JOURNAL OF MATERIALS SCIENCE **39** (2004) 6263 – 6269

# Studies on the formation of whiskers and platelets of $B_4C$ and BN

R. V. KRISHNARAO, J. SUBRAHMANYAM
*Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad-500058, India*
*E-mail: rvkr4534@yahoo.com*

The formation of whiskers and platelets of $B_4C$ and BN has been studied through carbothermal reduction of $B_2O_3$. In the absence of any additive, neither whiskers nor platelets have formed from $B_2O_3$ and carbon black. $K_2CO_3$ which forms a low melting liquid and $NiCl_2$ which act as catalyst in gasification of carbon were used to facilitate the growth of whiskers and platelets. $NiCl_2$, $K_2CO_3$, carbon black and $B_2O_3$ were reacted in a weight ratio ($NiCl_2$:$K_2CO_3$:C:$B_2O_3$ = 5:5:12:17.4) and studied the formation of $B_4C$ and BN in the temperature range of 940°C to 1500°C in 1-atm. argon and 1-atm. nitrogen respectively. Whiskers and platelets of different sizes have formed at 1100–1500°C. The whiskers have been observed to form by vapor-liquid-solid growth mechanism. The effect of $NiCl_2$ and $K_2CO_3$ on the morphology of $B_4C$ and carbon has been studied. $NiCl_2$ and $K_2CO_3$ have been found to accelerate the growth of whiskers and platelets.


## 1. Introduction

Whiskers are used to reinforce metallic, ceramic, and polymeric materials. Though ceramic whiskers have been synthesized with a variety of chemistries, including SiC, AlN, TiC, TiN, $Si_3N_4$, $B_4C$, and $Al_2O_3$, the most developed and commercial whiskers are those based on SiC [1]. $Al_2O_3$ reinforced with 25–30 wt% SiC whiskers is the material of choice for inserts used in high-speed cutting of high-nickel-content alloys. Cutting speeds of up to 450 m/min with reasonable life times could be achieved [2]. The superior behavior of the $Al_2O_3$-SiC composite is not observed when machining steels. Recently attempts were made to develop other whisker materials that are more chemically stable than SiC and suitable for cutting stainless steel [3]. Whisker materials with different thermal expansion coefficients are required to reinforce different metallic materials.

The development of new whisker materials has focussed mainly on carbides, nitrides and carbonitrides of transition metals such as Ti, Ta, and Nb [4–7]. There are few reports [8–13] on formation of TiC and TiN whiskers. Nygren *et al.* [8] used $TiO_2$, carbon, and MCl ($M$ = Li, Na, or K) as raw materials, and Ni as a catalyst. TiN whiskers were formed in nitrogen, whereas argon is used for TiC whiskers. Recently, Krishnarao *et al.* reported a process involving vapor-liquid-solid (VLS) growth mechanism for the formation of TiC [12] and TiN [13] whiskers. However, not much attention has been paid to produce boride whiskers particularly $TiB_2$ and $B_4C$ whiskers. $TiB_2$ and $B_4C$ are very useful refractory compounds with outstanding hardness, excellent wear resistance and high strength. $B_4C$ is a light-weight (2.52 g cm$^{-3}$), and very hard (microhardness 2840 Kg mm$^{-2}$) high temperature refractory material with a melting point 2447°C. It exhibits high flexural strength (380 MPa) and Young's modulus (574 GPa). It possesses a moderate co-efficient of thermal expansion $5.73 \times 10^{-6}$ K$^{-1}$.

$B_4C$ is known to retain its hardness up to a temperature of 1300°C in a reducing atmosphere [14]. It is highly resistant to erosion and abrasion [15]. Typical applications of $B_4C$ are light-weight armor, high-temperature thermoelectric conversion elements, sliding bearings, seal rings, and wear parts such as nozzles. Chapmam *et al.* [16] developed aluminium boron carbide cermet brake pads for automotive brake applications. In contrast to asbestos or semimetallic brake materials, Al-B-C has very high strength, stiffness, hardness and thermal conductivity.

There are few reports [17–19] on the growth of $B_4C$ whiskers and filaments. Zhang *et al.* [20] reported a process for the growth of $B_4C$ nanowires and arrays of nanoparticles by plasma-enhanced chemical vapour deposition. Recently Carlsson *et al.* [21, 22] reported a carbothermal reduction process for synthesis of $TiB_2$ and $B_4C$ whiskers. They [22] used $B_2O_3$, and carbon as basic raw materials. Metallic powders of Co/Fe/Ni were used to form liquid catalyst to grow $B_4C$ whiskers by VLS mechanism. NaCl was used to supply Co and B as $CoCl_3$(g) and BOCl(g) to catalyst liquid droplet. More recently, Krishnarao *et al.* [12, 13, 23] reported a process involving vapor-liquid-solid (VLS) growth mechanism for the formation of TiC, TiN and $TiB_2$ whiskers. Similarly in the present work, $K_2CO_3$ which forms a low melting liquid, $NiCl_2$ which is well known

TABLE I Purity of reactants used for synthesis of $B_4C$ and BN

| Chemical | Manufacture | Impurity level | |
|---|---|---|---|
| $K_2CO_3$ | Johnson Matthey, U.K., England | Sr | 3 ppm |
| | | Mg, Na | 1 ppm |
| | | Ca, Fe, Li | <1 ppm |
| $NiCl_2$ | Qualigens Fine Chemicals, Ltd., Mumbai, India | $SO_4$ | 0.005% |
| | | Co | 0.002% |
| | | Fe | 0.002% |
| $H_3BO_3$ | Qualigens Fine Chemicals, Ltd., Mumbai, India | $SO_4$ | 0.04% |
| | | Cl | 0.01% |
| | | Pb | 0.002% |
| | | As | 0.0001% |
| C. Black | Philips Carbon Black Grade N220, ISAF-HM Durgapur, India | | |

as a catalyst in carbon gasification, were used to aid the formation of $B_4C$ and BN whiskers. Where as $B_2O_3$, and carbon black were used as precursor raw materials for the synthesis of $B_4C$ and BN.

