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HIGH RESOLUTION ELECTRON MICROSCOPIC CHARACTERIZATION OF INTERFACES IN CERAMICS

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August 1984

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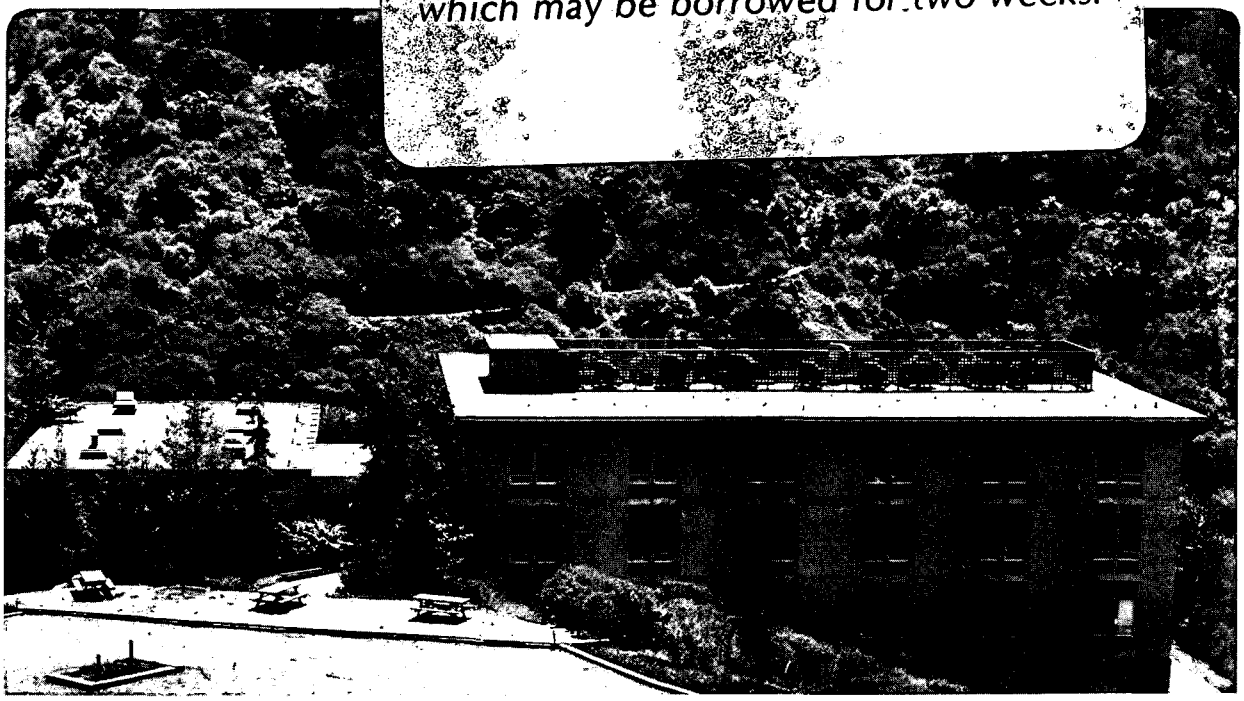

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This work was supported in part by the U.S. Department of Energy under Contract number DE-AC03-76SF00098; by NSF under Contract number DMR-83-1317239; and by AFOSR/DARPA under Contract number 83-0375.

HIGH RESOLUTION ELECTRON MICROSCOPIC CHARACTERIZATION OF INTERFACES IN CERAMICS

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ABSTRACT

High resolution electron microscopy (HREM) is useful in bringing out the microstructural variations, such as structural details at grain boundaries, at very high resolutions, even at atomic levels. An important aspect is the examination of the surface irregularities at the boundary regions which provide information on the transformation characteristics of the phases. In this paper, we present data on the microstructural characteristics of some high temperature ceramics (silicon nitride, mullite, and aluminum nitride) with particular emphasis on the detection of grain boundary amorphous phases. Furthermore, the HREM technique is reevaluated with reference to other techniques.

