Journal of the European Ceramic Society 17 (1997) 1849–1854
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PII: S0955-2219(97)00070-8
0955-2219/97/$17.00 + 0.00

Interphase Boundaries between Hexagonal Boron Nitride and Beta Silicon Nitride in Silicon Nitride–Silicon Carbide Particulate Composites

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Abstract

Interphase boundaries between hexagonal boron nitride and β-Si_3N_4 in hot isostatically pressed Si_3N_4–SiC particulate composites, in which boron nitride appears as a trace contaminant, have been examined using high resolution transmission electron microscopy. A number of characteristic orientation relationships were observed between these two phases. Significantly, high resolution transmission electron microscopy showed that the interphase boundaries tended not to contain any intergranular films. © 1997 Elsevier Science Limited.

1 Introduction

The addition of hexagonal boron nitride (*h*-BN) to engineering ceramic matrices can have a number of important consequences. For example, it has been reported that increasing the amount of *h*-BN particulate dispersion in matrices such as alumina[1] and silicon nitride[2] increases the thermal shock resistance of the ceramic matrix. This can be attributed to micro-cracking of the *h*-BN grains along their relatively weak (0 0 0 1) basal planes, thereby enabling the large thermal strains that arise during cooling of the composites to be accommodated. Such micro-cracking has been observed experimentally in a number of *h*-BN-based composites such as BN-SiC, BN-Si_3N_4 and BN-sialon,[3] BN-B_4C[4] and also in Si_3N_4 particulate reinforced SiC composites containing *h*-BN as a trace contaminant.[5]

A second consequence of the incorporation of *h*-BN into a matrix is that it can improve the fracture toughness, both of oxide matrices[6–8] and, at low addition levels of *h*-BN, Si_3N_4.[9] The addition of BN has been shown to improve the fracture toughness of oxide matrix composites by micro-cracking and/or crack-particle interaction mechanisms.[6–8] In contrast, the fracture toughness of Si_3N_4 matrix composites has been reported to decrease with the addition of BN at levels of BN of 10–40 wt% due to increasing porosity associated with BN content,[2] but recently it has been claimed that at 2·5 and 5 wt% additions of *h*-BN to Si_3N_4, the fracture toughness measured either by the single edged notched beam method or by the indentation fracture toughness method increases.[9]

Evidence suggests that *h*-BN is also a very promising material to replace graphite as an interface material in fibre-reinforced ceramics, since the oxidation of BN in air starts at 800°C, whereas the oxidation kinetics of graphite are already significant at 600°C. For example, Lowden and More[10] have shown that BN could be used as a coating between a SiC fibre and the surrounding matrix.

In contrast to the amount of work on mechanical behaviour, the nature of interphase boundaries between BN and likely engineering ceramic matrix materials such as SiC and Si_3N_4 has received comparatively little attention, although Ruh, Kearns, Zangvil and Xu have recently reported transmission electron microscope obsevations on BN–B_4C boundaries.[4] During the detailed characterisation of Si_3N_4–SiC composites, small *h*-BN inclusions were found at grain boundaries, interphase boundaries and inside SiC and Si_3N_4 grains.[5,11,12] These inclusions were introduced unintentionally during the densification of the composites. The purpose of this paper is to present and discuss transmission electron microscope observations on the structures of h-BN–β-Si_3N_4 interphase boundaries in these composites. The nature of interphase boundaries between h-BN and SiC in these composites will be reported elsewhere.[13]

2 Experimental Procedure

Sample preparation has already been reported in detail.[5,11,12] Briefly, Si_3N_4–SiC composites with either 10 or 20 wt% Si_3N_4 were prepared by first mixing commercially available SiC and Si_3N_4 powders without the addition of any sintering aids and then hot isostatically pressing the powder compacts in tantalum cans at 200 MPa and 2373 K for 1 h. The h-BN inclusions arose indirectly during the densification process from boron oxide present on the surface of fine particles of boron nitride sprayed onto the internal surface of the tantalum can to prevent an unwanted chemical reaction between SiC and the tantalum.[12]

Slices from the hot isostatically pressed composites were thinned mechanically and ion milled to perforation for transmission electron microscopy. The high resolution transmission electron microscope (HRTEM) observations of the specimens were carried out at 400 kV in a JEOL 4000EX-II which has a spherical aberration coefficient, C_s of 1 mm and a point-to-point resolution of $\approx 1{\cdot}7$ Å.