## 2. Experimental procedure

### 2.1. Materials

Laboratory reagent grade $NiCl_2$ was supplied by Qualigens Fine Chemicals, Bombay-400075, India. Specpure $K_2CO_3$ was procured from Johnson Matthey Chemicals Limited, Hertfordshire, England. Carbon black of grade N774 was obtained from Philips Carbon Black Ltd., Durgapur, India. $B_2O_3$ was prepared from SQ grade boric acid obtained from Qualigens Fine Chemicals, Mumbai, India.The level of impurities in above chemicals is given in Table I.

### 2.2. Experimental

Initially, 12 g of carbon black and 17.4 g of $B_2O_3$ were taken in a plastic container and dry mixing using agate balls was done for 5 h. This mixture was designated as CB. No whisker formation was noticed in the CB samples reacted in argon at

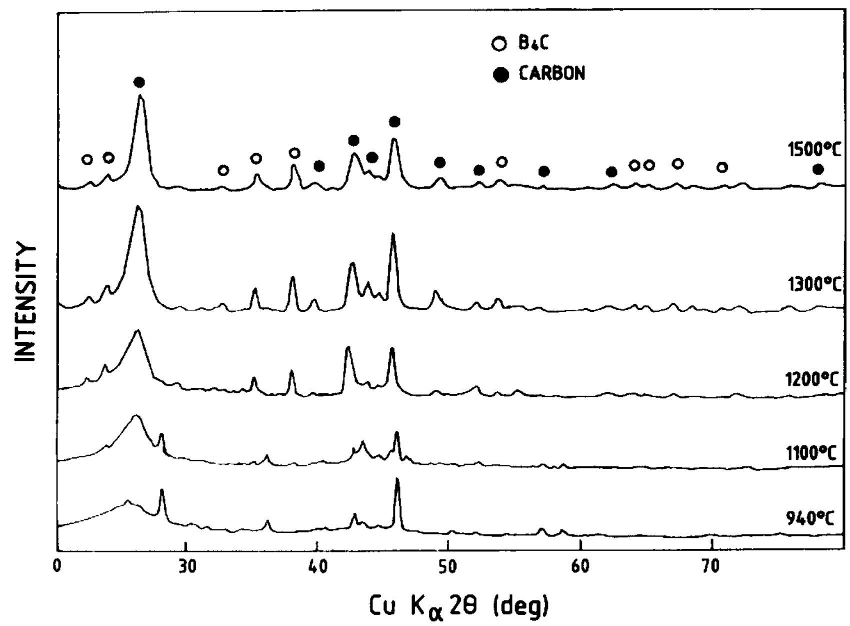


*Figure 1* XRD patterns of NKCB after reaction in argon at different temperatures.

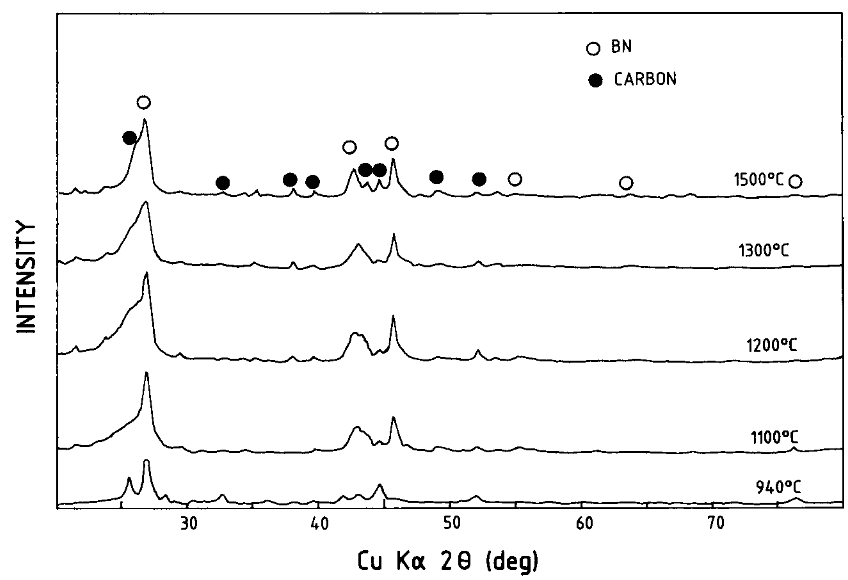


*Figure 2* XRD patterns of NKCB after reaction in nitrogen at different temperatures.

different temperatures. In the next mixture $K_2CO_3$ and $NiCl_2$ were added to aid the formation of whiskers. $NiCl_2$, $K_2CO_3$, carbon black and $B_2O_3$ were taken in weight ratio ($NiCl_2$:$K_2CO_3$:C:$B_2O_3$ = 5:5:12:17.4). Its equivalent molar ratio is ($NiCl_2$:$K_2CO_3$:C:$B_2O_3$ = 0.15:0.144:4:1). Initially 5 g of $K_2CO_3$ and 17.4 g of $B_2O_3$ were taken in an agate container and mixing using agate balls was carried out for 5 h. 5 g of $NiCl_2$ and 12 g carbon black were added and mixing was continued for another 5 h. This powder mixture was designated as NKCB. After reviewing the results three more mixes were prepared to study the effect of potassium and nickel on the morphology of carbon and boron. $NiCl_2$, $K_2CO_3$, carbon black and $B_2O_3$ were taken in weight ratio similar to that of NKCB. These three-component mixes are designated as NKC, KCB, and NCB.

