Section 3: Ceramic materials

INVITED

# **INTERPHASE BOUNDARIES IN ENGINEERING CERAMICS**

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Interphase boundaries in engineering ceramics invariably contain thin intergranular films arising from the method of manufacture. Experimental evidence and theoretical understanding of these films is presented and discussed, with particular attention paid to circumstances where such films are not seen. In addition, evidence for and against the development of preferred orientation relationships and good lattice matching at intergranular and interphase boundaries is presented and discussed. This is relevant when developing models for the strength and toughness of engineering ceramics, and it can also be a reason for the absence of intergranular films.

*Keywords*: Engineering ceramics, Interfaces, Amorphous thin films, High-resolution transmission electron microscopy

# 1. Introduction

Intergranular and interphase boundaries in structural engineering ceramics such as silicon nitride and silicon nitride – silicon carbide particulate composites usually contain silica-rich glassy phases which arise as a consequence of impurities and additives present in the starting powders used to make the ceramics [1,2]. The more glass there is present in an engineering ceramic, the more it will be expected to creep at high temperatures, because of the exponential decrease in the viscosity of glasses with increasing temperature. However, at temperatures below 1000 °C, glassy phases can actually be beneficial, as they can increase the strength and toughness of ceramics though stress relaxation at crack fronts. In the recently developed ceramic nanocomposites, which have very large internal surface areas per unit volume, interphase boundaries, with or without glassy phases, necessarily have an important influence on composite performance.

In this overview, I will first consider various aspects of these intergranular glassy phases. I will show how transmission electron microscopy techniques can be used to determine the presence or absence of such glassy phases at interphase boundaries in structural engineering ceramics. When these are present, they show a narrow distribution of thicknesses of the order of 1 - 2 nm. I will show how this can be reconciled with theoretical models of the attainment of an equilibrium film thickness from suitable competing attractive and repulsive forces at interphase boundaries. Finally, I will summarise evidence for and against the development of preferred orientation relationships and good lattice matching at intergranular and interphase boundaries, as such considerations are relevant for the development of models for the strength and toughness of engineering ceramics.

# 2. Experimental evidence for intergranular glassy phases at interphase boundaries

In contrast to grain boundaries and interphase boundaries in metals, in which grains make intimate contact at the atomic level regardless of the orientation relationship across the boundary [3], the manufacturing processes used to make engineering ceramics encourage the development of liquid phases during sintering (both pressureless and pressure-assisted), and their retention as remanent glass at triple junctions and along grain boundaries and interphase boundaries after cooling to room temperature.

Such remanent intergranular glassy phases at grain boundaries and interphase boundaries cannot be seen by scanning electron microscopy and instead require transmission electron microscopy (TEM) procedures to show their existence. In these procedures, the boundary under examination is oriented so that it is parallel to the electron beam. The intergranular glassy phases can then be revealed by (i) dark field imaging from the part of reciprocal space into which there is scattering from the intergranular glassy phase, (ii) the behaviour of Fresnel fringes at the boundary as a function of defocus and (iii) high resolution transmission electron microscopy (HRTEM) [4]. Of these three techniques, the dark field technique is the least likely to give accurate quantitative information on the thickness of the glassy phases [4]. It is also the technique most likely to produce artefacts, most notably from preferential etching from ion beam thinning of the boundaries and subsequent sputter deposition or damage in these regions.

HRTEM requires that grains either side of the boundary have at least a one-dimensional lattice image to distinguish them from the intergranular glassy phases. If such conditions pertain, it is then possible to measure the width of the glassy phases to an accuracy of 1 Å [4]. Systematic studies on large numbers of high angle grain boundaries using this procedure show that, to within experimental error, the thickness of these glassy phases is remarkably uniform for a given material of a specific chemical composition (e.g., [5,6]), and that film thicknesses are typically of the order of 1 - 2 nm.