INTRODUCTION

Interfaces are of great fundamental and technological importance in polycrystalline ceramics since their properties, such as electrical and mechanical, depend largely on the interfacial characteristics. In the characterization of interfaces in ceramic systems, electron microscopy provides a unique opportunity. In the conventional mode, bright-field (BF) imaging does not have sufficient resolution for interfacial details, especially in very thin regions of second phases which may be present at grain boundaries. However, high resolution electron microscopy (HREM) is an advanced imaging technique which can provide invaluable information on the

details of the interfaces, e.g., interfacial steps, and lattice arrangements at or near the interfaces at atomic levels.[1,2] Especially important is the detection of thin film amorphous grain boundary second phases which usually occur in sintered ceramics.[3,4]

The presence of amorphous grain boundary phases in ceramics is generally associated with additives that are used as processing aids. For instance, in the case of silicon nitride ceramics, as a result of reactions between the surface silica present on the matrix powder and the processing aids (such as alumina, yttria, and magnesia) a liquid phase, which wets the grains and acts as a densifying agent, is formed during sintering.[3-7] A similar situation also arises during the sintering of aluminum nitride with (e.g., silica or calcia) additives.[8] In the case of mullite, a metastable liquid phase may be present during the course of densification.[9] In all cases, this amorphous grain boundary phase, with a low softening temperature, becomes responsible for the loss of strength at elevated temperatures.

The goal of this paper is two-fold. First, the technique of high resolution electron microscopy is discussed. Second, the use of HREM in the characterization of grain boundaries in ceramics is illustrated with case studies on silicon nitride, mullite, and aluminum nitride.

TECHNIQUE

An ideal condition for imaging an interface between two grains exists when the interface is parallel to the incident electron beam direction.[3,4,10] In this way, the details of both surfaces on either side of the boundary will be clearly revealed. For example, such a configuration of the grain boundary with a thin amorphous film is schematically illustrated in Fig. 1. Here, the boundary is seen edge-on with respect to the incoming electron beam. In order to image the boundary,

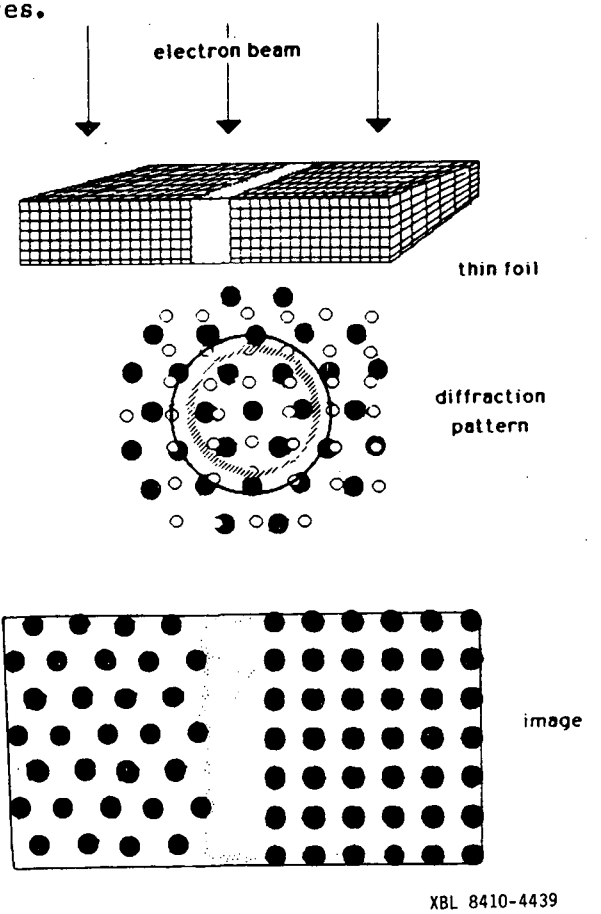

Figure 1. Schematic illustration of an edge-on configuration in imaging of an interface where the grains are in z.a. orientation.

an objective aperture is used which encompasses the diffraction spots due to both grains, as well as the diffuse ring (hatched) due to the inelastically scattered electrons from the amorphous region. Under favorable conditions consistent with the specimen-electron beam orientation discussed here and proper performance of all electron-optical alignments, a lattice image of the boundary region can be resolved in a sufficiently thin region of the foil. If both of the grains are in the zone axis (z.a.) orientation, then the atomic periodicities are resolved as schematically shown in Fig. 1, provided also that the correct defocus value has been set with an objective lens with sufficiently high resolving power (~0.2-0.3 nm). The presence of an amorphous layer can then be discerned from the lack of any atomic periodicity right at the boundary, even if the layer is 1.0 nm thick. The sensitivity of this image also depends on the boundary tilt and the defocus value of the image.

