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Proceedings of the 14th University
Conference on Processing of
Crystalline Ceramics, North Carolina
State University, Raleigh, NC,
November 7 - 9, 1977

UC-25
LBL-6985
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SILICON NITRIDE BASED ALLOYS

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David R. Clarke and G. Thomas

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THE STRUCTURE OF GRAIN BOUNDARIES
IN SILICON NITRIDE BASED ALLOYS

David R. Clarke
Structural Ceramics Group
Rockwell International Science Center
Thousand Oaks, California 91360

and

G. Thomas
Materials Science and Mineral Engineering
University of California
Berkeley, California 94720
Lawrence Berkeley Laboratory

Abstract

Grain boundaries in silicon-based ceramics have been characterized by high resolution electron microscopy including the technique of lattice fringe imaging, and this work is illustrated with examples from both hot-pressed silicon nitrides (MgO and Y_2O_3 fluxed) and a magnesium-sialon ($\text{Mg}_{1.86}\text{Si}_{1.67}\text{Al}_{2.47}\text{O}_{3.19}\text{N}_{3.81}$). Room temperature observations of the glassy phase are consistent with it being only a partially wetting phase, indicating that it cannot form a continuous film. The atomic configuration of the grain boundaries in both materials is presented together with lattice fringe observations of segregation at grain boundaries in the magnesium-sialon.

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INTRODUCTION

Grain boundaries and phase boundaries have long held a special significance for the ceramist. In part this is because of their profound influence on both the fabrication of components from powders and on the resulting mechanical and electrical properties. Partly this is also because so little is known about them from existing experimental techniques. However, this situation is changing with the advent of two techniques that promise to revolutionize our understanding of boundaries in ceramics: high resolution transmission electron microscopy and Auger electron spectroscopy. The importance of high voltage electron microscopy must not be overlooked as this method whilst not yet at the resolution capabilities of 100 kV offers advantage of increased penetration, reduced ionization damage, and better statistical data. In this present paper the characterization of boundaries in silicon-based ceramics will be described using 100 kV electron microscopy exclusively.

The application of high resolution electron microscopy to the investigation of grain boundaries is still very much in its infancy; the first results were reported at two international conferences just a year ago.(1,2) Consequently, the correlation between processing variables and microstructure of the grain boundary regions is very undeveloped in comparison to those that will be presented in other papers at this meeting.

After a brief account of the techniques of electron microscopy, three aspects of the structure of grain boundaries pertinent to ceramics will be discussed: the location and distribution of intergranular phases, the crystalline structure of the boundary itself, and the segregation of solute to the grain boundary.

TECHNIQUES AND MATERIALS

Two principal techniques of high resolution electron microscopy have been used to investigate the nature of boundaries in ceramics: lattice fringe

imaging and high resolution bright and dark field imaging. As they have been described at length in a recent review,⁽³⁾ they will only be mentioned in outline here.

In lattice fringe imaging, the microscope is operated in a phase contrast mode by recombining two or more diffracted beams, enabling one or more sets of atomic planes in the sample to be imaged directly. As a result, microstructural detail down to an atomic spacing can be examined, for instance, grain boundary ledges in hot-pressed silicon nitride 3.3A high can be readily resolved. The other mode, that of high resolution bright field/dark field imaging, the electron microscope is operated in an amplitude contrast manner by imaging the transmitted beam alone or in dark field imaging one of the diffracted beams. In this case, image detail results from variations in relative scattering of the electron beam produced by adjacent regions and the resolution is limited by contrast variations. Nevertheless, intergranular films 10A in width in hot-pressed silicon nitride have been detected in this way under favorable conditions.

Results from an investigation of three different types of ceramic are used here: commercially available silicon nitrides based on additions of MgO (Norton Company HS110, HS130, and NC132), a 10 m/o Y_2O_3 hot-pressed silicon nitride (kindly provided by Dr. F. F. Lange), and a magnesium-sialon ($Mg_{1.86} Si_{1.67} Al_{2.47} O_{3.19} N_{3.81}$, kindly supplied by Professor K. H. Jack).

INTERGRANULAR FILMS

The properties of a number of materials of contemporary interest appear to depend critically on the presence of an intergranular phase. For example, the nonlinear electrical conduction of the ZnO based varistors is attributed to the existence of a Bi_2O_3 rich phase at the ZnO grain boundaries;⁽⁴⁾ the lowering of eddy current losses in soft magnetic ferrites can be explained by a thin film layer between the ferrite grains;⁽⁵⁾ and the presence of a glassy phase at the grain boundaries has been held responsible for the high

temperature strength degradation of MgO fluxed and hot-pressed silicon nitride.(6,7) In each case, good agreement is found between the observed properties and those calculated on the basis that there is a continuous intergranular film separating the grains. However, whether or not the intergranular phase does indeed coat the individual grains is important to know in both suggesting ways of improving the material properties and in furthering our understanding of the origin of these properties.