In this context, examples such as the interfaces shown in the HRTEM micrographs in Figure 1, which seem to go against other experimental observations, require explanation. In this micrograph taken from a SiC – Si<sub>3</sub>N<sub>4</sub> particulate composite, a 3C SiC grain abuts two  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains either side of a triple junction where there is a pool of amorphous material. The enlarged views of the interphase boundaries (IB(b) and IB(c)) in Fig. 1(a) shown in Fig. 1(b) and Fig. 1(c) respectively show that here the two film thicknesses are noticeably different, despite their meeting at the *same* triple junction. From enlargements of these micrographs, the film thicknesses at interfaces IB(b) and IB(c) were found to be  $19 \pm 1$  Å and  $14 \pm 1$  Å, respectively.

Such a clear difference can be explained in terms of highly non-equilibrium film thicknesses, different local film compositions (e.g., [6]), or as an effect arising from the orientation relationships between the  $Si_3N_4$  grains and the common 3C SiC grain. The recent analysis of the dependence of equilibrium film thickness on grain orientation at interphase boundaries in ceramic-ceramic composites by Knowles and Turan [7] concluded that such an orientation dependence will only arise if one or more phases is highly anisotropic optically, as will be the case for materials like graphite and hexagonal boron nitride. Silicon nitride is anisotropic, but the magnitude of this anisotropy is not sufficient to account alone for the marked differences seen in the interfaces in Fig. 1 [7].

Thus, other than suggesting that Fig. 1 actually represents a highly non-equilibrium situation, in which amorphous material has simply been trapped at interface IB(b), we are left with an interesting explanation, albeit one which is speculative, given the high diffusion rates which will be present during sintering: since during sintering the rate of re-precipitation of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> from the nitrogen-rich siliceous liquid is highly anisotropic, with growth parallel to [0001] faster than growth in the (0001) plane, it is possible that growth was slower at interface IB(b), thus leaving behind a more nitrogen-saturated amorphous silica phase. This would have the effect of increasing the refractive index of the glass locally, leading to a smaller attractive force between the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grain and the SiC grain at this interface, and enabling more amorphous material to be retained than at IB(c) [8].



Fig. 1. (a) An HRTEM image of two interphase boundaries between a 3C SiC grain and two  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains attached to the same triple junction. (b) and (c) are the enlarged views from the interfaces labelled as IB(b) and IB(c) in (a), showing clear differences in the film thickness.

## 3. Theoretical understanding of equilibrium film thicknesses

Theoretical understanding of the attainment of equilibrium film thicknesses at grain boundaries in ceramics was first addressed by Clarke [9] extending concepts from colloid science. He showed that an equilibrium film thickness arises from the competition between attractive dispersion forces determined by the dielectric properties of the grains, and repulsive disjoining forces, which can be steric forces and/or double-layer forces.

The most general condition which applies when there is an applied pressure, P, and a capillary pressure,  $P_{CAP}$ , is:

$$P + P_{CAP} + \Pi_{DISP} + \Pi_{ST} + \Pi_{EDL} + \Pi_{ADS} + \Pi_{HB} = 0 \tag{1}$$

where  $\Pi_{DISP}$  is an attractive dispersion force per unit area of interface arising from van der Waals forces,  $\Pi_{ST}$  is a repulsive steric force per unit area,  $\Pi_{EDL}$  is a repulsive electrical double-layer force per unit area,  $\Pi_{ADS}$  is a repulsive force per unit area arising from the effects of any solute absorption and  $\Pi_{HB}$  is an attractive force per unit area arising from any hydrogen bonding present.

Clarke [9] examined the form of equation (1) for the situation where  $\Pi_{EDL} = \Pi_{ADS} = \Pi_{HB} = 0$ , in which case the repulsive force per unit area enabling an equilibrium film thickness to arise is simply  $\Pi_{ST}$ . Subsequently, Clarke *et al.* [10] examined the situation where  $\Pi_{EDL}$ ? 0,  $\Pi_{ADS} = \Pi_{HB} = 0$  for zero and finite values of  $\Pi_{ST}$ . In this latter paper, two approaches were used to calculate the relevant electrical double-layer force: (i), the weak overlap approximation for the interaction between two similar surfaces at constant potential and (ii) solving the Poisson-Boltzmann equation. Both these approaches are discussed in detail by Israelachvili [11].