Compared to other imaging techniques, such as diffuse dark-field imaging (DDF)[10] in which the objective aperture is placed on the diffuse ring produced in the diffraction pattern due to the presence of an amorphous layer at the boundary, higher spatial resolution is achieved by the lattice imaging technique. In addition, an amorphous layer might be caused due to external effects, such as excessive carbon accumulation at the boundary groove which occurs during the carbon evaporation to the surface of the foil, a process used to prevent decharging during electron microscopy observation of insulators.

INTERFACE CHARACTERIZATION IN CERAMICS

Case I: Silicon Nitride

The silicon nitride compact used in this study was prepared with high purity powders of β-Si_3N_4, α-Al_2O_3, and Y_2O_3 with the use of an aqueous colloidal filtration route.[12] Densification was achieved by liquid phase sintering at 1750°C and 725 KPa nitrogen pressure.[12] The fully dense microstructures produced after this liquid phase sintering process displayed uniform distribution of β-Si_3N_4 grains (Fig. 2(c)). Two different second phases were determined within the microstructure: one crystalline and the other amorphous. Since there is no morphological difference between these two phases, geometrical effects in the crystallization behavior may be disregarded. However, a compositional analysis by energy dispersive x-ray spectroscopy (EDS) indicated a higher yttria content in the crystalline second phase than in the glassy regions, while electron energy loss spectroscopy (EELS) showed higher oxygen content in the glassy regions.[13]

The distribution of amorphous phase is homogeneous as revealed in the DDF micrograph of Fig. 2(b). Although the regions

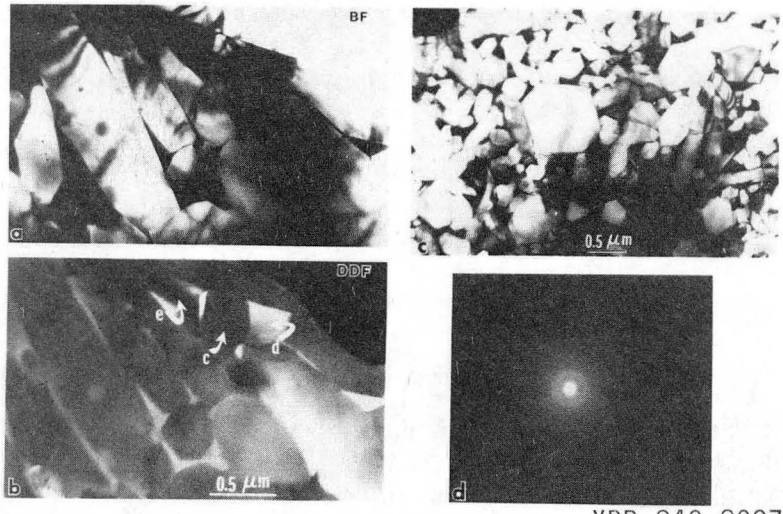

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Figure 2. (a) BF and (b) DF images from a thin foil showing the distribution of glassy phase; (c) low magnification BF image showing the general microstructure; (d) microdiffraction pattern from glassy region revealing only diffuse scattering.

indicated as e and d produce similar contrast in the BF image of Fig. 2(a), only the region d changes contrast in the DDF image. In fact, microdiffraction from region e produces elastic scattering while diffuse scattering is produced from region d (Fig. 2(d)).