Thus, as part of an investigation into the microstructure of silicon-nitride based ceramic alloys, the distribution and location of the intergranular phases in silicon nitrides hot pressed with magnesia and with yttria have been extensively examined. The main findings of those studies(1,2,8,9) have been that (1) the intergranular phase is inhomogeneously distributed throughout the microstructure with it located principally at three- and four-grain junctions, (2) many of the grain boundaries examined are devoid of any phase separating the grains, and (3) intergranular films as narrow as 8A are seen at some boundaries and, in many of these cases, the boundary is formed by the low-index plane in one of the two adjacent grains.

Observations illustrating these findings have already been published(1,8,9) so, rather than repeat them with other similar micrographs of silicon nitride, the opportunity is taken here to present observations from another silicon nitride alloy that also contains a glassy phase. The alloy, a magnesium substituted silicon-aluminum-nitrogen-oxygen alloy(10) has the composition $Mg_{1.86} Si_{1.67} Al_{2.47} O_{3.19} N_{3.81}$ but for brevity is referred to here simply as a magnesium-sialon. It was originally investigated as a part of a study into compositionally controlled polytypism, described elsewhere in these proceedings,(11) but it is found that the distribution of the glassy phase is the same as that in the hot-pressed silicon nitrides.

The magnesium-sialon consists of long interlocking plates several microns in length and about one micron across as may be seen in Fig. 1 of the

accompanying paper (Shaw and Clarke, these proceedings). In addition, at the three- and four-grain junctions, a glassy phase is frequently seen. Because of the exaggerated plate-like morphology of the grains, the three-grain junctions are typically wedge shaped in cross-section, as is shown in Fig. 1. These regions are generally too small for selected area electron diffraction to be used to determine whether they are glassy or crystalline, but as they remain featureless on tilting the sample in the microscope, it can be concluded that they are probably glassy.

In many of these glassy triple-grain junctions, secondary crystallization has occurred, as in Fig. 1. Unfortunately, again the regions are too small to obtain electron diffraction patterns from so it is impossible to determine what phase they consist of. Interestingly, however, these secondary crystallites have an ill-formed morphology in contrast to the highly faceted adjoining grains, and they lack the long stacking periodicities characteristic also of the adjacent sialon grains. This secondary crystallization is not unique to this material; it is also observed in magnesia hot-pressed silicon nitride where small grains of the silicon oxynitride $\text{Si}_2\text{N}_2\text{O}$ can be seen surrounded by glass at three-grain Si_3N_4 junctions.

As with the silicon nitride, many grain boundaries and occasionally even a three-grain junction are free of any glass. This may be vividly seen in Fig. 2 in which the long period polytype fringes have been imaged. The micrograph also illustrates a number of general features concerning the structure of grain boundaries and will be referred to in the following section.

Another example of a three-grain junction is Fig. 3. Here the glassy phase can be clearly seen, and also the fact that it has a nonzero contact angle with the sialon grains, suggesting that it has been trapped at the junction by the growing plates rather than wetting them.

Inevitably, these observations in both hot-pressed silicon nitride and hot-pressed magnesium-sialon raise doubts as to the generally interpreted

morphology and distribution of the glassy phase in these materials, in which it is envisaged that the glass forms a continuous layer surrounding and separating each grain.(7,12) Geometry alone indicates that such an interpretation is a gross simplification except for the case in which the intergranular phase occupies a large volume fraction of the microstructure or when the surface energy of the glassy phase--crystalline phase σ_{GS} --is much less than that between two crystalline grains σ_{GG} .

Firstly, it is necessary to recognize that at equilibrium, the extent to which one phase wets another, will be entirely determined by their relative surface energies. Only when σ_{GS} is less than σ_{GG} will the minor phase completely wet and surround the grains of the major phase. Secondly, there are three distinct types of intergranular regions to be considered: that associated with four grains is a point, with three grains is a line, and with two grains is a surface. Corresponding to these three regions a minor amount of intergranular phase will appear as isolated particles, open network, or as a closed cell foam, respectively.(13)

Since the dihedral angles formed by the glassy phase against the nitride and sialon grains at three-grain junctions are observed to be normally nonzero,(1-3,8,9) these geometric considerations imply that the glassy phase will be distributed between the grains in the same way as any other partially wetting phase will do as was argued by C. S. Smith over a quarter of a century ago.(13) This is schematically illustrated, following Smith, in Fig. 4 and is in agreement with the observations made by electron microscopy.