If, for a general grain boundary, we have a repulsive steric force per unit area and repulsive electrical double-layer forces describable by the weak overlap approximation, then in the absence of any forces arising from solute absorption and hydrogen bonding, equation (1) takes the form:

$$P + P_{CAP} + \frac{H}{6\pi L^3} - \frac{a\eta^2}{\sinh^2(L/2\xi)} - \frac{16k_BT}{z^2\pi b_L} \tanh^2\left[\frac{ze\Psi_s}{4k_BT}\right]\kappa^2 \exp(-\kappa L) = 0$$
(2)

where *L* is the film thickness,  $\xi$  is a molecular correlation distance,  $a\eta^2$  is a constant which is the free energy difference between ordered and disordered states of the film, *z* is the ion charge, *e* is the electronic charge,  $b_L$  is the Bjerrum length,  $\Psi_s$  is the electrostatic potential on the surface of the grains, *T* is temperature,  $k_B$  is Boltzmann's constant,  $\kappa^{-1}$  is the Debye screening length and *H* is the Hamaker constant of the interface containing the amorphous film [9,10].

When considering covalently bonded materials such as SiC and  $Si_3N_4$  interacting across a thin film of amorphous silica, the ionic contribution from any electrical double-layer forces is likely to be extremely modest. Given that Clarke *et al.* [10] establish that it is only under certain restricted conditions that it is plausible for an electrical double-layer force to contribute significantly to the total repulsive force, it is safe to neglect this contribution when discussing interfaces in nitride and carbide ceramics, the materials where most experimental data are available on equilibrium film thicknesses. Thus, equation (2) simplifies to the situation:

$$P + P_{CAP} + \frac{H}{6\pi L^3} - \frac{a\eta^2}{\sinh^2(L/2\xi)} = 0$$
 (3)

Israelachvili [11] discusses the various approximate and analytic formalisms for H, with the conclusion that where two macroscopic isotropic phases 1 and 2 interact across an isotropic medium 3, a suitable approximation to the relevant Hamaker constant valid for L greater than molecular dimensions is:

$$H_{132} \approx \frac{3}{4} k_{\rm B} T \left( \frac{\varepsilon_1(0) - \varepsilon_3(0)}{\varepsilon_1(0) + \varepsilon_3(0)} \right) \left( \frac{\varepsilon_2(0) - \varepsilon_3(0)}{\varepsilon_2(0) + \varepsilon_3(0)} \right) + \frac{3h v_{el}}{8\sqrt{2}} \frac{\left(n_1^2 - n_3^2\right) \left(n_2^2 - n_3^2\right)}{\left(n_1^2 + n_3^2\right)^{1/2} \left(n_2^2 + n_3^2\right)^{1/2} \left\{ \left(n_1^2 + n_3^2\right)^{1/2} + \left(n_2^2 + n_3^2\right)^{1/2} \right\}}$$
(4)

where  $\varepsilon_1(0)$ ,  $\varepsilon_2(0)$  and  $\varepsilon_3(0)$  are the zero frequency dielectric permittivities of phases 1, 2 and 3,  $n_1$ ,  $n_2$  and  $n_3$  are the refractive indices in the visible of the three phases, h is Planck's constant and  $v_{el}$  is the characteristic electronic absorption frequency in the ultraviolet, assumed in the analysis of Israelachvili to be the same for all three materials, with a value  $\sim 3 \times 10^{15} \text{ s}^{-1}$ .

Hence, when 1, 2 and 3 are isotropic, an equilibrium film thickness can be found by substituting equation (4) into equation (3) and solving for L. It follows from this analysis that L will be zero if the Hamaker constant is sufficiently high, i.e., if the attractive dispersion forces arising from van der Waals forces are sufficiently high, or if the magnitude of the repulsive forces is too low. It also follows from equation (3) that the equilibrium film thickness will not depend on the misorientation across the interphase boundary, but is determined instead solely by the relative dielectric properties. In practice for ceramics, the dispersion energy term containing the refractive indices in the visible of the respective phases dominates the right hand side of equation (4), so that the dielectric properties at optical frequencies are the most important.

Recently Knowles and Turan [7] have considered the extension of Clarke's theory to the situation where phase 1 is optically uniaxial, and have shown that if this exhibits very strong anisotropy, as in the case of *h*-BN and graphite, *H* will be a sensitive function of the interface crystallography, so that a noticeable dependence of equilibrium film thickness on crystallographic orientation is to be expected. The trends they calculated for *h*-BN – 3C SiC interfaces were found to be in accord with experimental observations.