3 Results and Discussion

An example of an interface edge-on to the electron beam between an h-BN particle and an adjacent β-Si_3N_4 grain is shown in the high resolution transmission electron micrograph in Fig. 1. In this micrograph, the $(0001)_{h\text{-BN}}$ planes are parallel to $(10\bar{1}0)_{\beta\text{-}Si_3N_4}$, and while the electron beam is parallel to $[\bar{2}4\bar{2}3]_{\beta\text{-}Si_3N_4}$, the electron diffraction pattern from the h-BN particle only showed the systematic row of $000l$ reflections and was not near to a low index zone. The limited tilting facilities in the high resolution electron microscope and the small size of the h-BN particle precluded a more detailed crystallographic assessment.

This micrograph is of interest for a number of reasons. First, in engineering ceramics where there are liquid phases at high temperatures, such as when Si_3N_4 is sintered, it is found that in general, high-angle grain boundaries observed in the transmission electron microscope are wet with thin amorphous films because of the competition between attractive van der Waals dispersion forces and a repulsive disjoining pressure, arising either from steric forces or electrical double layers.[14,15] Good examples of this phenomenon are grain boundaries between Si_3N_4 grains, where typically amorphous films of the order of 10 Å are seen.[11]

It is apparent from the way in which the lattice fringes from the two phases meet at the interface in Fig. 1 that the amorphous phase present at the triple junction arrowed in (a) does not spread along the interface between the h-BN particle and the β-Si_3N_4 grain. It is also relevant that the $(0001)_{h\text{-BN}}$ planes with an interplanar spacing of 6·66 Å are parallel to $(10\bar{1}0)_{\beta\text{-}Si_3N_4}$ planes, which are 6·58 Å apart (for h-BN $a = 2{\cdot}50$ Å, $c = 6{\cdot}66$ Å and for β-Si_3N_4 $a = 7{\cdot}60$ Å and $c = 2{\cdot}91$ Å). Thus, it would appear that this interface is somehow 'special', in the sense that it could be argued that the epitaxial nature of the interface, manifested in the way in which the $(0001)_{h\text{-BN}}$ and $(10\bar{1}0)_{\beta\text{-}Si_3N_4}$ planes are parallel both to one another and to the interface has given rise to an interface of low energy. This would certainly be consistent with Clarke's model of the way in which such a low energy interface would expel amorphous films.[16] The single step of

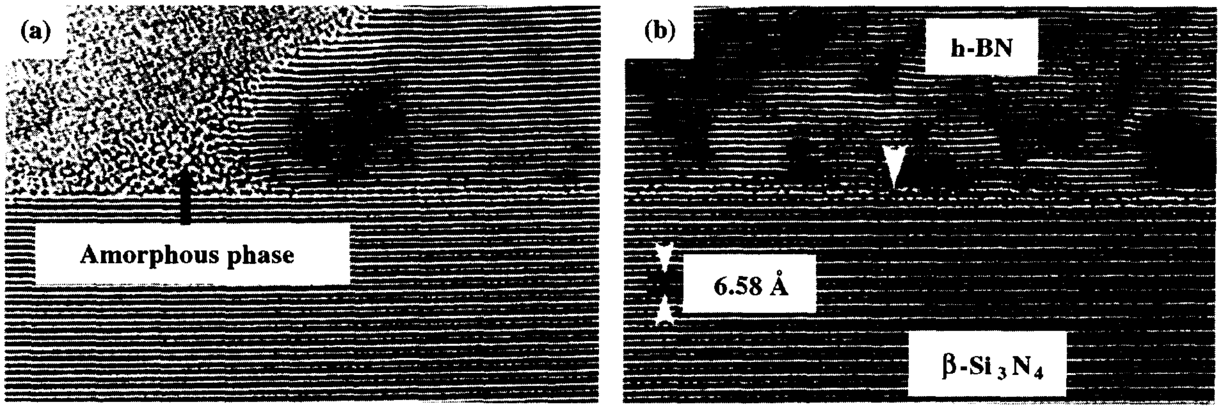


Fig. 1. (a) and (b) A typical example of an interphase boundary between an h-BN particle and a β-Si_3N_4 grain for which $(0001)_{h\text{-BN}} \parallel (10\bar{1}0)_{\beta\text{-}Si_3N_4}$; (b) is taken from a region to the right of the part of the interface in (a) and shows a single step (arrowed) of height 3·3 Å. It is apparent that the amorphous phase at the triple junction arrowed in (a) does not extend along the interphase boundary.

height 3·3 Å seen in (b) gives rise to little strain in the interface, again consistent with the low degree of misfit between the $(0\,0\,0\,1)_{h\text{-BN}}$ and $(1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$ planes and a low energy interface.