At low resolutions and magnifications (Fig. 2(c)), it is not possible to reveal whether or not grain boundaries are also covered with a thin (usually 2-10 nm thick) amorphous phase, which is usually the case in all liquid phase sintered silicon nitrides.[5,6] Therefore, it becomes necessary to perform HREM. The example given

in Fig. 3 is of interest for several reasons: First, one of the grains is Si-Al-Y-oxynitride and the other is Si_3N_4. Second, both of the grains are in the z.a. orientations. An amorphous phase is clearly seen in the lower portion as indicated by Am. However, as one follows this amorphous region towards the boundary, it is seen that several nanometers inside the boundary the amorphous phase ends. At this portion of the grain boundary, atomic periodicities in both grains continue right to the boundary and stop when they reach each other. The absence of any discontinuity at the boundary then indicates the absence of an amorphous phase. Fig. 4

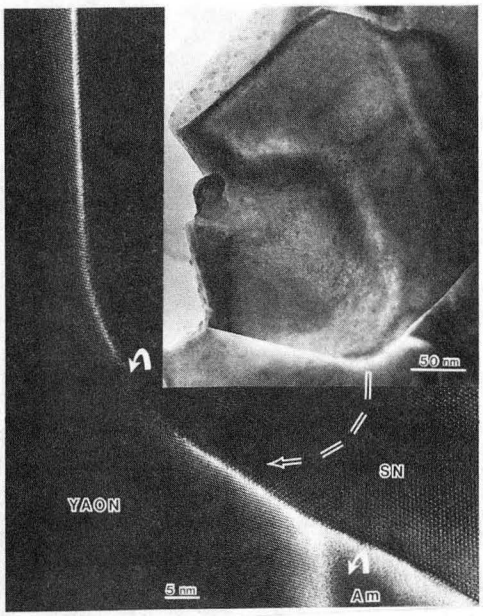

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Figure 3. HREM image of an interface between a Y-Si-Al-oxynitride and silicon nitride grains.

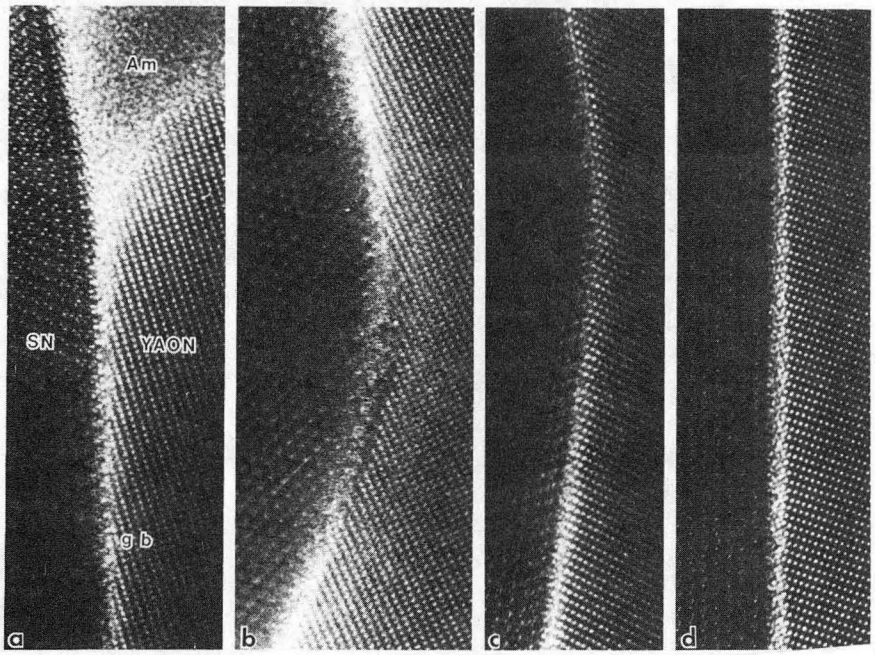

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Figure 4. Details of the interface shown in Figure 3.

presents a series of images along the boundary revealing the details at very high magnifications. Again, the absence of any amorphous phase film is made obvious by the presence of rows of atoms in both grains at the points of contact.

