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IMAGING OF THIN INTERGRANULAR PHASES
BY HIGH RESOLUTION ELECTRON MICROSCOPY

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ABSTRACT

As a result of the processing methods used, many ceramics such as silicon nitrides often contain amorphous (glassy) phases that wet most grain boundaries. These phases can be extremely thin ($5\text{-}15\text{\AA}$), and their detection by electron microscopy is not trivial. We assess the merits of high resolution dark field and lattice imaging for this application. In general, dark field imaging is more convenient for the detection of the glassy phases than lattice imaging because it is much less sensitive to the boundary orientation and microscope defocus, and because it enables many boundaries to be examined in a few micrographs, and the boundary thickness to be determined with good accuracy. We also present evidence for a strong inelastically--elastically doubly scattered image contribution in silicon nitride, and show how this contribution can be utilized to supplement the high resolution information when imaged axially at around $3000\text{\AA}$ underfocus.

I. INTRODUCTION

The presence of second phases at grain boundaries usually has dramatic effects on the properties of polycrystalline materials. It affects their mechanical, electrical and transport properties, and their sintering and hot-pressing behavior. An important example is that of silicon nitride (Si_3N_4) prepared by hot-pressing or sintering, where the presence of amorphous (glassy) grain boundary phases with a low melting point prevents the attainment of the intrinsically excellent strength characteristic of pure Si_3N_4 ⁽¹⁾. Further examples can be found in ZnO varistors where grain boundary phases are thought to control the materials' highly non-Ohmic electrical behavior^(2,3), WC-Co abrasives, etc.

Conventional bright field electron microscopy does not have sufficient resolution to detect the very thin phases⁽⁴⁾. Lattice imaging can detect the thin boundary phase^(5,6), and the phase can also be detected by high resolution dark field imaging^(7,8). Lattice images can however misleadingly conceal an existing boundary phase when the boundary is not viewed exactly edge-on⁽⁹⁾, or when the boundary is curved in the direction of the beam. High resolution dark field imaging would therefore be preferable if it could be used to give precise values of the boundary thickness which the correct lattice images yield very directly. In this paper we present a convenient method for determining the film thickness by comparing the intensity in the dark field image of the thin boundary film with that of a nearby pocket of the glassy material, compare the sensitivity of the dark field and lattice techniques to defocus and boundary tilt, and discuss some interesting features that appear in axial lattice images and are due to inelastically-elastically doubly scattered electrons.

II. EXPERIMENTAL

Several silicon nitrides prepared by sintering and hot-pressing with various additives were used for the present experiments. The details of their overall microstructure and chemical composition will be described elsewhere⁽¹⁰⁾. Thin foils prepared by the usual ion-beam milling technique were examined at 125 kV in a Siemens 102 electron microscope equipped with a double-tilting specimen stage.

The two imaging techniques employed, lattice imaging and high resolution dark field imaging, are shown schematically in Fig. 1. It can be seen that with the correct diffraction geometry set up and no Bragg beams contributing through the objective aperture, the dark field image will simply give a bright line where the amorphous phase is, and defocus and tilting will only broaden the line, but not affect its total intensity. The bright field image, on the other hand, must be taken under exactly controlled conditions since either defocus change or specimen tilting could make the two sets of fringes extend into the gap and thus obscure the amorphous phase.

The sensitivity of lattice imaging to boundary tilt has been documented by Lou, Mitchell and Heuer⁽⁹⁾. The sensitivity to defocus is demonstrated in Fig. 2. Here a dark field image (Fig. 2a) shows segments of three silicon nitride grains and a large pocket of amorphous material (upper left). All the grain boundaries in the image appear bright and are therefore penetrated by the amorphous phase. Fig. 2b-e are lattice images of the boxed region of Fig. 2a, taken at four different defocus values. Although the boundary was accurately end-on, only the Scherzer defocus⁽¹¹⁾ image (2c) shows clear evidence of the intergranular phase, whilst in the second contrast transfer interval⁽¹²⁾ under focused image (d), and

especially the first interval overfocused image (b), the amorphous phase seems to disappear. This defocus range corresponds roughly to that reached during standard imaging. The series shows that the lattice fringes "spill" outside the crystal when the defocus does not coincide with the optimum value, making image interpretation unreliable. The whole series (b-e) also shows that in accordance with the standard results of contrast transfer theory^(12,13), smaller spacings are imaged with increasingly better contrast at greater underfocus conditions.