A second example where $(0\,0\,0\,1)_{h\text{-BN}} \parallel (1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$ was found is shown in Fig. 2. Here, the interface is also parallel to the electron beam and again the interface plane is $(0\,0\,0\,1)_{h\text{-BN}} \parallel (1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$ for most of the interface. In this case the electron beam was parallel to $[1\,1\,\bar{2}\,0]_{h\text{-BN}}$ and $[\bar{1}\,2\,\bar{1}\,3]_{\beta\text{-}Si_3N_4}$, although it should be noted that the high resolution image from the *h*-BN particle shows small angular deviation away from $[1\,1\,\bar{2}\,0]$ which are caused by the highly strained nature of the particles.[5] The interface contains a number of steps which rotate the macroscopic interface between the *h*-BN particle and the β-Si_3N_4 grain away from $(0\,0\,0\,1)_{h\text{-BN}} \parallel (1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$. Once again, it is significant that the interface appears to be free of any amorphous film.

In contrast to these two examples, cases were also found where the $(1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$ planes were not parallel to $(0\,0\,0\,1)_{h\text{-BN}}$ planes. An example is shown in Fig. 3. As in Fig. 1, the β-Si_3N_4 grain is oriented parallel to a $<\bar{2}\,4\,\bar{2}\,3>$ direction. The *h*-BN inclusion is oriented approximately parallel to $[1\,1\,\bar{2}\,0]$ and the interfaces between the *h*-BN particle and the surrounding β-Si_3N_4 grain are $(0\,0\,0\,1)_{h\text{-BN}}$. However, the angle between the $(1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$ planes and the $(0\,0\,0\,2)_{h\text{-BN}}$ planes is ≈72°, and a close examination of the micrograph shows once again that the interfaces contain at most ≈ 3 Å thick intergranular films, the uncertainty caused by the serrated nature of the contrast on the β-Si_3N_4 side of the interface, interface roughness and the possibility that the interface may not be exactly oriented parallel to the electron beam.

A final example is shown in Fig. 4. Here, there appears to be a series of ledges one atomic plane high and 70–100 Å long along the 1000 Å length of