Local variations, such as complete wetting for certain combinations of grain boundary orientations, occur when the model is refined to include the crystallographic anisotropy of the surface energy. Such an anisotropy exists as observations of (10T0)(1,9) and (1120)(14) habits for silicon nitride crystals indicate and would account for the observations of a continuous grain boundary film in hot-pressed silicon nitride seen at some boundaries, notably those in which a low index plane in one of the adjacent grains forms the

boundary. Interestingly, a similar observation⁽¹⁵⁾ is made in the ZnO varistor material, a material in which the intergranular phase is easier to distinguish than in the silicon nitride alloys. Here the Bi₂O₃ rich phase appears only to form an intergranular film when the grain boundary is parallel to the basal plane in one of the adjacent ZnO grains.

The other important factor determining the distribution of the glassy phase in the microstructure is the local microscopic volume fraction of the glass, as this determines the extent to which it encroaches from the three- and four-grain junctions into the two-grain junctions. Although in a fully equilibrated structure this should be a constant, observations indicate that it rarely is, as is illustrated by the electron micrographs of Figs. 5a and 5b. Both of these were taken from the same microscope sample cut from the same billet of a 10 m/o Y₂O₃ hot-pressed silicon nitride. Clearly, the local volume fraction of the yttrium-rich phase (the black phase) is different in these two regions despite the contact angle remaining the same; in one case the yttrium-rich phase is entirely localized at the three-grain junctions whereas, in the other case it surrounds the silicon nitride grains.

GRAIN BOUNDARY STRUCTURE

There are two grain boundary structures of interest in ceramics, the interface between a crystalline and an amorphous grain and the interface between two crystalline grains.

Details of the crystal-crystal interface can again be illustrated with examples drawn from the magnesium sialon system. In those instances where the boundary is straight, it is found that the boundary plane is formed by a low-index plane in one or other of the two grains forming the boundary. This is seen in regions A, and B of Fig. 2, and has been seen when imaging the fundamental lattice planes in both MgO and Y₂O₃ hot-pressed silicon nitride, Mg-sialon and in ZnO. In some cases, the boundary is straight but for unit cell high ledges or multiple atomic high ledges.

Those boundaries that are macroscopically curved are seen using lattice fringe imaging to be made up of short segments parallel to a close packed plane in one or other of the grains, as may be seen in region D of Fig. 2. This seems to be a general fact though not unexpected. The curvature of low-angle grain boundaries similarly is made up of short flat segments, but when the lattice planes across the boundary are examined, as in Fig. 6, terminating fringes can be seen with an accompanying strain field contrast. Although image contrast theory has not been fully developed for this particular geometry, there is every reason to believe that these terminating fringes represent grain boundary dislocations.

Only a few observations have been made of the interface between a crystalline and an amorphous region, and until microscopes having atomic resolution are available, it is unlikely that much structural information will be forthcoming. Nevertheless, a common feature of many of the interfaces examined is the presence of ledges one interplanar-spacing high. Examples of these have been presented elsewhere.(3,8,9)

SEGREGATION TO GRAIN BOUNDARIES

Auger electron spectroscopy combined with sputter ion etching has, in less than ten years, proved to be a remarkably versatile tool for investigating segregation of solute to grain boundaries in both metals and alloys.(16) However, it is limited to studying only those boundaries exposed by intergranular fracture. For this reason, we have begun to explore whether lattice fringe images can be used to detect and measure segregation, in the same way that periodic compositional variations due to spinodal transformation have recently been measured from lattice fringe micrographs.(17) By this method, changes in composition would be manifest as changes in local lattice fringe spacings, and measurement of these changes would be related to compositional changes.

In order that the maximum effect be seen, it is necessary that a set of lattice planes parallel to the boundary plane be imaged and the boundary

observed edge on. This has been done in producing the lattice fringe image of Fig. 7 taken of a boundary in the magnesium-sialon in which one set of fringes are imaged in the grain to the right. The spacing of the fringe adjacent to the boundary plane is noticeably larger than the spacing between fringes in the interior of the grain. The spacing of the second fringe is also larger but is less perceptibly so. Together, those indicate a change in composition adjacent to the boundary. The scale of segregation is quite large since the fringe periodicity in this case corresponds to the polytype spacing in magnesium-sialon and not to the fundamental close packed layer spacing. Nevertheless, it is still on a very much finer scale than has been possible with electron-optical methods to date, e.g., the electron micro-probe. The change in spacing of the first fringe corresponds to a 20% alteration in the lattice spacing. What change in composition this relates to is, at the time of writing, unclear since the compositionally controlled polytypism in this alloy is not fully understood.(11)

Another example of a change in fringe spacing in the vicinity of a magnesium-sialon grain boundary is shown in Fig. 8. The spacing in the band adjacent to the boundary is clearly finer than it is in the rest of the grain, indicative again of a local compositional change. This is a frequent observation in this material and suggests that the compositional change due to segregation effects does not occur smoothly away from the boundary as usually indicated by Auger electron spectroscopy but rather changes discretely.

