deposition of Turbostratic and Hexagonal Boron Nitride*. Materials Science Forum Vols 54 and 55 Trans Tech, Switzerland, 1990, pp. 141-152.
13. Cholet, V., Vandenbulcke, L., Rouan, J. P., Baillif, P. and Erre, R., Characterization of boron nitride films deposited from BCl_3–NH_3–H_2 mixtures in chemical vapour infiltration conditions. *J. Mater. Sci*, 1994, **29**, 1417–1435.
14. Nyquist, R. A. and Kagel, R. O., *Infrared Spectra of Inorganic Compounds*. Academic Press, London, 1971.
15. Shen, L., Tan, B. J., Willis, W. S., Galasso, F. S. and Suib, L. S., Characterization of dip-coated boron nitride on silicon carbide fibers. *J. Am. Ceram. Soc.*, 1994, **77**, 1011–1016.