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Interfacial microstructure and reaction of BN-coated single crystal Al_2O_3 fiber reinforced NiAl matrix composites

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Analytical electron microscopy was carried out on BN-coated 125 μm single crystal Al_2O_3 fiber reinforced NiAl matrix composites fabricated by diffusion bonding. NiAl was observed to react with BN to form a layer of AlN with a thickness of about 100 nm at the NiAl/BN interface during fabrication of the composite. The BN layer, deposited on Al_2O_3 fibers using chemical vapor deposition, exhibited a turbostratic structure with {002} planes of BN showing highly preferred orientation. Perfect bonding was obtained at the BN/Al_2O_3 interface with the BN {002} basal planes locally parallel to the surface of Al_2O_3.

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1. Introduction

NiAl is an attractive intermetallic compound for high temperature structural applications because of its high melting point, low density and excellent oxidation resistance. The lack of low-temperature toughness and poor high-temperature strength have been the main drawback for commercial applications. One strategy to improve low temperature toughness and high temperature strength is to introduce reinforcements into the NiAl matrix. In recent years, many studies were conducted on NiAl matrix composites reinforced with polycrystalline [1] or single crystal [2] continuous Al_2O_3 fibers. The composites were fabricated by diffusion bonding, powder cloth process or similar powder metallurgy techniques.

It has been established that fiber/matrix interfacial properties play an important role for the performance of the composite. There is excellent chemical compatibility between Al_2O_3 fiber and NiAl matrix with no chemical reaction [3]. TiB_2 and Al_2O_3 particles or whiskers reinforced NiAl composites were reported to show significant improvement of high temperature strength compared to the monolithic matrix material [4]. No improvement of high temperature performance, however, was achieved for single crystal continuous Al_2O_3 fiber reinforced NiAl composites, both with strong or weak fiber/matrix interfacial bonding [2].

Applying a coating on the fiber surface is an important way to control the structure and properties of the fiber/matrix interface. The species, microstructure and thickness of the coating can be tailored to achieve an optimum bond for the desired application. Coating is also expected to protect the fiber from strength degradation during the processing of composites. Recently, BN coated SCS-6 SiC fiber reinforced ceramic matrix composites have shown improved strength and toughness at both room and elevated temperatures [5]. This may be also a viable way to improve the mechanical properties of Al_2O_3 reinforced NiAl. The purpose of this paper is to explore the interfacial reaction and microstructure of BN coated single crystal continuous Al_2O_3 fiber reinforced NiAl matrix composites fabricated by diffusion bonding.

2. Experimental procedure

The matrix for the present study was an as-cast NiAl intermetallic compound with a composition of Ni-48.9at.% Al. The reinforcement consisted of 125-μm diameter, *c*-axis-oriented, continuous single crystal Al_2O_3 fibers* with a BN coating of about 1-μm thickness. A BN coating was deposited on the fiber by chemical vapor deposition (CVD) at a temperature of ∼1000°C. The composites were fabricated by placing one layer of fibers between two NiAl plates, and then subjecting the assemblage to a temperature of 1400°C

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*Saphikon, Inc.

at a pressure of 7–10 MPa in a vacuum of ~5×10^{-3} Pa for two hours.

The interfacial microstructure of the composites was characterized using scanning electron microscopy as well as analytical and high resolution transmission electron microscopy. Foils for TEM observations were prepared in a conventional way of mechanical grinding, dimpling and ion milling, The plane of the foils was perpendicular to the filaments. Conventional TEM work was performed on a JEOL 2000 FX microscope equipped with an energy dispersive x-ray spectrometer and an electron energy loss spectrometer. High-resolution transmission electron microscopy was carried out on a JEOL 2000EX electron microscope. Both TEMs were operated at a voltage of 200 kV.