### 4. Experimental evidence for preferred orientation relationships

Low angle grain boundaries in ceramics are examples of situations where the solid-solid interfacial energy,  $\gamma_b$ , is low, or equivalently where the magnitude of the repulsive forces between adjacent grains is low. In such cases, films are expected to be absent, the rationale being that  $\gamma_b$  is less than that of the wetted boundary,  $2\gamma_l$ , where  $\gamma_l$  is the liquid-solid interfacial energy [12]. Other low energy boundaries such as twin boundaries might similarly be expected not to have thin intergranular films. Qualitatively, this is consistent with experimental observations of boundaries free of intergranular films [13-15].

It might therefore be expected that boundaries where no evidence can be found for the presence of an intergranular glassy phase might be considered to be 'special'. Generalising this concept to interfaces between particles and surrounding matrices, a situation which arises in ceramic nanocomposites, it is relevant to determine whether or not preferred orientation relationships occur, and the consequences which follow.

The most widely studied ceramic nanocomposite system is that of SiC nanoparticles dispersed in alumina [16]. Different workers on SiC –  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanocomposites have drawn contrasting conclusions from their studies: while Ohji *et al.* [17] have developed a model for toughening in SiC – $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanocomposites on the basis of the good lattice matching they infer arises at SiC –  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interfaces from their own work and that of others (e.g., [18]), others have drawn the conclusion that there is no characteristic orientation relationship between the SiC particles and the surrounding  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> grains, even though they found no evidence for glassy phases [19]. The detail of the SiC –  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interfaces is important in developing models of the fracture toughness of ceramic nanocomposites: Ohji *et al.* [17] made estimates of interface strength on the basis of their TEM observations which they then incorporated into their crack-tip bridging model of toughening in ceramic nanocomposites.

In other ceramic nanocomposite systems, evidence for preferred orientation relationships is unambiguous. Two examples from recent work on the microstructural characterisation of SiC – Si<sub>3</sub>N<sub>4</sub> particulate composites, in which Si<sub>3</sub>N<sub>4</sub> was added at levels either of 10 wt% or 20 wt%, are shown in Fig. 2 and Fig. 3. In these composites, nanoscale inclusions of both Si<sub>3</sub>N<sub>4</sub> and *h*-BN were found [20]. The sub-micron size *h*-BN grains 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 [21].

The example in Fig. 2 of an interface between an *h*-BN particle and a  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grain shows that a non-random orientation relationship has arisen here. The (0001) *h*-BN planes are parallel to the interface, which makes an angle of  $3.5 - 4^{\circ}$  with the (1010)  $\beta$ -Si<sub>3</sub>N<sub>4</sub> planes. Overlapping electron diffraction patterns and an examination of Fig. 2 by eye at an inclined angle both show that this orientation relationship enables a symmetrically equivalent set of {1010}  $\beta$ -Si<sub>3</sub>N<sub>4</sub> planes to be parallel to the (1102) *h*-BN planes [22]. There is also a striking absence of an amorphous intergranular film. The stepped nature of the interface on the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> 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 (1010)  $\beta$ -Si<sub>3</sub>N<sub>4</sub>.

The {1010 } faceted  $\beta$ -Si<sub>3</sub>N<sub>4</sub> precipitate in a 3C SiC grain shown in Fig. 3 also has a characteristic orientation relationship with the surrounding SiC grain. Here, the [110] 3C SiC and [0001]  $\beta$ -Si<sub>3</sub>N<sub>4</sub> directions are ~ 4° apart. It is evident from Fig. 3(b) and Fig. 3(c) that the (001) 3C SiC and (1010)  $\beta$ -Si<sub>3</sub>N<sub>4</sub> planes are almost parallel, but there is a definite measurable small rotation of ~ 2° between these two sets of planes about the 'common' zone axes. Interfaces IB1 and IB4 between the precipitate and the surrounding grain in Fig. 3(a) are parallel to [0001]  $\beta$ -Si<sub>3</sub>N<sub>4</sub> within experimental uncertainty, while interfaces IB2, IB3, IB5 and IB6 are almost parallel to the electron beam. Examination of these interfaces at a higher magnification and after suitable specimen tilting to make them parallel to the electron beam showed that both IB1 and IB4 contained thin intergranular films, but that interface IB6 and the interface between IB1 and IB6 appeared to be free of intergranular film [8].