Cylindrical graphite holder of 2.5-mm wall thickness and 40-mm inner diameter was filled with the powder mixture. The holder was closed with a graphite lid having a small hole allowing exchange of gasses between reactants and furnace chamber. The graphite reactor (sample holder) was placed in the hot zone of high-temperature graphite resistance furnace (ASTRO, U.S.A., Model 1000-3060-FP20). The furnace was evacuated to a moderate vacuum ($5 \times 10^{-2}$ torr) and back filled with 1 atm. argon or 1 atm. nitrogen. Experiments were conducted at 940, 1100, 1200, 1300 and 1500°C for 40 min. Temperature was maintained with a Model 939A3 Honeywell radiation pyrometer.

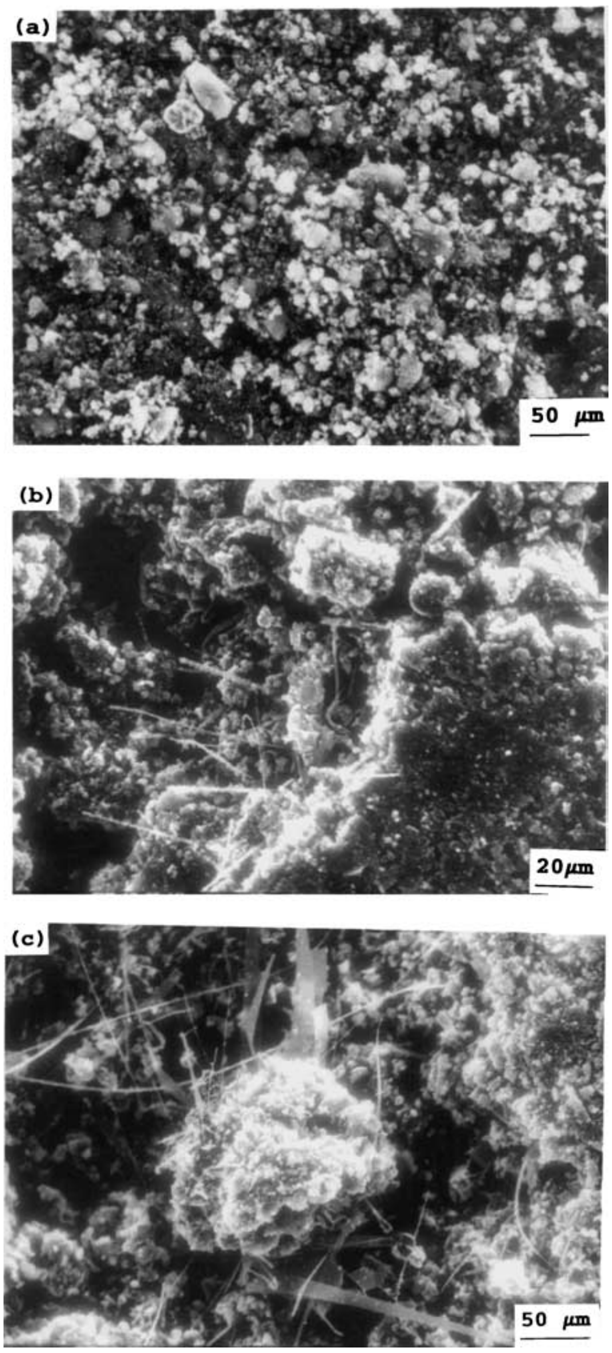


*Figure 3* SEM photographs showing the morphology of: (a) CB reacted in argon at 1500°C, (b) and (c) NKCB reacted in argon at 1100 and 1200°C respectively.