3. Results and discussion

3.1. NiAl/BN interface

Fig. 1 shows a SEM micrograph of the interface between matrix and fiber. Perfect contact between matrix and fiber was achieved after diffusion bonding. The cracks apparent at the Al_2O_3/BN interface were introduced during mechanical grinding and polishing. At higher magnification, a subtle contrast variation at the BN/NiAl interface was observed, but no distinct interlayer could be detected. The TEM micrograph in Fig. 2 shows clearly a reaction layer with a thickness of about 100 nm at the NiAl/BN interface. Some of the grains in the reaction layer have a columnar shape and have grown from the NiAl/BN interface into the BN layer, but most of the grains exhibit an irregular form. EDS analysis, which is incapable of detecting light elements such as B and N, pretended that aluminum was the only element present in the reaction layer. An EELS spectrum (Fig. 3) collected from the reaction layer proved that the reaction layer actually contained nitrogen, oxygen and aluminum. Fig. 4a shows an electron diffraction pattern obtained from a grain in the reaction layer, the grain has an irregular form as shown in Fig. 4b. The pattern in Fig. 4a can be indexed as $[2\,\bar{1}\,\bar{1}\,0]$ zone axis pattern of AlN. A large number of electron diffraction examinations were conducted on different grains of the reaction layer in several TEM samples, and all the grains were identified to consist of AlN. The K-edge of oxygen in Fig. 3 probably arose from the oxygen adsorbed on the surface of the foils, because similar K-edges were also observed in the spectra collected from both NiAl matrix and BN layer.

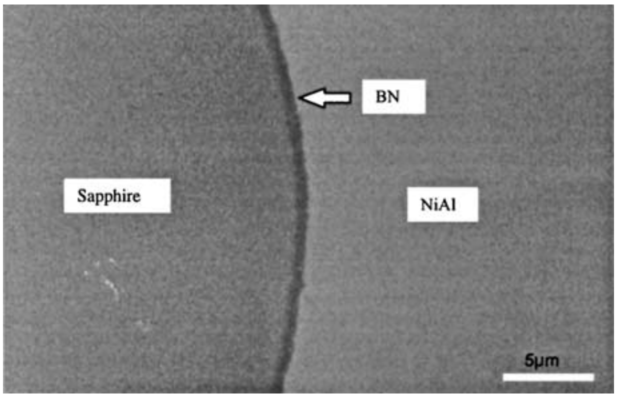


Figure 1 SEM image exhibiting alumina fiber with ~1 μm BN coating in NiAl matrix.

It was noted that all the electron diffraction patterns obtained were $[2\,\bar{1}\,\bar{1}\,0]$ zone axis patterns of AlN, within a range of ±12 degrees. This indicates a pronounced texture with the c-axis of the hexagonal AlN approximately perpendicularly to the fibers. A similar texture was also observed in other systems, e.g. the basal planes of hexagonal $CaAl_{12}O_{19}$ were found to align with the fiber axis [6].

Fig. 5 shows a lattice image of AlN, which was observed to have grown in BN. No interlayer was observed at the boundary between AlN and BN. The AlN layer (Fig. 6) found between the NiAl matrix and Al_2O_3 fiber, was probably due to the fact that most of the BN coating had fallen off before diffusion bonding, and the