Fig. 2. A regularly stepped interphase boundary between an h-BN particle and a  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grain where the beam direction was [1120] *h*-BN || [0001]  $\beta$ -Si<sub>3</sub>N<sub>4</sub>. Here, the (0001) *h*-BN planes make an angle of  $3.5 - 4^{\circ}$  with the (1010)  $\beta$ -Si<sub>3</sub>N<sub>4</sub> planes and the interphase boundary is parallel to (0001) *h*-BN.

#### 5. Theoretical understanding of preferred orientation relationships

Given experimental evidence for preferred orientation relationships under suitable circumstances, such as between nanoscale ceramic precipitates of one phase and adjacent grains of a second ceramic phase, it is reasonable to hypothesise the reasons for these. For  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> – 3C SiC interfaces where a preferred orientation relationship could be identified, Unal and Mitchell [23] proposed that matching of SiN<sub>4</sub> and SiC<sub>4</sub> tetrahedra dominated the tendency for (1010)  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> to be parallel to the {111} surfaces of underlying 3C SiC substrates. They accounted qualitatively for small rotations away from the ideal orientation relationship of [110] 3C SiC || [0001]  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> that they observed experimentally in terms of the relief of structural mismatch arising from the large misfit between corresponding crystal planes of the two structures, as shown in Table 1 of [23]. However, this explanation does not address the question of why the orientation relationship approximating to [110] 3C SiC || [0001]  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and (001) 3C SiC || (1010)  $\beta$ -Si<sub>3</sub>N<sub>4</sub> also dominates other experimental observations of Si<sub>3</sub>N<sub>4</sub> – SiC interfaces where {111} 3C SiC substrates are not used [24,25].

A first approach to the general problem of understanding the basis for preferred orientation relationships is through the near-coincidence concept, whereby misfits can be specified between supercells of two crystal lattices [26,27]. While obvious caution must be exercised in the use of geometric criteria such as low misfit for implying low interfacial energies (see, for example, Sutton and Balluffi [28] who conclude that no geometric criterion for low interfacial energy can be regarded as wholly reliable), there is at present no suitable atomistic modelling algorithm which can be used

to examine structures and energies of interfaces between crystalline phases where one or more phase is covalently bonded.

In the near-coincidence site lattice (NCSL) approach, the details of atomic bonding at the interfaces are necessarily of secondary importance, although ultimately the adoption of any particular three-dimensional orientation relationship and the energetics of the interface will be determined by the way in which atoms bond at the interfaces. Recent computations of near-coincident cells between 3C SiC and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> have shown that while there are no orientation relationships between Si<sub>3</sub>N<sub>4</sub> and 3C SiC which have extremely low misfits and relatively small supercell volumes, there are orientation relationships for which the misfits are reasonably low and the supercell volumes reasonably small, and which can account for the preferred orientation relationships seen between particles and surrounding matrices when either there are no intergranular films present at interfaces, or incomplete interfacial coverage [8]. Similar calculations also give support to the suggestion that the orientation relationship in Fig. 2 between *h*-BN and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> is one of low misfit [29].

Further NCSL calculations on other systems contrast with these two examples. Interfaces between small h-BN particles and 3C SiC consistently show a favoured orientation relationship where (0001) h-BN planes are parallel to (111) 3C SiC planes, even though is clear evidence for ~1.2 nm thick intergranular films at the interfaces [30,31]. However, NCSL calculations demonstrate that there are no low misfit descriptions which can explain such a dominant experimental observation [29]. Instead, it turns out that there is a simple explanation for the alignment of these planes in the composites examined by Turan [20]: since a number of SiC grains in the composites were bounded either by  $\{111\}\ \beta$ -SiC or (0001)  $\alpha$ -SiC planes, the chemical reactions forming the h-BN particles do so in a manner whereby basal plane 'meshes' of h-BN are deposited on available low energy SiC planes, leading to inclusions where growth normal to [0001] is relatively difficult, but where the meshes can grow relatively rapidly within the (0001) planes. This qualitative explanation can account for the further observation that this alignment occurs both with and without the presence of intergranular amorphous films, depending on whether or not there is a deoxidation step in the processing route chosen for the composites [31]. It is also in accord with observations of the deposition of crystalline thin films on glass substrates, where preferred orientations are also seen, in which relatively dense close packed planes of the thin films are deposited parallel to the substrate surfaces [32,33].