One of the objectives in reducing the detrimental effects of the amorphous phase is to crystallize it during cooling. This crystallization can be achieved when the liquid phase, which is present at the sintering temperature, reaches a composition of one of the complex yttrium-aluminum-silicon oxynitride phases. Many factors can affect this process, such as compositional variations due to inhomogeneities in mixing, and the temperature and pressure of sintering. An example of such a case is shown in Fig. 5. At the triple junction of Fig. 5, where normally an amorphous phase would be present, lattice fringes are revealed which indicate that the amorphous phase has crystallized. However, upon a close examination of the boundary between this crystalline phase and the silicon nitride grains, one can still see a thin layer of amorphous film. Micrographs taken along the boundary region between the silicon nitride grains indicate that this film is discontinuous and the rest of the boundary is free from any amorphous layer.

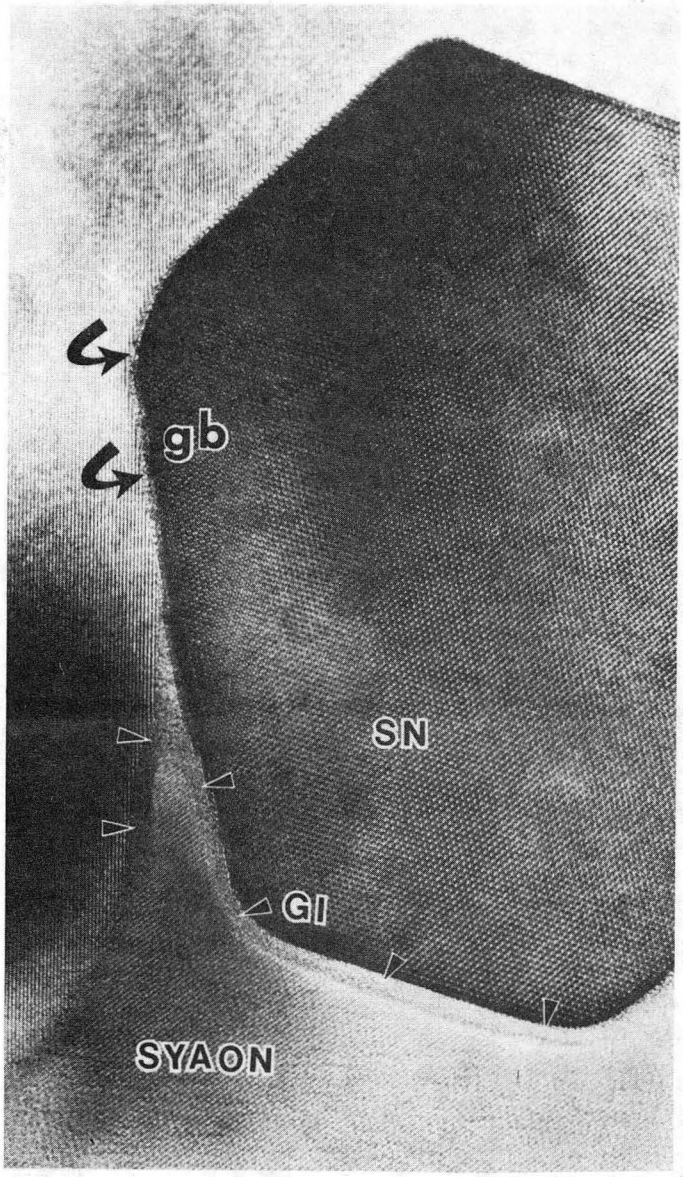

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Figure 5. Low magnification HREM image revealing a crystalline phase, formed from the amorphous phase, at a three-grain junction.

Case II: Mullite

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is the only stable intermediate compound in the silica-alumina binary system.[14] Mullite's main importance as a structural material comes from the fact that it has favorable thermal shock resistance, low specific gravity, good corrosion resistance, and especially high creep resistance.[15]

In the processing of mullite, recent trends have favored the use of submicron size particles or molecularly mixed systems in order to enhance the mullitization process during densification.[9,16] The mullite compact that was examined in this current study was similarly prepared by a colloidal filtration process of submicron size alumina and kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$).[17] The premise of the work was to show that if diffusion distances were shortened, diffusion controlled reactions could be completed at relatively low temperatures (<1550°C) to form liquid free mullite. The results of the electron microscopy observations are as follows.