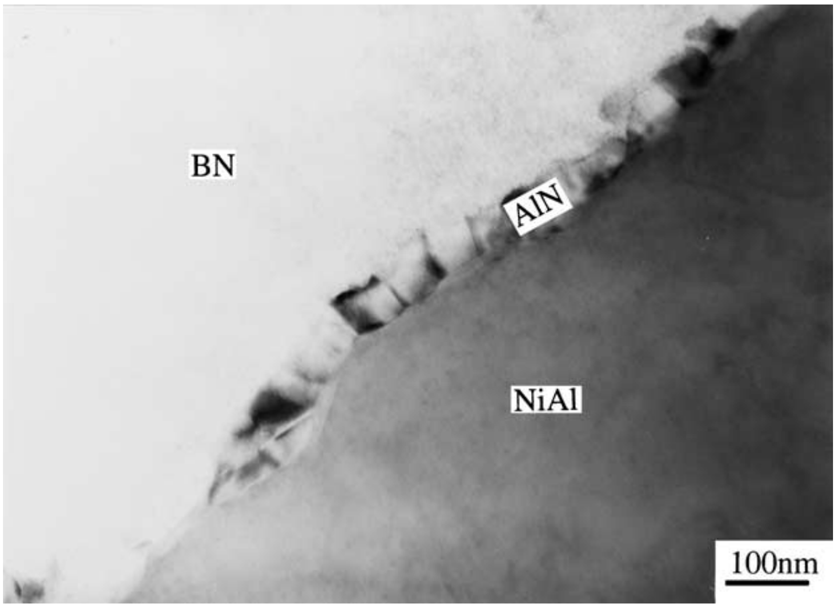


Figure 2 TEM image of AlN layer between NiAl and BN after diffusion bonding.

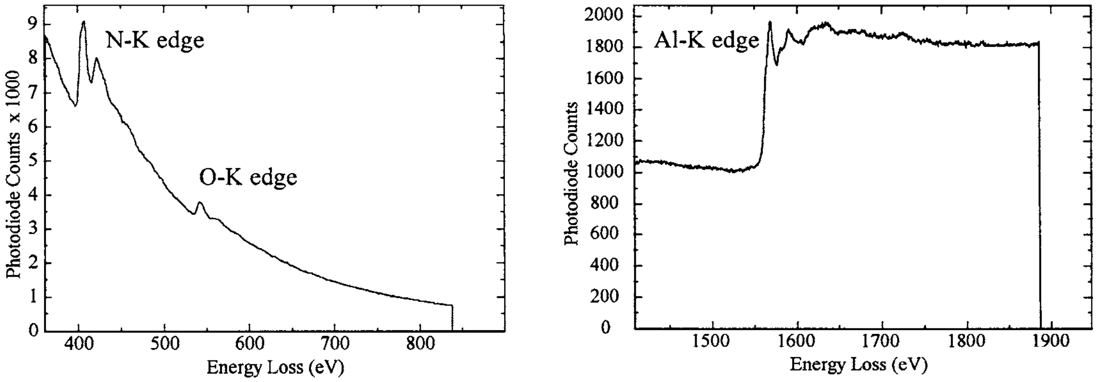
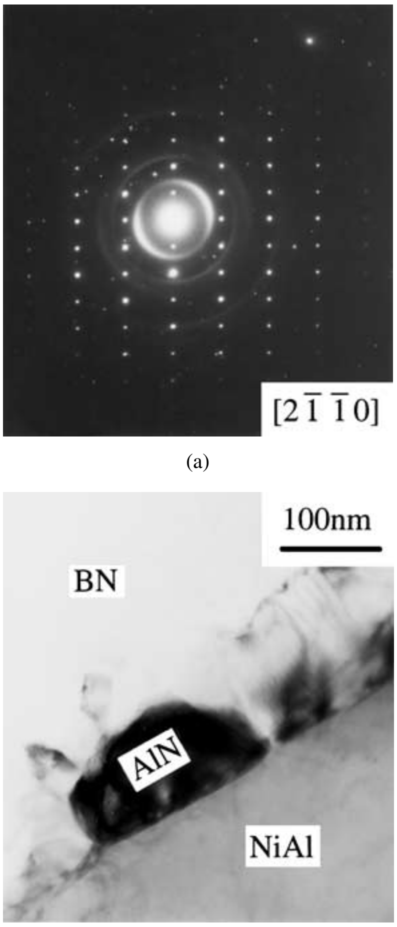


Figure 3 EELS spectrum from AlN.



(a)

(b)

Figure 4 $[2\bar{1}\bar{1}0]$ zone axis electron diffraction pattern of AlN (a) and the corresponding AlN grain (b).

remaining BN had reacted completely with the NiAl matrix to form AlN.

Because no phase other than AlN was observed at the NiAl/BN interface, the reaction

$$(1+x)\,\mathrm{NiAl} + x\mathrm{BN} \rightarrow x\mathrm{AlN} + \mathrm{Ni}_{1+x}\mathrm{Al} + x\mathrm{B}_{\mathrm{NiAl}}$$

is proposed to have occurred between NiAl matrix and BN coating at their interface during fabrication of the composites.