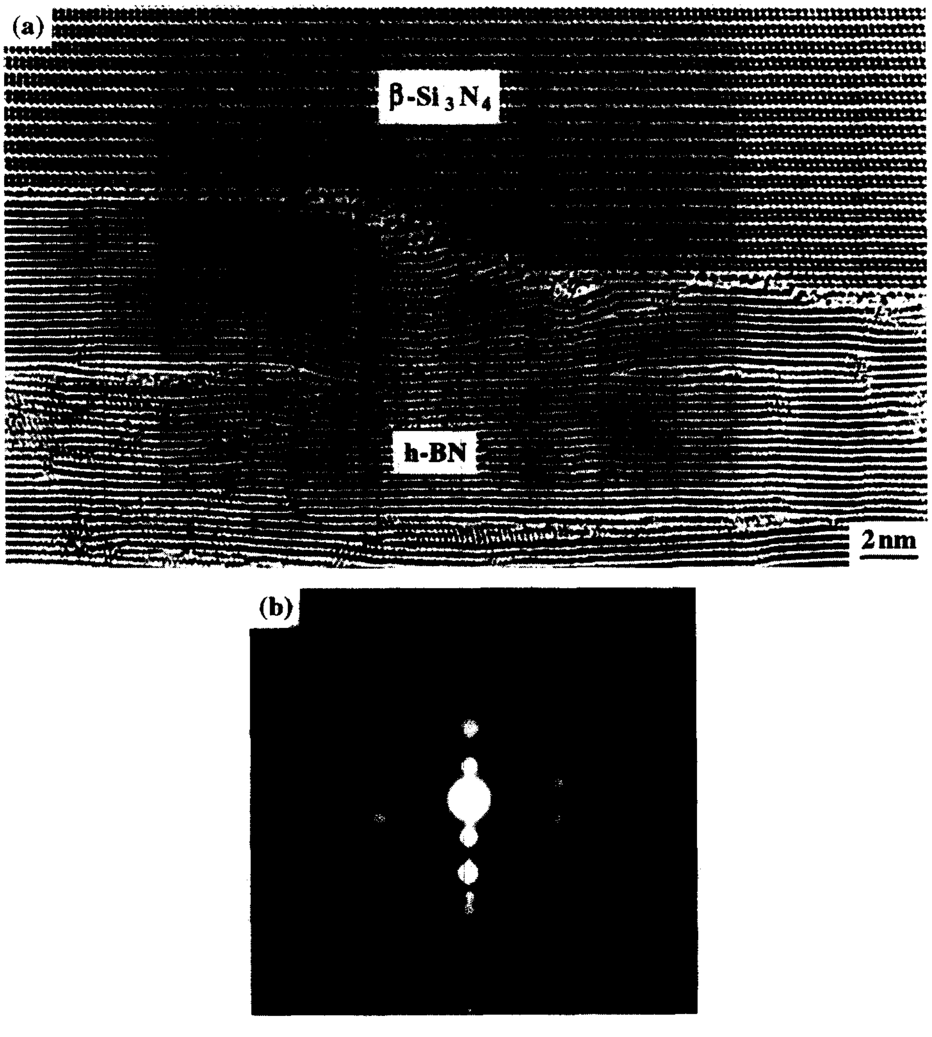


Fig. 2. (a) A large step at an interphase boundary between an *h*-BN particle and a β-Si_3N_4 grain imaged with $[1\,1\,\bar{2}\,0]_{h\text{-BN}} \parallel [\bar{1}\,2\,\bar{1}\,3]_{\beta\text{-}Si_3N_4}$ and $(0\,0\,0\,1)_{h\text{-BN}} \parallel (1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$. Any amorphous material at the grain boundary is clearly confined to within about 3 Å of the interface plane. (b) Selected area electron diffraction pattern from the region where (a) was taken. Arrowed spots along the central row of common reflections show $0\,0\,0\,2_{h\text{-BN}} \parallel 2\,0\,\bar{2}\,0_{\beta\text{-}Si_3N_4}$ systematic reflections. Spots arrowed in the faint streaks parallel to the central row are from *h*-BN. These are faint because of the small dimensions of the particle in comparison with the size of selected area aperture. Spots labelled 'E' are extra spots from adjacent grains and not from either the *h*-BN particle or the β-Si_3N_4 grain.