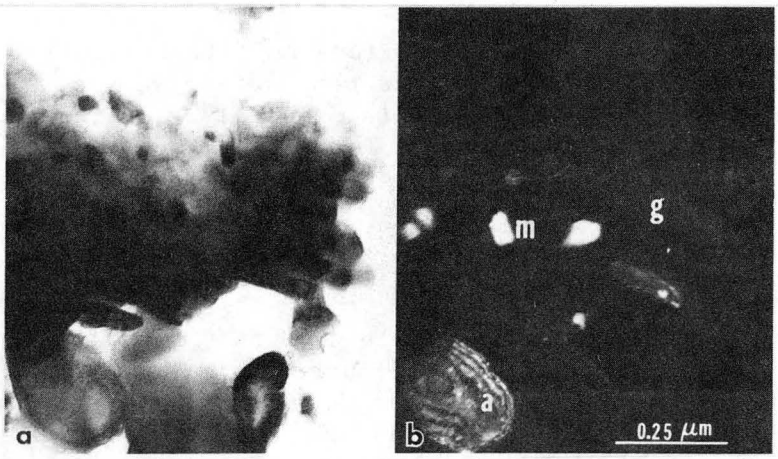

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Figure 6. (a) BF and (b) DF micrographs from 1300°C sample. The amorphous phase, G, surrounding the crystals, M, are also revealed. Alumina crystals are still present as indicated by A.

In Fig. 6, the pair of TEM micrographs displays a characteristic region of a sample that was heat treated at 1300°C for 1 hr to achieve partial densification. In the BF image, small mullite crystals with well defined rectangular shapes are seen in various orientations. This is more clear in the dark-field (DF) micrograph (b), which was taken by using a superimposed reflection formed by the diffraction from those crystals which change contrast. The size of these crystals ranges from 10 to 100 nm. Mullite particles are embedded in an amorphous matrix which is mostly SiO_2. (It should be noted here that because of experimental difficulties and uncertainties, quantitative chemical analysis by EDS method was not performed.) The distribution of this glassy phase is seen as a

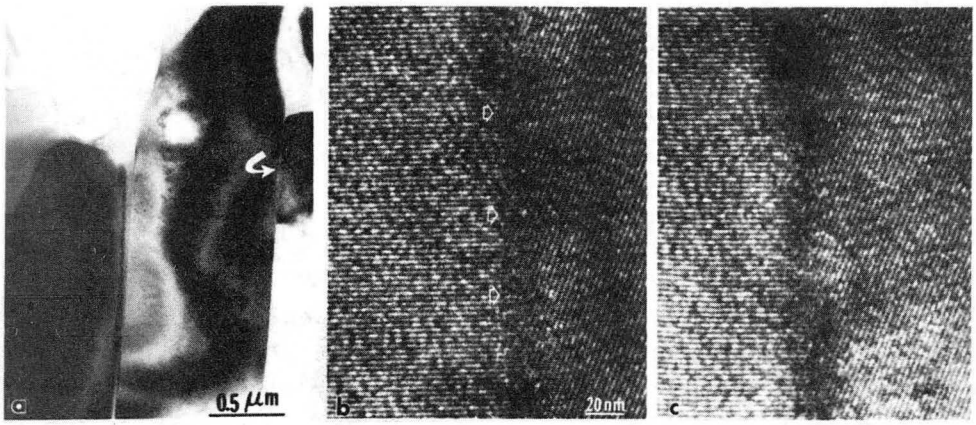

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Figure 7. (a) BF image from 1500°C sample. (b) and (c) are are HREM images taken along the boundary shown by arrow in (a) revealing the absence of any amorphous layer.

faint bright background in the DF image (due to diffuse scattering). The duration of sintering at this temperature was not sufficiently long enough to result in complete dissolution of the alumina grains within the amorphous matrix. Therefore, some alumina still remained in the compact (as indicated by letter A in the micrograph).

A portion of the microstructure evolved after a densification treatment at 1500°C, for 1 hr, is shown in Fig. 7(a). In comparison to the 1300°C treatment, considerable growth of mullite crystals has occurred at the expense of the surrounding matrix. Although an amorphous phase could still be detected in certain portions, the amount is reduced considerably and many mullite-mullite grain boundaries appear to be free of the amorphous phase. HREM is utilized to examine the mullite grain boundaries. A favorable configuration of imaging is presented in Fig. 7, where the boundary between grains B and C, each exhibiting one set of fringes, was examined. The fringes in grain C are continuous up to the interface where the fringes in grain B are also revealed. It was ascertained from this and other micrographs that many grain boundaries were free from an amorphous phase.