According to the binary Al-Ni phase diagram, NiAl can exist over an extended compositional range. The free Ni atoms resulting from the formation of AlN are therefore expected to diffuse into the NiAl matrix. EDS measurement substantiated that there was no significant difference between the Ni concentration at the interface in NiAl and that away from the interface in NiAl.

No solubility data of B in NiAl is available. The average concentration of boron on the grain boundaries of NiAl doped with 300 wt.ppm boron was estimated to be about 2.7 at.% on one-half of the fracture surface [7]. Outside of the BN layer, EELS analysis revealed no measurable boron content at the interface. The boron atoms liberated through the interface reaction probably had segregated to the grain boundaries of NiAl.

There are a series of nickel boride compounds in the Ni-B binary phase diagram [8]. In boron-carbide-coated boron (B_4C/B) fiber reinforced Ni_3Al (IC-221) matrix composites, Ni was seen throughout the B layer after 6 h at 980°C in form of a nickel boride network, which are Ni_3B_2- and NiB_2-based precipitates [9, 10]. No nickel boride precipitate, however, was observed at the NiAl/BN interface in this study. There are two possible reasons for the lack of nickel boride formation at the NiAl/BN interface. (i) the nickel borides are not stable at the temperature the composite was fabricated, (ii) since the chemical activities of the constituents in a binary alloy system strongly depend on composition, the chemical activity of Ni in NiAl is three orders of magnitude lower than that of Ni_3Al [9].

Ni was found to be the predominant diffusing species during the interaction between SiC and various nickel aluminides [9] and in Al_2O_3 reinforced Ni_3Al matrix composites [11]. In the present study, however, the predominant diffusing species seemed to be Al. In Fig. 2, AlN grains were observed to nucleate at the NiAl/BN interface and to grow into the BN layer. Accompanying the nucleation and the growth of AlN, a diffusion flow of atoms in opposite directions occurred in the NiAl matrix with Ni atoms diffusing from the interface into the matrix and Al atoms of the NiAl matrix diffusing from the matrix into the the NiAl/BN interface and through the interface into the BN layer. AlN grains were also observed to nucleate and grow in the BN matrix very near the NiAl/BN interface, indicating that nucleation of AlN was not difficult. The intrinsic diffusion coefficients D_{Ni} and D_{Al} are very small [12] and the ratio of the intrinsic diffusion coefficients, $D_{\mathrm{Ni}}/D_{\mathrm{Al}}$, was reported to be 3 to 3.5 for NiAl with Al concentration below 50 at.% at 1100°C [13]. The small

