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OF HIGH ANGLE TWIST BOUNDARIES

II. HIGH RESOLUTION ELECTRON MICROSCOPY STUDY

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Cornell University

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T.Y. Tan, S.L. Sass and R.W. Balluffi
Department of Materials Science and Engineering
and Materials Science Center
Cornell University, Ithaca, New York 14850

ABSTRACT

High resolution electron microscopy was used to image directly the 0-lattice of $\langle 001 \rangle$ twist boundaries with misorientations up to 25° and 0-lattice spacings as small as $7\text{\AA}$. The results were entirely consistent with the conclusions reached on the basis of the diffraction experiments described as Part I. An experimental method was devised for determining whether the 0-lattice was imaged by conventional diffraction strain contrast or by interference strain contrast which arises from interference between f.c.c. and 0-reflections resulting from the periodic structure of the boundary (Part I). It was demonstrated that spacings down to about $34\text{\AA}$ were imaged mainly by means of diffraction strain contrast, while networks with spacings of about $16\text{\AA}$ or less were imaged mainly by means of interference strain contrast. Efforts were also made to detect secondary grain boundary dislocation networks and such networks were observed in the vicinity of $\Sigma=5$, 13 and 17 boundaries over a larger range of misorientations than detected previously.

1. INTRODUCTION

In Part I (Sass, Tan and Balluffi 1974) we demonstrated using electron diffraction techniques that $\langle 001 \rangle$ twist boundaries are periodic over the entire possible range of misorientations. The periodicity associated with the strong extra reflections from the grain boundary structure was always that of the 0-lattice of the unrelaxed boundary structure. While previous studies (Schober and Balluffi 1970) have demonstrated directly the existence of periodic arrays of secondary grain boundary dislocations (GBD's) in certain high Σ boundaries, no evidence was obtained from the diffraction study in Part I for the existence of these GBD's.

In the present work high resolution electron microscopy was used to image the 0-lattice directly and to confirm the conclusions reached in Part I on the basis of diffraction experiments. In addition, strong efforts were made to image secondary GBD's and to extend the range of misorientations over which these dislocations are observed.

2. ORIGINS OF IMAGE CONTRAST FROM GRAIN BOUNDARIES

2.1 Diffraction Strain Contrast

Any crystal defect possessing a significant displacement field perturbs the periodic lattice potential by which Bragg beams from the perfect crystal are excited. Electrons scattered by the perturbed potential appear as diffuse intensity in the vicinity of the Bragg beams. The amount of the diffuse intensity included in the objective aperture with a Bragg beam is usually too small to influence any defect image contrast. The perturbed potential also causes the Bragg beams to undergo phase shifts which introduce sufficient amplitude changes of the Bloch waves to produce observable intensity differences from that of a perfect crystal. This effect is called diffraction strain contrast and is

the usual mechanism by which defects are imaged.

Thölén (1970) has calculated the diffraction strain contrast resulting from a square grid of screw dislocations in a $\langle 001 \rangle$ twist boundary* and has concluded that the image of the dislocation network becomes more difficult to separate from the Moiré pattern as the dislocation spacing, d_0 , decreases. He estimated experimentally that it is not possible to resolve individual dislocations as d_0 becomes smaller than about 0.3 of an extinction distance, ξ_g , which corresponds to about $54\text{\AA}$ in Au at 100kV, if the 200 reflection is used. Schober and Balluffi (1970) observed square grids of screw dislocations with d_0 's down to $20\text{\AA}$ and, therefore, it is apparent that an additional contrast mechanism must be operative at small d_0 .

2.2. Interference Strain Contrast

In the case where the defect possesses an extended periodic structure, as in the case of a grain boundary, extra reflections associated with the defect periodicity are produced in addition to the usual Bragg crystal reflections. As pointed out in Part I, $\langle 001 \rangle$ twist boundaries possess a square 2 dimensional periodicity, and strong grain boundary reflections are located very close to the Bragg reflections in square patterns which correspond to the reciprocal lattice of the 0-lattice (See Fig. 6 Part I). When a dark field image is formed several of these reflections will typically be included within the objective aperture. Since the spacing between these reflections is inversely related to the 0-lattice period the interference of the 0-reflections with the Bragg reflections will produce square fringe patterns which

* We note that the square grid of screw dislocations delineates the 0-lattice in this case (see Part I).

possess the 0-lattice periodicity. We will call this type of contrast, interference strain contrast*. As we shall demonstrate, the strength of this type of contrast increases relative to the strength of the usual diffraction strain contrast as the 0-lattice spacing decreases, and it eventually becomes the main source of contrast.