Although we have deliberately chosen a material in which there is a direct crystallographic relationship between a polytype spacing and composition to demonstrate the applicability of lattice fringe imaging, these and similar observations indicate that the technique will have widespread utility for measuring segregation profiles. One outstanding advantage of the technique is that the segregation can be related directly to the crystallographic orientation of the boundary.

CONCLUSION

Although the techniques of high resolution electron microscopy, and in particular, that of lattice fringe imaging, are only just being brought to bear on ceramics, the information already obtained clearly demonstrates that they will have an important role to play in investigating the effects processing variables have on the microstructure and, hence, properties of ceramics.

Using these techniques, it has been possible to show that the distribution of the glassy phase in both hot-pressed silicon nitride and hot-pressed magnesium-sialon at room temperature is consistent with that obtained for any partially wetting phase in a polyphase material. The next step is to determine which combinations of grain boundary orientations and grain surface orientations are completely wet by the glassy phase so that a more realistic microstructure model based on an only partially wetting phase can be used for formulating high temperature strength degradation theories.

The crystalline grain boundaries in both silicon nitride and magnesium-sialon are concluded to be faceted, to contain interplanar high ledges, and to be formed by low-index planes in the adjacent grains. Furthermore, segregation effects in hot-pressed magnesium-sialon have been detected opening up the way for detailed measurements to be made of segregation profiles in ceramics.

ACKNOWLEDGEMENTS

This work was initiated while both authors were supported by the National Science Foundation (Grant DMR-75-11352). One of us (D. R. C), also gratefully acknowledges the financial support of the Rockwell International Independent Research and Development Program for this work. This work was also done with support from the US Department of Energy.

We also wish to thank Professor K. H. Jack of Newcastle University for kindly supplying us with the magnesium-sialon alloy, and it is a pleasure for us to acknowledge useful discussions with our colleagues T. Shaw and Dr. F. F. Lange.

FIGURES

- Figure 1 A glassy phase at a three-grain junction in a magnesium-sialon. Secondary crystallization has occurred from the glassy phase, B, to form the crystallites, A.
- Figure 2 A three-grain junction in magnesium-sialon in which the polytype fringes have been imaged. In addition to there being no glassy phase in the intergranular regions, the crystalline and stepped nature of the boundaries can be seen. The fine fringe spacing is 18.8Å.
- Figure 3 A three-grain junction in which a glassy phase is present. The glass has not spread along the boundaries and the dihedral angles are clearly nonzero. Magnesium-sialon (courtesy of T. M. Shaw)
- Figure 4 Schematic illustration of the location of a partially wetting phase for which the dihedral angle is 60° based on surface energy considerations. It also represents the observed distribution of the glassy phase in hot-pressed silicon nitride, magnesium-sialon, and the ZnO based varistor material (after C. S. Smith).
- Figure 5 The two extreme cases for the distribution of the yttrium-silicon oxynitride phase (appearing black) in a 10 m/o Y_2O_3 hot-pressed silicon nitride; a low local volume fraction situation (a) and a high local volume fraction (b).
- Figure 6 A lattice fringe micrograph of a low angle grain boundary in MgO hot-pressed silicon nitride in which a set of (10T0) planes have been imaged across the boundary. Note the presence of a number of terminating fringes. The fringe spacing is 6.6Å.
- Figure 7 A lattice fringe micrograph of a grain boundary in magnesium-sialon. The fringes (32.4Å) have only been revealed in the grain to the right, and the grain boundary is located at the position of the furthest left fringe. The interfringe spacing is greater at the boundary than to the right of the boundary indicative of segregation to the boundary.
- Figure 8 Another grain boundary region in magnesium-sialon with the boundary at B. Due to the recording conditions, the second grain, S, appears black. There is a band $\sim 100\text{Å}$ wide at the grain boundary in which the polytype spacing is smaller than that in the rest of the grain indicative, again, of a segregation effect. The broad fringe spacing is 32.4Å.

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FIG. 1

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FIG. 2

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FIG. 3

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FIG. 4

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FIG. 5

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FIG. 6

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FIG. 7

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FIG. 8

This report was done with support from the United States Energy Research and Development Administration. 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 United States Energy Research and Development Administration.