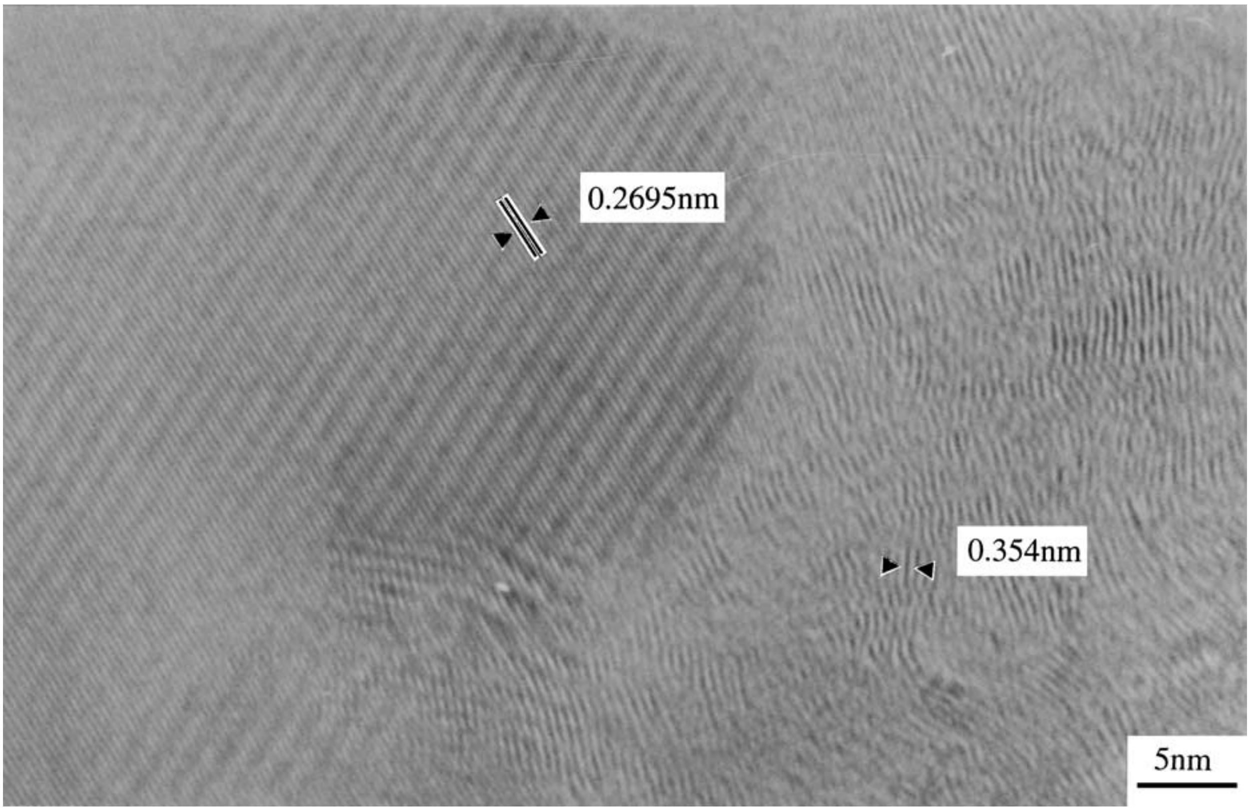


Figure 5 TEM image of AlN layer between NiAl and Al_2O_3.

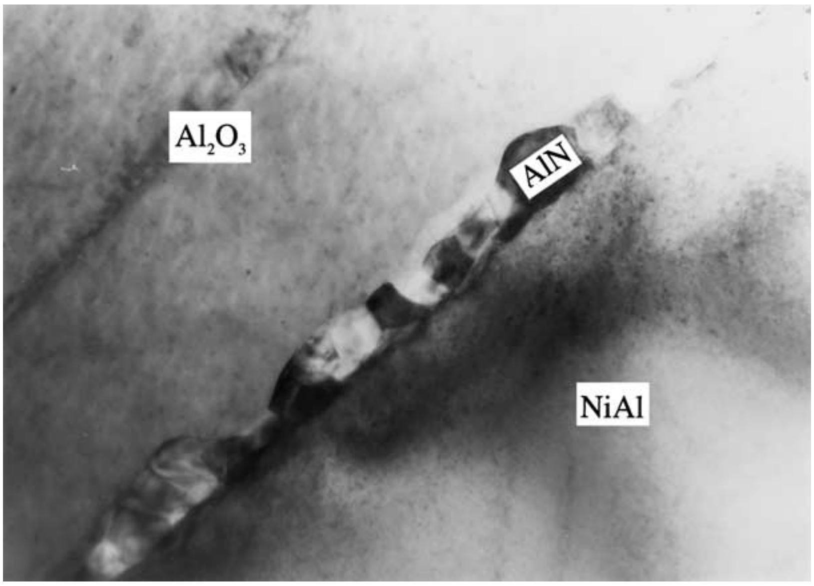


Figure 6 (HREM image of AlN in BN.) TEM image of AlN layer between NiAl and Al_2O_3.

intrinsic diffusion coefficient of D_{Al} probably accounts for the relatively slow growth kinetics of the AlN layer when considering the temperature and the duration of the fabrication process.