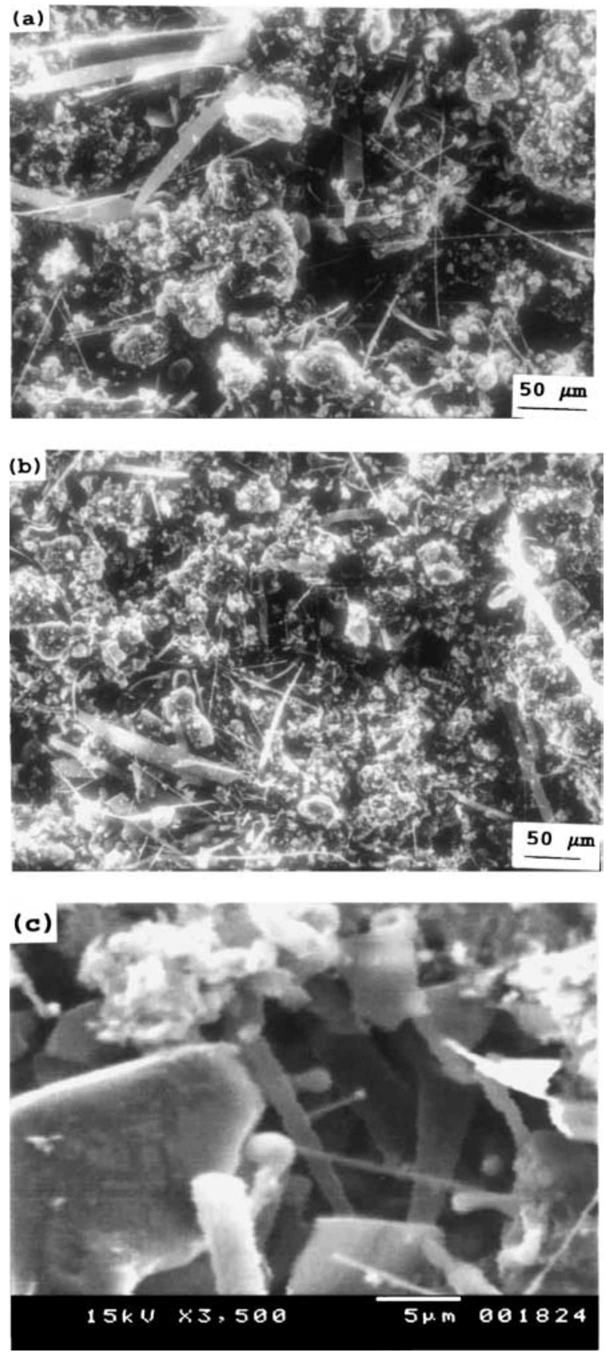


*Figure 4* SEM photographs showing the morphology of NKCB reacted in argon at: (a) 1300°C, (b) 1500°C and (c) vapor-liquid-solid grown whisker formed at 1300°C.

Heating rate employed was ≈40°C min$^{-1}$. The samples of NKC, KCB, and NCB were reacted at 1300°C in argon.

Reacted samples were analysed by X-ray diffraction (XRD). A Philips X-ray diffractometer, Model PW3710, with Cu $K_\alpha$ radiation through Ni filter was used. The morphology of the reacted powders was examined with a Leo 440i, scanning electron microscope (SEM). Scanning electron probe microanalysis (SEPMA) was carried out with CAMECA (model CAMEBAX-MICRO, France) equipment.

## 3. Results and discussion

After reaction at 940°C in argon/nitrogen samples appeared like unreacted dried powders. After reaction at 1200°C and above 1200°C, they formed fluffy sponge like cake. All samples except CB samples contained glittering particles. Peaks corresponding to $B_4C$ were observed in all samples of CB and NKCB after reaction at different temperatures in argon (Fig. 1). Peaks of strong intensity corresponding to graphitic carbon were also observed. The intensities of $B_4C$ peaks increased with increase in reaction temperature. However, the intensities of $B_4C$ peaks of CB samples were lower than that of NKCB samples. In the XRD patterns of NKCB samples reacted in nitrogen, peaks corresponding to BN were observed (Fig. 2). In BN samples peaks of strong intensity corresponding to graphitic carbon were also observed. The intensities of BN peaks increased with increase in reaction temperature from 1100 to 1500°C.

The morphology of samples after reaction in Ar at different temperatures is shown in SEM photomicrographs (Fig. 3). Neither whiskers nor platelets were observed in the CB samples reacted at different temperatures. The typical morphology of particulates of $B_4C$ formed in CB sample is shown in Fig. 3a. After reaction at 940°C, the NKCB sample appeared like unreacted mass. Whisker formation was observed in the NKCB sample reacted at 1100°C. Typical vapour-liquid-solid (VLS) whiskers formed at 1100 and 1200°C are shown in Fig. 3b and c. At higher reaction temperature (1300 and 1500°C) thick and long platelets were formed (Fig. 4a and b). The formation of whiskers and platelets increased with increase in reaction temperature from 1100 to 1500°C.

The presence of potassium and nickel in the spherical tip (Fig. 4c) of whisker was identified through energy dispersive X-ray analysis (EDAX). Since the detection of boron through EDAX was difficult electron probe micro-analysis (EPMA) was used. The typical $B_4C$ platelet formed at 1300°C is shown in BSE image in Fig. 5a. EPMA analysis of the platelet revealed the presence of boron and carbon. Nickel was observed in bright spherical particles only (Fig. 5d).