The third contrast transfer interval image (e) also contains lattice fringes that meet and in fact overlap, but superimposed on these there is a bright band about $6\text{\AA}$ wide. This feature could possibly arise by superposition of Brogg beams originating in the two different grains, but it is much more likely due to the inelastically-elastically scattered image contribution⁽¹⁴⁾ for which the effective defocus in a microscope of the Siemens 102 type is some $2000\text{-}3000\text{\AA}$ higher than for the elastic image^(15,16), on account of the energy lost by the electrons in the dominant plasmon scattering process and the chromatic aberration of the objective lens. This difference means that the $-3300\text{\AA}$ defocus image (e) effectively shows the first plasmon inelastic-elastic contribution as if obtained at Gaussian defocus. The rough similarity of Figs. 2c and 2e is therefore not surprising.

III. DETERMINATION OF THE BOUNDARY FILM WIDTH

Quantitative results on the width of the amorphous film can be obtained by measuring the total intensity in the bright line appearing in the dark field image of the boundary, and comparing it with the average intensity of the image of an adjacent glassy pocket. Because of the highly linear response of photographic emulsions to electrons⁽¹⁷⁾, the

intensity can be determined directly from a recorded negative by using a microdensitometer. A pair of microdensitometer traces is shown in Fig. 3, one across the boxed region of the grain boundary show in Fig. 2, and one across the neck of the glassy phase pocket above the box. Measuring the area A under the first trace and dividing it by the height (h) of the second trace gives the boundary thickness as $t \sim 12 \pm 4 \text{ \AA}$, in good agreement with the $8 \pm 2 \text{ \AA}$ determined from the optimum lattice image.

The insensitivity of the dark field intensity method to variations of the angle which the boundary makes with the electron beam is illustrated in Fig. 4. Here a grain boundary in the dark field image (a) is seen to twist away from being edge-on. The microdensitometer traces taken along A-A' and B-B' reflect this by the second peak being wider than the first one. However, the areas under the two peaks are the same, and the widths derived by the method given above will also be the same. This shows that the thickness of the boundary phase did not vary in a distance of a few hundred angstroms, an observation consistent with the results derived in a thorough characterization of this and similar materials⁽¹⁰⁾.

It is perhaps worth mentioning that when the grain size is small and it is impossible to arrange the diffraction conditions so that all the crystalline grains in the observed area appear dark simultaneously, one can distinguish the glassy phases from the diffracting crystals by recording images at two or more different specimen tilts. The contrast of the crystalline phases will change while that of the glassy ones will not. One must however ensure that neither of the two grains adjacent to any particular boundary being examined diffracts through the aperture, as even quite weak diffraction from either grain is liable to give misleading results.

IV. DISCUSSION

The apparent disappearance of the amorphous phase at the wrong defocus is an electron-optical effect. In order that the lattice fringes terminate exactly at the crystal edge, the two Bragg beams (plus and minus) and the main beam must coincide precisely, a condition fulfilled exactly at only one defocus value⁽¹⁸⁾. The displacement of the Bragg beam is given by the gradient of the aberration function at the Bragg beam, as

$$\begin{aligned}\underline{r} &= \underline{\nabla}X(q_B) \\ &= c_s \lambda^3 q_B^3 + \Delta f \lambda q_B\end{aligned}\quad (1a, b)$$