3.2. Microstructure of BN coating and Al_2O_3/BN interface

Fig. 7 shows a high-resolution micrograph of the BN layer. BN exhibits a turbostratic structure, which is a two-dimensional structure with the hexagonal layers stacked with a rotational disorder and these small stacks forming domains [14]. Discrete and wavy lattice fringes corresponding to {002} of BN can be seen (Fig. 7) to tend to align parallel to the interface. This preferred orientation of the basal planes gave rise to the arcing of the diffuse rings in the electron diffraction pattern of BN shown in the inset of Fig. 7. At the Al_2O_3/BN interface, the BN {002} lattice fringes within a thickness of 5–10 nm are seen to be locally parallel to the surface of Al_2O_3 and closely adhere to the fiber, as shown in the high-resolution micrograph of Fig. 8. A similar structure was observed by Borek *et al.* [15], who found that mixtures of amorphous BN power with oxides particles such as MgO, Al_2O_3, and

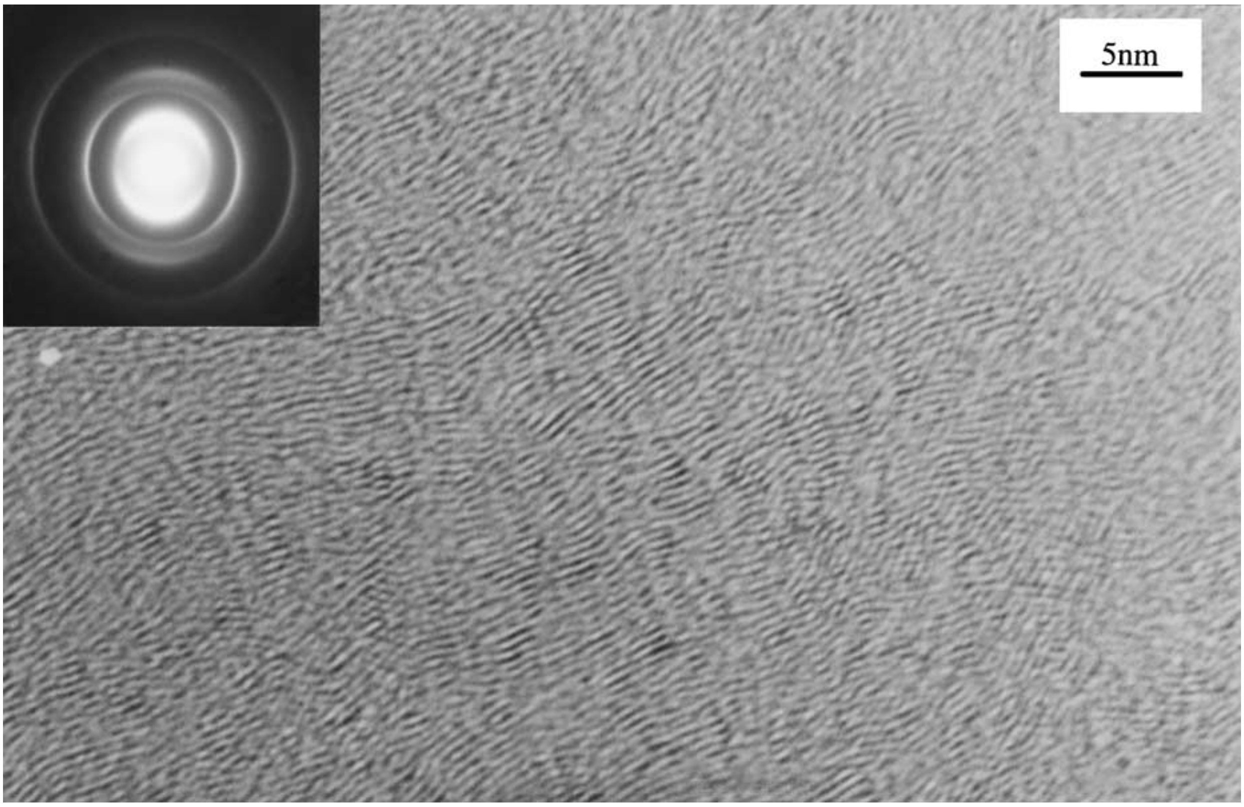


Figure 7 HREM image of BN coating.