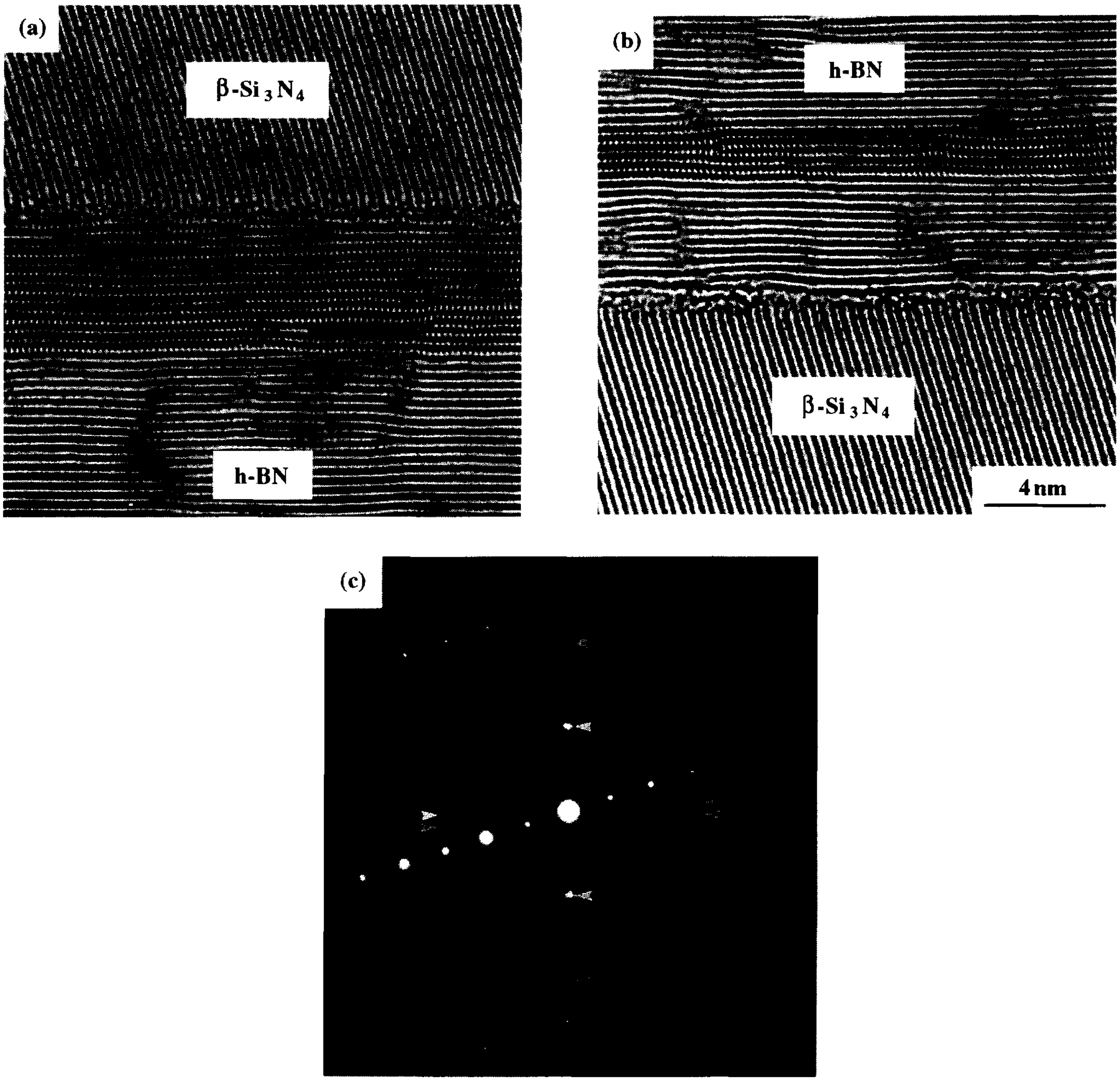
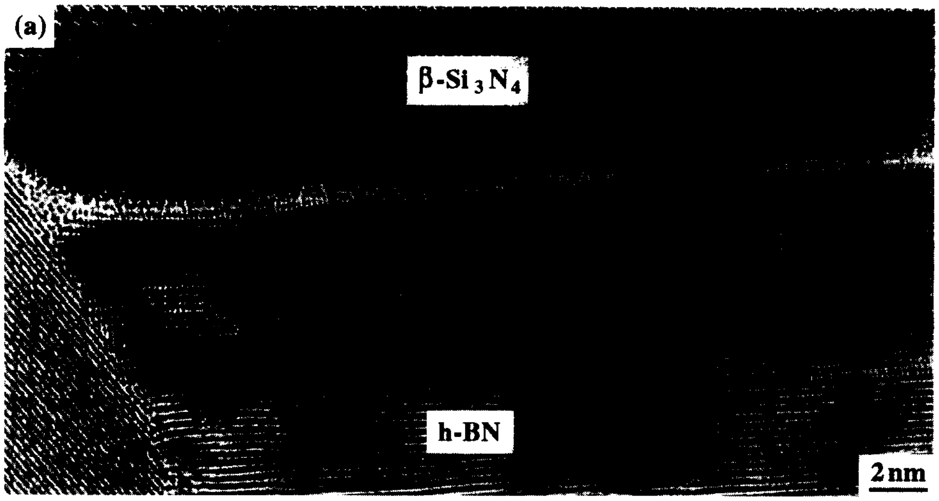


Fig. 3. HRTEM images of interphase boundaries from opposite sides of an *h*-BN inclusion in a β-Si_3N_4 grain. In (a), the *h*-BN particle is oriented parallel to $[1\,1\,\bar{2}\,0]_{h\text{-BN}}$ at the interface, whereas in (b) it is oriented parallel to $[1\,1\,\bar{2}\,0]_{h\text{-BN}}$ some 40 Å away from the interface and there is a low angle twist boundary evident within the *h*-BN particle which causes a local rotation of material from $[1\,1\,\bar{2}\,0]_{h\text{-BN}}$ at the interface with β-Si_3N_4. The selected area diffraction pattern from the region where (a) and (b) were taken is shown in (c). Arrowed reflections are from *h*-BN. Weak *h*-BN reflections are shown by double arrows.