Application of the NCSL methodology to SiC –  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interfaces summarised elsewhere [29] shows that there is no orientation relationship between either 3C SiC and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or 6H SiC and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> which has extremely low misfits and low values of supercell volumes, although there are a number of NCSL descriptions that have plausible misfits and reasonably small supercell volumes. However, a comparison of NCSL pairs with available experimental evidence is inconclusive. None of the experimental high resolution TEM work reported on SiC –  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interfaces in ceramic nanocomposites interfaces provides electron diffraction evidence [19, 34-36].



20 nm



Fig. 3. (a) Low magnification high resolution image with the [0001]  $\beta$ -Si<sub>3</sub>N<sub>4</sub> direction parallel to the electron beam showing a cross section of a {1010} faceted  $\beta$ -Si<sub>3</sub>N<sub>4</sub> precipitate embedded in a 3C SiC grain. (b) Electron diffraction pattern from (a) with the SiC spots arrowed. There is a relative rotation of 90° with respect to the image in (a). (c) Electron diffraction pattern from SiC and the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> precipitate after tilting 4° away from (b) to make the electron beam close to [110] SiC.

The proposition of Kaplan *et al.* [19] that simple orientation relationships between  $\alpha$ -SiC particles and surrounding  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> grains do not occur does not preclude more complex preferred orientation relationships, but these authors have not given details of the orientation relationships they found, and so their proposition cannot be tested. The same is true of the high resolution TEM work reported by Ohji *et al.* [34]: without a more comprehensive description of the orientation relationship between the SiC particles and the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> grains, it is simply not possible to infer that there is poor lattice match where the angle between lattice fringes is near 90° (e.g., Fig. 9 of [34]). Indeed, a more reasonable interpretation is that it is highly likely that there is some preferred orientation to enable lattice fringes to be obtained at the same orientation of the electron beam in both the particle and the grain.

Thus, more careful and systematic work needs to be carried out on SiC –  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interfaces in ceramic nanocomposites before it can be established beyond reasonable doubt whether or not 'special' orientation relationships between SiC and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are established, irrespective of the presence or absence of amorphous intergranular film. The generally accepted notion that the bonding between SiC and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is strong [7,8] has some high resolution TEM work to rely upon, but it is apparent that at present the interpretation of this TEM work is highly subjective.

## **6.** Conclusions

Interphase boundaries in engineering ceramics are of research interest, not only for the detection of thin intergranular films relevant to creep behaviour at high temperatures, but also because of the strength of the bonding at interfaces affects the strength and toughness of these materials. HRTEM is now a routine technique for the observation of such thin films. Preferred orientation relationships between nanoparticles and surrounding matrices, can arise both when intergranular films are present and when they are absent. If films are absent, or if there is incomplete coverage of intergranular film, as for example between  $\beta$ -Si<sub>3</sub>N<sub>4</sub> particles and 3C SiC grains where residual glassy phase is trapped at the interfaces and cannot completely escape, observed orientation relationships can be shown to have suitable NCSL descriptions and to have low misfits relative to other NCSL descriptions.

However, we cannot infer on the basis of geometry alone that low energy interfaces necessarily occur when such NCSL orientation relationships are adopted. It cannot be overemphasised that low misfits do not imply that interfaces necessarily have low energies, in contrast to such an assumption all too frequently made in the literature without any supporting evidence in the form of atomistic calculations. In this context, it would clearly be worthwhile to attempt to determine by atomistic simulation in the future once suitable methods are established whether, for example, low energy Si<sub>3</sub>N<sub>4</sub> –  $\beta$ -SiC interfaces are indeed generated when observed orientation relationships arise, in comparison with other possible orientation relationships.

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