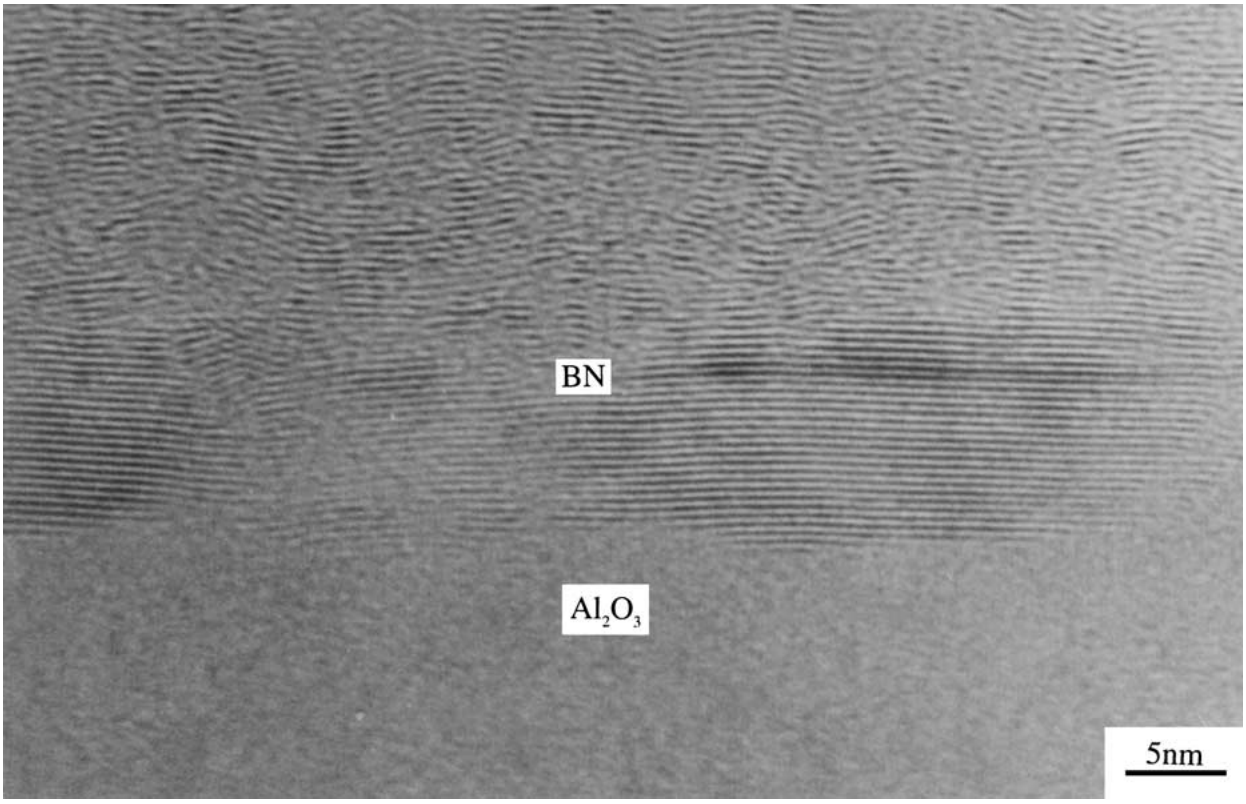


Figure 8 HREM image of Al_2O_3-NiAl interface.

TiO_2 yielded crystalline, tightly adherent coatings of hexagonal BN on the oxide surfaces after heat treatments, with the BN {002} basal planes parallel to the oxide surfaces. Using the structure of AlN as an internal reference for magnification, the interplanar spacing of BN was measured to be 0.354 nm. The 0.352–0.356 nm range is typical for a turbostratic structure of BN [16]. A few small domains with subtle two dimensional lattice fringes can be seen in Fig. 7. These domains, with a size of only several atomic layers, appear to have a degree of three-dimensional crystalline order in the layered structure.