interface. The β-Si_3N_4 grain is oriented parallel to $[0\,0\,0\,1]$ and the *h*-BN inclusion is oriented parallel to $[1\,1\,\bar{2}\,0]$, and so the *c*-axes of the *h*-BN particle and the β-Si_3N_4 grain are, respectively, perpendicular and parallel to the electron beam. Here, the $(1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$ planes make an angle of 3·5–4° with the interface plane, whereas once more the $(0\,0\,0\,1)_{h\text{-BN}}$ planes are parallel to the interface. Overlapping electron diffraction patterns and an examination of Fig. 4 by eye at an inclined angle both show that this orientation relationship enables a symmetrically equivalent set of $\{1\,0\,\bar{1}\,0\}_{\beta\text{-}Si_3N_4}$ planes to be parallel to the $(\bar{1}\,1\,\bar{0}\,2)_{h\text{-BN}}$ planes. Again, it can be argued that the orientation relationship observed is 'special' and the interface plane is also 'special', in the sense that it is a low index plane with respect to the *h*-BN particle, so it is not surprising that here too there is little evidence of the interface being wet by any amorphous film. The stepped nature of the interface on the β-Si_3N_4 side of the interface can be rationalised simply in terms of a step of height 6·58 Å perpendicular to the interface being required at regular intervals to accommodate the angular deviation of the interface plane away from $(1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$. The observed d_{ledge} = 70–100 Å spacing of the ledges is in accord with a calculation of 95–110 Å from the formula $d_{\text{ledge}} = 6{\cdot}58$ Å/ tan θ where $\theta = 3{\cdot}5$–4°.



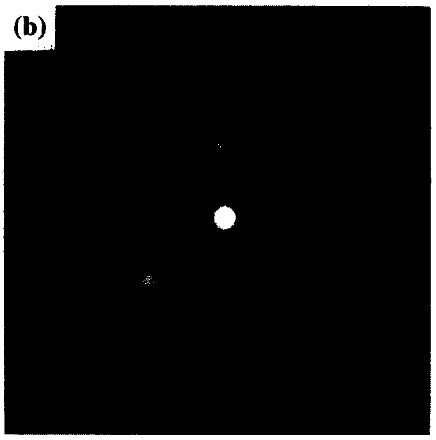


Fig. 4. (a) A regularly stepped interphase boundary between an h-BN particle and a β-Si_3N_4 grain where the beam direction was $[1\,1\,\bar{2}\,0]_{h\text{-BN}} \parallel [0\,0\,0\,1]_{\beta\text{-}Si_3N_4}$. Here, the $(0\,0\,0\,1)_{h\text{-BN}}$ planes make an angle of 3·5–4° with the $(1\,0\,\bar{1}\,0)_{\beta\text{-}Si_3N_4}$ planes and the interphase boundary is parallel to $(0\,0\,0\,1)_{H\text{-BN}}$. (b) Selected area electron diffraction pattern from the region where (a) was taken. Spots arrowed are all from h-BN. Spots labelled 'E' are extra spots from the β-Si_3N_4 grain on the left hand side of (a).

4 Conclusions

The experimental results presented here show convincingly that interphase boundaries between h-BN and β-Si_3N_4 observed in silicon nitride–silicon carbide particulate composites, in which h-BN particles arise as a trace contaminant by way of a chemical reaction at high temperature, can show a number of non-random orientation relationships. Interphase boundaries are dominated by $(0\,0\,0\,1)_{h\text{-BN}}$ planes. HRTEM of these interfaces shows that it is highly likely that they are free of amorphous intergranular films.

These observations are not in accord with a relatively high equilibrium film thickness between h-BN and β-Si_3N_4 grains which might be expected for general h-BN–β-Si_3N_4 interfaces wet by amorphous silica films on the Clarke model,[14,15] on the basis of a relatively low value of Hamaker constant, calculated to be 29×10^{-21} J for a silica film sandwiched between h-BN and β-Si_3N_4 with the interface parallel to $(0\,0\,0\,1)_{h\text{-BN}}$.[17] This compares with a Hamaker constant of 50×10^{-21} J for a silica film sandwiched between h-BN and β-SiC with the interface parallel to $(0\,0\,0\,1)_{h\text{-BN}}$ and where clear evidence of amorphous phases has been found at such interfaces in these silicon nitride–silicon carbide particulate composites.[18,19]

Acknowledgements

The authors would like to thank Dr S. M. Winder of The Carborundum Company, Niagara Falls, for the provision of the samples and for useful discussions. We would also like to thank Professor C. J. Humphreys for the provision of laboratory facilities during the course of this work.

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