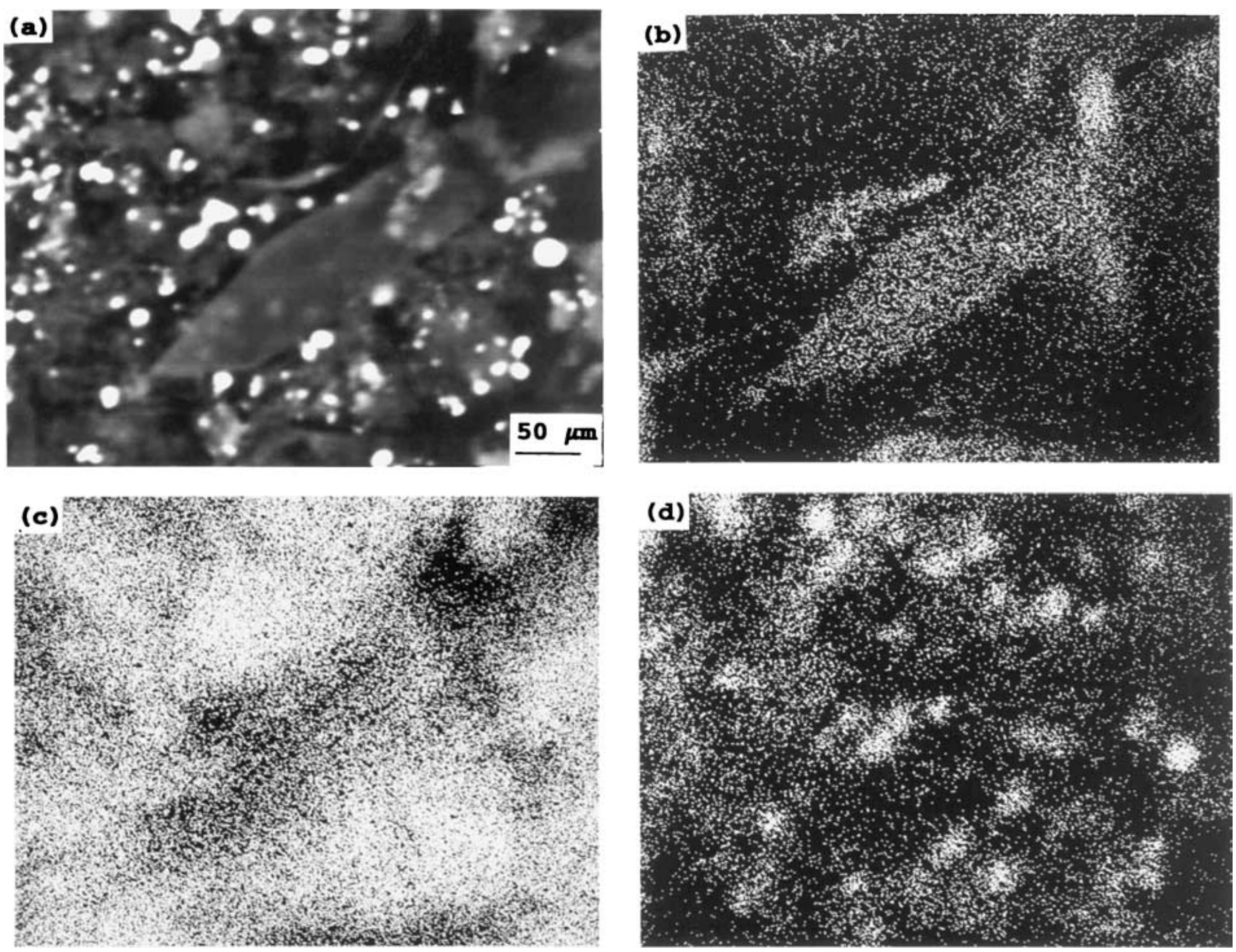


*Figure 5* EPMA analysis of $B_4C$ platelet formed in NKCB after reaction in argon at 1300°C: (a) BSE image, (b), (c) and (d) X-ray maps of boron, carbon and nickel respectively.

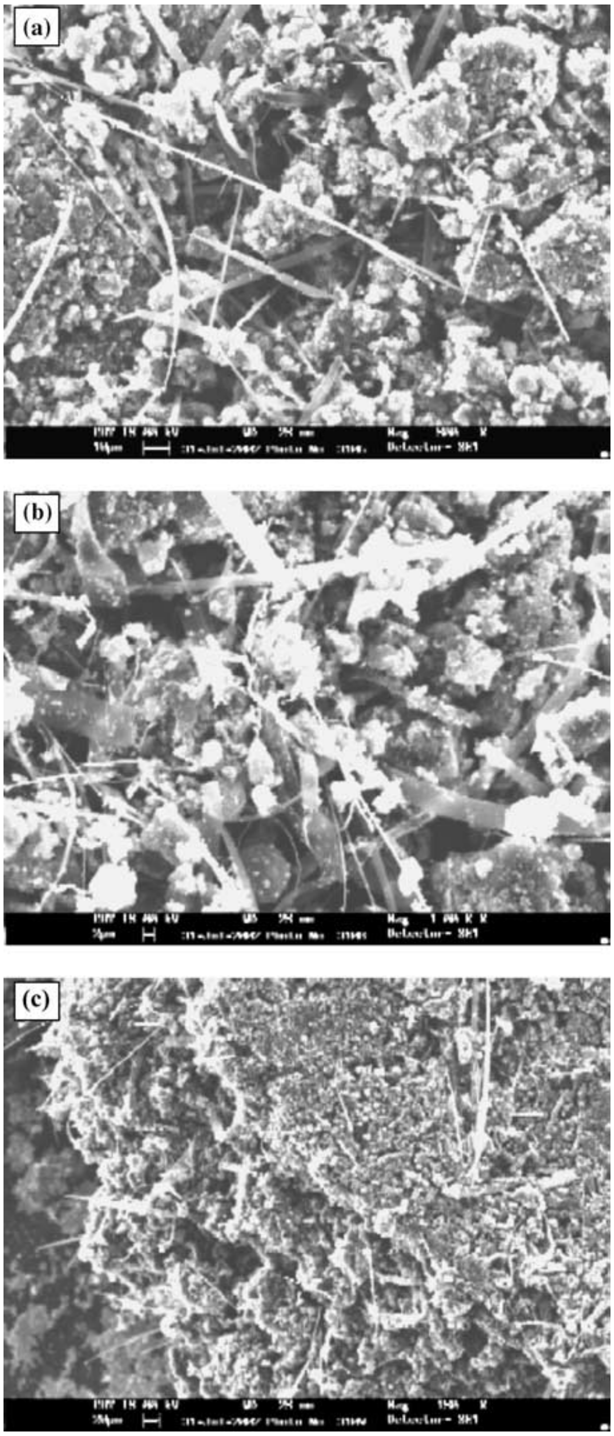


*Figure 6* SEM photographs showing the morphology of NKCB after reaction in nitrogen at: (a) 1200°C, (b) 1300°C and (c) 1500°C.

The morphology of NKCB samples after reaction in nitrogen at different temperatures is shown in SEM photomicrographs (Fig. 6). After reaction at 940°C it appeared like unreacted mass. Whisker formation was observed in the sample reacted at 1200°C. At higher reaction temperature (1300 and 1500°C) thick and long platelets were formed (Fig. 6b). Typical VLS whiskers and platelets formed at 1500°C are shown in Fig. 6c.