Case-III: Aluminum Nitride

AlN is a member of the SiAlON system and is used for high temperature applications.[18] Only limited work has been reported on the Al rich corner of the SiO_2-Al_2O_3-Si_3N_4-AlN system.[18-20] Similar to the silicon nitride ceramics, AlN can be sintered with the aid of sintering additives such as silica and calcia. Small amounts of silica (5-10 %) produce alloys near the 2H phase field.[8] The

samples in the present investigation (with 10% SiO_2 addition) were prepared by a two stage sintering process: First at 2000°C and then at 2100°C under 300 kg/cm^2 pressure in nitrogen atmosphere.[8] In this research, our intent was to study the 2H to polytypoid transformation. HREM was utilized to examine the details of the 2H/polytypoid interface.

Conventional characterization of the microstructure revealed high amounts of different types of polytypoids, in addition to the original 2H structure.[20,21] Polytypoids form because of the change in the stacking sequence. The reason for the local change in the hcp stacking sequence (ABABAB..) to cubic (ABCABC..) in AlN is because of the deviation of Al/N ratio from 1. As the Al/N ratio decreases, more N is taken into the structure. Together with N, Si and probably O are taken into the structure to keep the charge balance. In fact, a recent study with EELS indicated that oxygen is indeed incorporated into the polytypoid structure.[21] There is also 5-10% Si in polytypoids as measured by EDS and no Si in the original grains.[21]

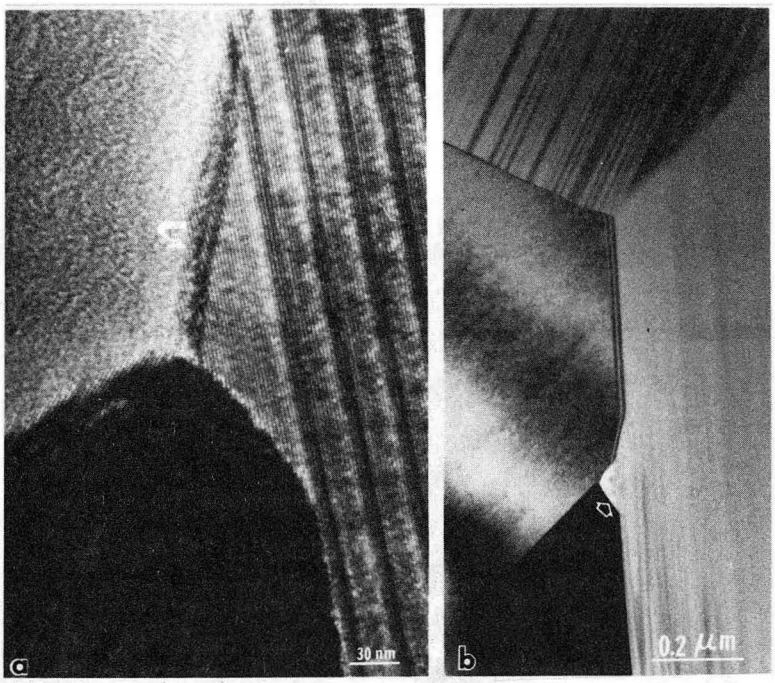

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Figure 8. (a) Lattice fringe image and (b) BF image taken from the AlN sample showing the details of a boundary region (arrow).

An example of the AlN microstructure examined in this study is shown in Fig. 8. In the low magnification BF micrograph (b), one can see a triangular projection of a three grain junction, which may be interpreted as a "glassy pocket" at this low magnification. However, the HREM micrograph in (a) reveals that this region is indeed crystalline and, interestingly enough, has an original 2H structure rather than the polytypoid seen on the right of the micrograph, which repeats itself through the whole grain. Another interesting feature in micrograph (b) is the presence of several different polytypoids in a grain seen at the top of the picture, which are frequently observed in these samples. Therefore, in this grain, faulting is

not a regular single type but is a combination of different types which repeat regularly throughout the structure.