where $\underline{r}$ is the displacement $\underline{\nabla}X(q)$ the gradient of the microscope aberration function, q the reciprocal space coordinate ($q_B = 1/d$), c_s the spherical aberration coefficient, λ the electron wavelength, Δf the defocus and d the lattice spacing. For $c_s = 2\text{mm}$, 125 kV, and the $\beta\text{-Si}_3\text{N}_4$ ($10\bar{1}0$) reflection ($d = 6.6\text{\AA}$),

$$r \approx (2.5 + \frac{\Delta f}{200})\text{\AA} \quad (2)$$

Therefore at the Scherzer defocus ($-800\text{\AA}$) the lattice fringes will extend by about $1.5\text{\AA}$ over the edge of the crystal. At $1000\text{\AA}$ away from the Scherzer defocus the fringes will easily fill up a $6\text{\AA}$ gap, provided of course that the lattice planes in at least one of the grains are roughly parallel to the grain boundary. Faithful imaging of the intergranular phase thus demands that the defocus be considerably more accurate than does lattice imaging of defects such as stacking faults in Si where image appearance depends periodically on defocus and there is, apart from coherence considerations, no exact preferred defocus value^(19,20,21).

In contrast, the dark field technique is relatively insensitive to any experimental variables. The values it yields for the thickness of the grain boundary film may still be in error when there is no large pocket of the glassy material close by the boundary examined, or if the boundary phase scatters differently from the glass concentrated in the larger pockets. Another problem is that the small intrinsic degree of disorder associated with any grain boundary will contribute to the dark field image intensity thus artificially increasing the determined thickness. However this contribution is so small as to be almost invisible in materials where no second phase exists, as shown in Fig. 5b, which is a dark field image of an edge-on grain boundary in polycrystalline, but glass-free SiC, and it will vary with specimen tilt so that with proper care it can be excluded altogether.

In materials where the intergranular phases have dramatic effects on properties and the main question is whether the phase does wet a particular boundary or not, the dark field technique therefore on the whole appears to be ideally suitable. In such materials the knowledge of the chemical composition of the intergranular phase is also essential, and here the high resolution techniques are ideally complemented by the STEM/EDX or ELS analysis methods⁽¹⁰⁾.

V. SUMMARY AND CONCLUSION

It has been shown that the detection of the thin amorphous intergranular phases in materials such as silicon nitride by lattice imaging may lead to false conclusions if the microscope defocus is not determined exactly. With grain boundaries properly oriented parallel to the electron beam and the defocus close to the Scherzer value the lattice imaging

technique is however very valuable in that it determines the thickness of the possibly very thin phase directly and accurately, especially in complex, multiphase materials⁽⁶⁾.

In contrast, high resolution dark field imaging of the grain boundary phases is relatively insensitive to specimen tilt and microscope defocus. It also enables one to study much larger specimen areas in just one image since the magnification of the recorded micrograph need not be as high as for lattice imaging. By measuring the intensity in the boundary image the thickness of the boundary phase can be determined quite accurately even when the boundary is not edge-on and the microscope defocus is in error. The technique therefore appears to be ideally suited for this highly specialized application.

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FIGURE CAPTIONS

- Fig. 1. High resolution bright field (lattice) and dark field imaging of amorphous intergranular phases.
- Fig. 2. Dark field (a) and bright field lattice images with their optical diffractograms (b-e) of an edge-on grain boundary in Si_3N_4 . Defocus values are b: $+300\text{\AA}$ c: $-800\text{\AA}$ d: $-2100\text{\AA}$ and e: $-3300\text{\AA}$.
- Fig. 3. A microdensitometer trace across the grain boundary imaged in Fig. 2a, and a trace across the adjacent glassy pocket.
- Fig. 4. A dark field image of a twisting grain boundary (a), and microdensitometer traces fallen along A-A' and B-B' (b and c).
- Fig. 5. A dark field image of a SiC grain boundary with an grain diffracting through the objective aperture (a), and a dark field image formed with diffuse scattering only (b) the aperture geometry for (b) is shown in the insert.

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Fig. 1

Fig. 2

XBB 788-9882

Fig. 3

XBB 786-6922A

Fig. 4

XBB 787-8724A

Fig. 5

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