The VLS whisker of BN formed at 1300°C was analysed trough EPMA (Fig. 7a). EPMA analysis of the whisker revealed the presence of boron and nitrogen. Nickel was observed in bright spherical particles only (Fig. 7d).

The XRD patterns of NKC, KCB, and NCB reacted at 1300°C in argon revealed the effect of nickel and potassium on carbon and boron (Fig. 8). In the presence of potassium and nickel the carbon black, which is basically amorphous, is converting into graphitic carbon. When $B_2O_3$ is added $B_4C$ is forming in the KCB system. In the NCB system, peaks of $B_4C$ as well as graphite were distinctly identified. From XRD patterns of NKC and NCB it is clear that nickel in combination with $K$ is very effective in forming the graphitic carbon and $B_4C$. From SEM analysis neither whiskers nor platelets were found in the NKC sample. Few very thick platelets and whiskers were seen in KCB sample (Fig. 9a). In NCB sample also whiskers and platelets were observed (Fig. 9b).

From the above results the formation of $B_4C$/BN whiskers can be explained as follows: The over all reactions of carbothermal reduction of $B_2O_3$ to form $B_4C$ or BN are

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO \qquad \text{(i)}$$

$$2B_2O_3 + 6C + 2N_2 \rightarrow 4BN + 6CO \qquad \text{(ii)}$$

When potassium and nickel are present in the system more complicated reactions take place. In CB samples no whiskers or platelets were formed (Fig. 3a). When $K_2CO_3$ was added few thick $B_4C$ platelets were formed in KCB sample. However, no whiskers were seen in KCB (Fig. 9a). $K_2CO_3$ dissociates into $K_2O$ and $CO_2$ at 891°C. $K_2O$ can form a thin liquid layer around other particles and react with it. The important role of potassium is formation of a low melting liquid. For the precipitation of $B_4C$ crystal, continuous supply of boron and carbon to the liquid droplet is required. $K_2CO_3$ alone could not accelerate the formation of platelets/whiskers. So the intensities of $B_4C$ peaks were low in the KCB sample (Fig. 8). The intensities of $B_4C$ peaks of NCB sample were higher than that of KCB sample.

This could be due to the catalytic affect of nickel in gasification of carbon. In the presence of $NiCl_2$ and $B_2O_3$ a complex K-Ni-B liquid droplet could form. This is confirmed from EPMA and EDAX analyses. Nickel increases the availability of carbon as CO and facilitates the growth of whiskers from a complex liquid droplet. The catalytic effect of nickel in carbon gasification is well known [24]. Iron, cobalt and nickel act as strong catalysts in gasification of carbon in carbon-carbon dioxide reaction [25], and in water vapor and hydrogen [26]. By introduction of metal atoms into the carbon structure, more carbon monoxide is produced. So more quantity of CO is available in presence of nickel. Further, chlorine available from $NiCl_2$ reacts with $B_2O_3$ to form BCl.

$$B_2O_3 + 3C + 2Cl \rightarrow 2BCl + 3CO \qquad \text{(iii)}$$

Thus CO and BCl are continuously supplied to the complex liquid droplet of K-Ni-B. So large number of whiskers and platelets were formed in NKCB samples. From SEM photographs (Figs 3 and 6) it is clear that whiskers were formed at low reaction temperatures