It is often very useful to find grains which are half-transformed. Examination of the interfaces between the transformed and the untransformed regions reveals valuable information about the nature of the interfaces which could be related to the mechanism of transformation. Both straight boundaries and boundaries containing ledges were observed in an earlier study.[21] Fig. 9 shows an example of the latter type. In the BF image of Fig. 9(a), the end part of the long grain is seen where, in either side of the grain, two small pockets of the original grain (shown by arrows) were left untransformed. The high resolution image in (b) reveals the details of the interface between the 2H and the polytypoid where the steps, or ledges, at the interface are clearly seen. It was hypothesized earlier[21] that the growth of polytypoids occurs when the concentration of nitrogen reaches a critical value in the original structure. Under a positive nitrogen atmosphere and high temperature, nitrogen is taken into the structure at the boundary by forming ledges. The size of the ledges and, therefore, the type of the polytypoid is then determined by the local concentration of nitrogen in the structure which dictates the Al/N ratio.

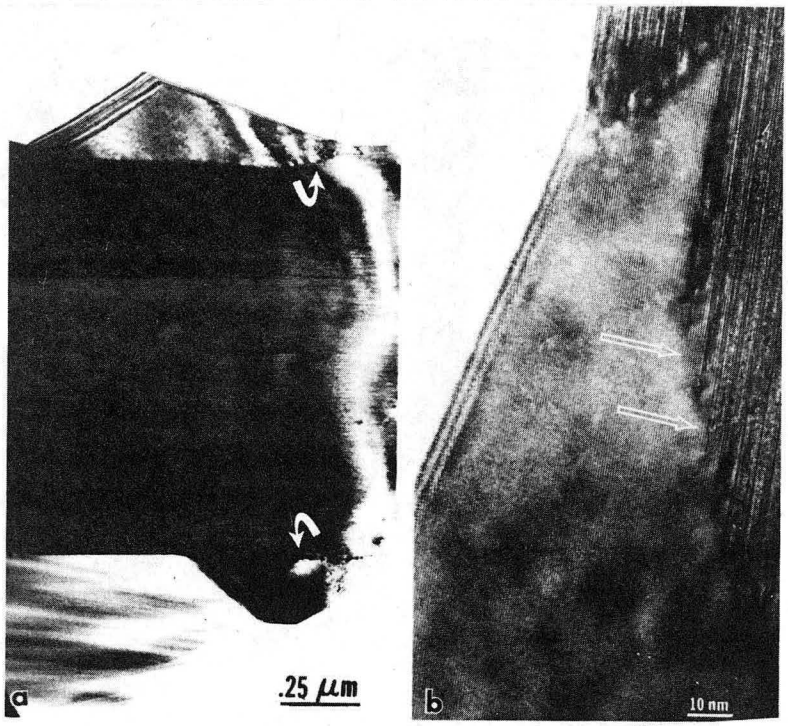

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Figure 9. (a) BF image showing 2H/Polytypoid boundaries containing ledges, and (b) HREM image revealing the details of the boundary indicated by B in (a).

CONCLUSIONS

High resolution electron microscopy technique was used to reveal microstructural details in some ceramic systems. Lattice image analysis resulted in the following conclusions:

(1) At some grain boundaries of silicon nitride ceramics (fluxed with alumina and yttria) a glassy phase is absent and in some cases even a crystalline second phase is observed at three grain junctions.

(2) In mullite ceramics, mullite-mullite grain boundaries are shown to be glass-free provided that sufficient time is allowed during the densification stage to achieve an equilibrium phase structure.

(3) AlN doped with 10% silica does not contain a glassy phase but has polytypoids in which the Al/N ratio deviates from the value in the original, 2H, structure. Stepped, or ledged, interfaces as well as straight boundaries can be formed between polytypoids/2H grains depending on the transformation stage.

ACKNOWLEDGEMENTS

Financial support from NSF (DMR-83-1317239) for the work on silicon nitride and aluminum nitride and from AFOSR/DARPA (83-0375) for mullite work is greatly acknowledged. We thank K. Komeya for providing the AlN samples.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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