It has been contended that there is no chemical bonding at a BN/MgO interface, and that the BN-Mg bonding is achieved by van der Waals interactions similar to those between BN layers [15, 16]. Similar conclusions may also be drawn for the BN/Al_2O_3 interface which has a structure similar to that of BN/MgO, yet BN seems to strongly adhere to the Al_2O_3 surface. The observation (Fig. 6) that the BN coating did not completely peel off during fabrication of the composite indicates such a tight bonding.

Ceramic matrix composites reinforced with BN coated SiC filaments have been reported to have a weak interfacial bonding and yet improved mechanical properties [5, 17]. The influence of BN coating on the interfacial shear strength and mechanical properties of single crystal Al_2O_3 fiber reinforced NiAl matrix composite is currently being studied, and the results will be reported elsewhere.

4. Conclusions

Tansmission electron microscopy studies were conducted on single crystal Al_2O_3 fiber reinforced NiAl matrix composites fabricated by diffusion bonding. The following conclusions were obtained:

(1) Chemical reactions occurred during the fabrication process at the NiAl/BN interface, resulting in the formation of an AlN layer with a thickness of about 100 nm. Aluminum was the dominant diffusion species in the interface reaction.

(2) The CVD-BN coating exhibited a turbostratic structure with a c-axis repeat greater than 0.7 nm. The BN {002} basal planes showed preferred orientation parallel to the fiber axis. The BN layer is therefore highly anisotropic.

(3) Perfect bonding was achieved at the BN/Al_2O_3 interface with the BN {002} basal planes locally parallel to the surface of Al_2O_3. No chemical reaction occurred at this interface.

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References

1. W. HU, W. WUNDERLICH and G. GOTTSTEIN, *Acta Mater.* **44** (1996) 2383.
2. R. R. BOWMAN, A. K. MISRA and S. M. ARNOLD, *Metall. and Mater. Trans.* **26A** (1995) 615.
3. L. WANG and R. J. ARSENAULT, *Metall. Trans.* **22A** (1991) 3013.
4. J. D. WHITTENBERGER, R. K. VISWANADHAM, S. K. MANNAN and B. SPRISSLER, *J. Mater. Sci.* **25** (1990) 35.
5. E. Y. SUN, S. R. NUTT and J. J. BRENNAN, *J. Amer. Ceram. Soc.* **79** (1996) 1521.
6. M. K. CINIBULK and R. S. HAY, *ibid.* **79** (1996) 1233.
7. E. P. GEORGE and C. T. LIU, *J. Mater. Res.* **5** (1990) 754.
8. T. B. MASSALSKI (ed.) "Binary Alloy Phase Diagrams" (ASM international, 1990) p. 508.
9. J. M. YANG, W. H. KAO and C. T. LIU, *Mater. Sci. Eng.* A **107** (1989) 81.
10. P. C. BRENNAN, W. H. KAO and H. A. KATZMAN, *J. Mater. Res.* **6** (1991) 355.
11. W. HU, P. KARDUCK and G. GOTTSTEIN, *Acta Mater.* **45** (1997) 4535.
12. M. M. P. JANSSEN, *Metall. Trans.* **4** (1973) 1623.
13. S. SHANKAR and L. L. SEIGLE, *ibid.* **9A** (1978) 1467.
14. X. BOURRAT, B. TROUVAT, G. LIMOUSIN and G. VIGNOLES, *J. Mater. Res.* **15** (2000) 92.
15. T. T. BOREK, X. QIU, L. M. RAYFUSE, A. K. DATYE and R. T. PAINE, *J. Amer. Ceram. Soc.* **74** (1991) 2587.
16. L. F. ALLARD, A. K. DATYE, T. A. NOLAN, S. L. MAHAN and R. T. PAINE, *Ultramicroscopy* **37** (1991) 153.
17. J. LLORCA and R. N. SINGH, *J. Amer. Ceram. Soc.* **74** (1991) 2882.

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