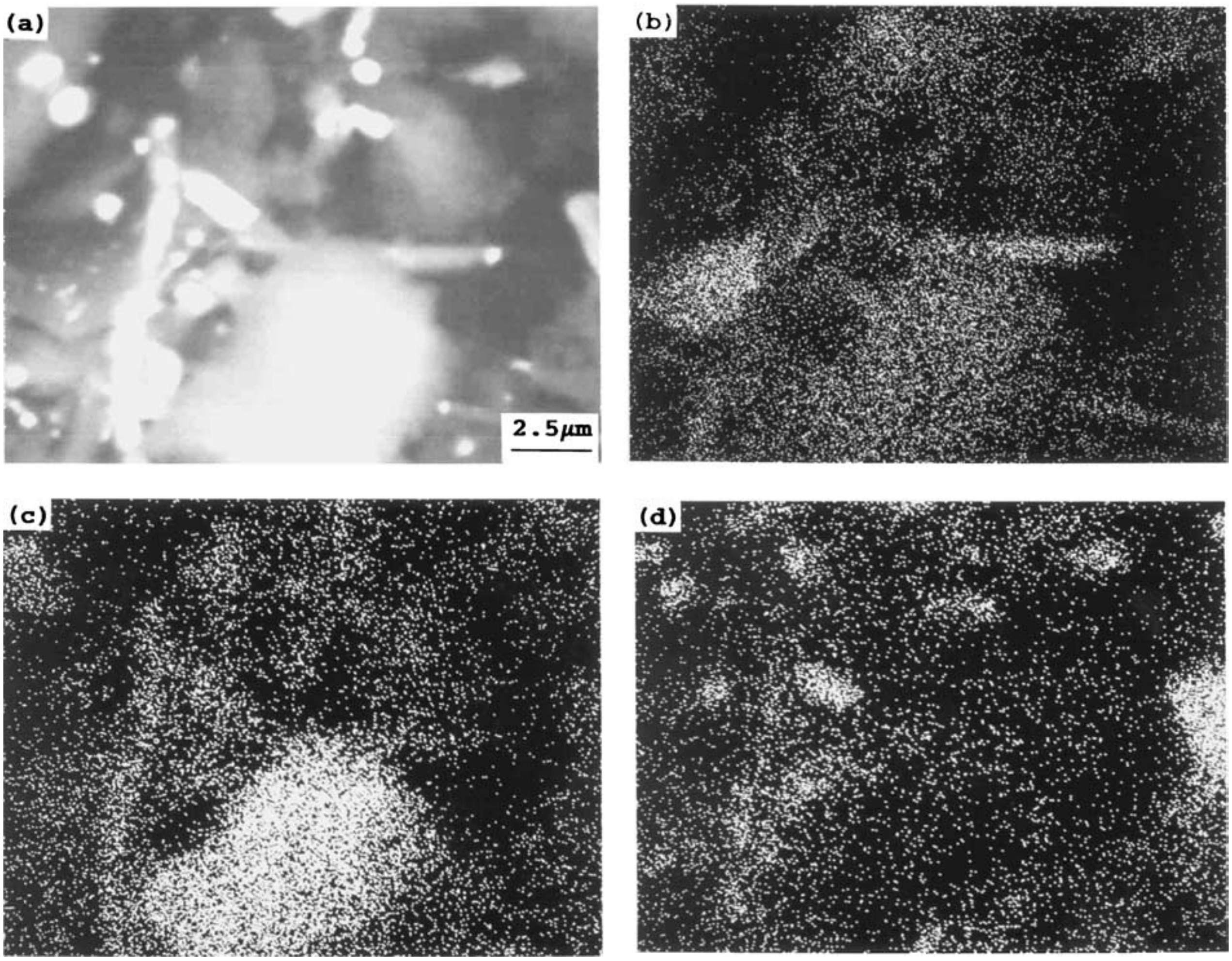


*Figure 7* EPMA analysis of BN whisker formed in NKCB after reaction in nitrogen at 1300°C: (a) BSE image, (b), (c) and (d) X-ray maps of boron, nitrogen and nickel respectively.

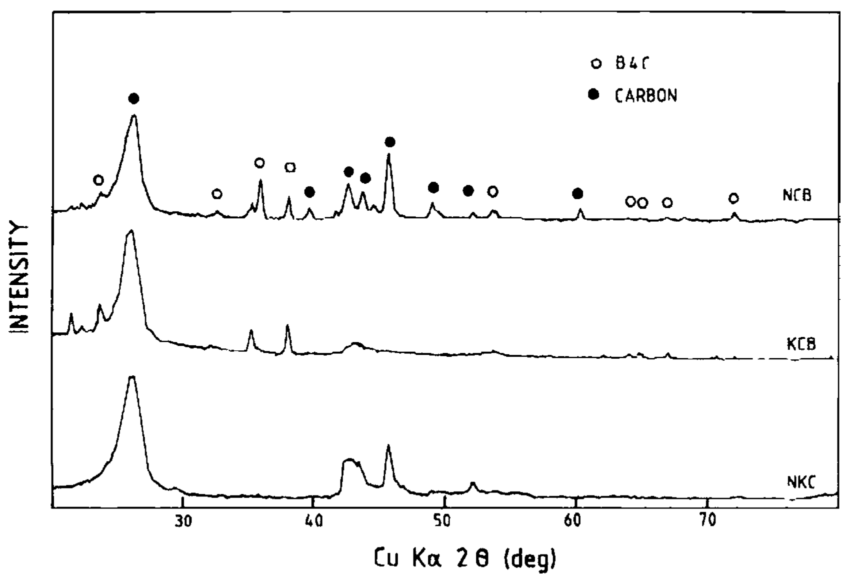


*Figure 8* XRD patterns of NKC, KCB, and NCB after reaction in argon at 1300°C.

up to 1200°C. At and above a reaction temperature of 1300°C the formation of platelets was a predominant phenomenon. Neither whiskers nor platelets were observed in the absent of $K_2CO_3$ or $NiCl_2$ (Figs 3 and 9). These results show that platelets have also formed by VLS growth mechanism. The reason for the formation of platelets at higher temperatures could be high rate of reaction and formation of large quantity of complex liquid. It appears that the formation of platelets can be avoided by decreasing the quantities of $K_2CO_3$ and $NiCl_2$. Further studies are required to establish optimum conditions to form either whiskers or

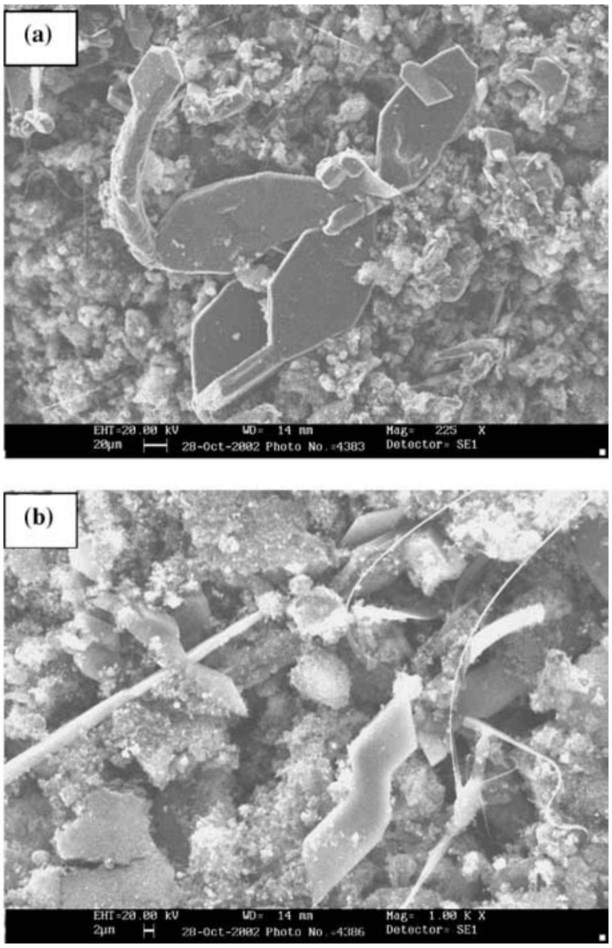


*Figure 9* SEM photographs showing the morphology of: (a) KCB and (b) NCB after reaction in argon at1300°C.

platelets. By incorporating these whiskers/platelets into ceramic/metal matrix their properties can be evaluated.

## 4. Conclusions

The formation of $B_4C$ and BN through carbothermal reduction of $B_2O_3$ has been studied in the temperature range of 940 to 1500°C in 1-atm. argon and 1-atm. nitrogen respectively. $B_2O_3$ and carbon black were used as source of boron and carbon. $K_2CO_3$ and $NiCl_2$ were used to aid the formation of whiskers and platelets. $NiCl_2$, $K_2CO_3$, carbon black and $B_2O_3$ were reacted in a weight ratio ($NiCl_2$:$K_2CO_3$:C:$B_2O_3$ = 5:5:12:17.4). Whiskers and platelets of different sizes have formed at 1100–1500°C. The whiskers have been observed to form by a vapor-liquid-solid growth mechanism. The effect of nickel and potassium on the morphology of $B_4C$ and carbon has been studied. $NiCl_2$ and $K_2CO_3$ have been found to accelerate the formation of whiskers and platelets.

## Acknowledgement

The authors thankfully acknowledge the financial support received from the Defence Research & Development Organisation, Govt. of India in order to carry out the present research study.

## References

1. D. J. BRAY, *Bull. Amer. Ceram. Soc.* **74** (1995) 152.
2. J. HOMENY, in "Ceramic Matrix Composites," edited by Richard Warren (Chapman & Hall, New York, 1992) p. 245.
3. M. CARLSSON and M. JOHNSSON, *Ceram. Engng. Sci. Proc.* **21** (2000) 375.
4. M. JOHNSSON and M. NYGREN, *J. Mater. Res.* **12** (1997) 2419.
5. J.-B. LI, G. Y. XU, E. Y. SUN, Y. HAUNG and P. F. BECHER, *J. Amer. Ceram. Soc.* **81** (1998) 1689.
6. N. AHLEN, M. JOHNSSON and M. NYGREN, *J. Mater. Sci. Lett.* **18** (1999) 1071.
7. M. CARLSSON, M. JOHNSSON and M. NYGREN, *J. Amer. Ceram. Soc.* **82** (1999) 1969.
8. M. NYGREN, M. JOHNSSON, N. AHLEN and M. EKELUND, Europ. Patent, EP 0 754 782 A1, Jan. 22 (1997).
9. N. AHLEN, M. JOHNSSON and M. NYGREN, *J. Amer. Ceram. Soc.* **79** (1996) 2803.
10. C. E. BAMBERGER, P. ANGELINI and T. A. NOLAN, *ibid.* **72** (1989) 587.
11. C. E. BAMBERGER, D. W. COFFE and T. A. NOLAN, *J. Mater. Sci.* **25** (1987) 4992.
12. R. V. KRISHNARAO, J. SUBRAHMANYAM and V. RAMAKRISHNA, *J. Mater. Synth. Process.* **9** (2001) 1.
13. R. V. KRISHNARAO, J. SUBRAHMANYAM and M. YADAGIRI, *J. Mater. Sci.* **37** (2002) 1693.
14. F. THEVENOT, *Key Eng. Mater.* **59** (1991) 56.
15. G. DE WITH, *J. Less-Common Met.* **95** (1983) 133.
16. T. R. CHAPMAN, D. E. NIESZ, R. T. FOX and T. FAWCETT, *Wear* **236** (1999) 81.
17. A. GATTI, C. MANUSCO, F. FEINGOLD and R. MEHAN, in Proceedings of International Conference on Crystal Growth, Boston, MA, June 1966 (Pergamon, Oxford, 1967) p. 317.
18. L. AHMED and G. G. CAPSIMALIS, in Proceedings of the 6th International Symposiumon on Reactive Solids, 1968 (Wiley-Interscience, New York, NY, 1969) p. 477.
19. I. D. R. MACKINNON and K. L. SMITH, in "Novel Refractory Semiconductors" (Mater. Res. Soc. Proc., Pennsylvania, 1987) Vol. 97, p. 127.
20. D. ZHANG, D. N. MCILROY, Y. GENG and M. G. NORTON, *J. Mater. Sci. Lett.* **18** (1999) 349.
21. M. CARLSSON, P. ALBERIUS-HENNING and M. JOHNSSON, *J. Mater. Sci.* **37** (2002) 2917.
22. M. CARLSSON, F. J. GARCIA-GARCIA and M. JOHNSSON, *J. Cryst. Growth* **236** (2002) 466.
23. R. V. KRISHNARAO and J. SUBRAHMANYAM, *Trans. Indian. Ceram. Soc.* **61** (2002) 3.
24. P. L. WALKER JR., M. SHELE and R. A. ANDERSON, in "Chemistry and Physics of Carbon," edited by P. L. Walker Jr. (Marcel Dekker Inc, New York, 1968) Vol. 4, p. 287.
25. J. T. GALLAGHER and H. HARKER, *Carbon* **2** (1964) 163.
26. D. W. MCKEE, *ibid.* **12** (1974) 453.

*Received 16 June 2003*
*and accepted 28 January 2004*