If the amplitude of the 0-reflection is ψ_0 and the amplitude of the f.c.c. reflections is ψ_{fcc} , then since $\psi_0 \ll \psi_{f.c.c.}$, the contrast of the fringe pattern is proportional to ψ_0/ψ_{fcc} (Heidenreich 1964). Thus, in principle it should be possible to increase the image contrast by decreasing ψ_{fcc} . This can be done by setting up the diffraction condition where the f.c.c. reflection has a large deviation parameter and the 0-reflection has a zero deviation parameter. This condition is possible to obtain because the reflections from the boundary form elongated relrods in reciprocal space (Cuan and Sass, 1973b).

3. EXPERIMENTAL PROCEDURE

As described in Part I, the bicrystal specimens were prepared by the welding method of Schober and Balluffi (1969). Fortunately, the boundaries produced by this technique in well equilibrated specimens contained bubbles ranging in size from 50 to a few hundred Å as illustrated schematically in Fig. 1. These bubbles served two important functions: (1) as an aid in making astigmatism and focusing corrections, and (2) as a means of distinguishing whether the image was due to diffraction from the periodic grain

* This procedure for imaging the 0-lattice is of course, completely analogous to the so-called direct lattice imaging method (Hirsch, et al. 1965) where several Bragg crystal reflections are collected in the objective aperture to form an image of the crystal lattice.

boundary or whether it was due solely to interference effects involving reflections resulting from double diffraction between the upper and lower crystals (Moiré effects). In the former case the image would appear only in the regions containing the grain boundary and not in the bubble regions where the boundary was absent. In the latter case the image would appear in both the grain boundary regions and the bubble regions. In this way it is easy to distinguish between grain boundary diffraction effects and purely crystal Moiré effects.

In order to image the 0-lattice by means of interference strain contrast it was desirable to have the row of 200-type reflections excited, so that both components of the square 0-lattice grid could be imaged simultaneously. Figure 2, which shows this diffraction condition, illustrates the typical complexity of the imaging conditions that exist for bicrystals containing twist boundaries. Here we see present at least 15 reflections including 000, f.c.c. reflections, 200_1 , 200_2 , $\bar{2}00_1$, $\bar{2}00_2$, and extra reflections, D_1 to D_{10} . Guan and Sass (1973a) have shown, for a low angle twist boundary, that the structure factors of 0-reflections around the origin are essentially zero. Comparison of Fig. 6 and 8b (Part I) confirms, in high angle twist boundaries, that the extra reflections observed around 000 result from double diffraction.

Micrographs were obtained by using either the reflections in the vicinity of 200 (dark field) or the reflections in the vicinity of 000 (bright field). In both cases the micrographs show fringes along the average $\langle 110 \rangle$ directions with spacings corresponding to the 0-lattice spacing and Moiré fringes along the average $\langle 100 \rangle$ direction, with a spacing which is $1/\sqrt{2}$ the 0-lattice fringe spacing. It is emphasized that although the 0-reflections around

000 are the result of double diffraction, the fringes formed with these reflections still reveal the true 0-lattice periodicity. The Moiré fringes result from interference effects due to either the two 200 reflections, or the 000 reflection and a double diffraction reflection such as D_g , depending upon the region of reciprocal space admitted by the objective aperture.

In order to obtain observable contrast for 0-lattice spacings of less than $10\text{\AA}$ ($\theta > 16^\circ$), it was necessary to image entirely using reflections in the vicinity of 200. Following the discussion in Section 2.2, we note that the image contrast could be increased by tilting the specimen about the average $\langle 100 \rangle$ direction in order to weaken the 200 reflections while maintaining the 0 reflections, r -s, r -s and r +s, r +s (see Part I) on the Ewald sphere. The f.c.c. reflections could not be made too weak, however, because in this resolution range it was necessary to be able to focus and adjust the objective lens astigmatism using the dark field image.

To image the secondary GBD's it was desirable to use a reciprocal lattice vector making a 45° angle with the two mutually perpendicular Burgers vectors of the GBD's. For example, for secondary GBD's in $\Sigma=5$ boundaries, the Burgers vector is of the type $\frac{a}{10} \langle 310 \rangle$ (Table 1, Part I), so that a f.c.c. reflection of the type 420 was chosen. For $\Sigma=13$ and 17 boundaries the secondary GBD's possess Burgers vectors of the type $\frac{a}{26} \langle 510 \rangle$ and $\frac{a}{34} \langle 530 \rangle$, respectively, (Table 1, Part I) and the desired f.c.c. reflections were of the type, 640 and 820, respectively. When Σ was larger than 5, however, it was not possible to obtain the desired diffraction condition without simultaneously exciting additional reflections lying close to the desired reflection. Because of this difficulty,

220 and 200 type reflections were used for imaging the $\Sigma=13$ and 17 boundaries, respectively.

The results described in this study were obtained using Philips EM300 and Siemens 102 electron microscopes operating at magnifications in the range 100,000 to 500,000X.

4. EXPERIMENTAL RESULTS

4.1 Imaging of the 0-lattice

Figure 3a-h shows images obtained using the diffraction conditions discussed above. We see that a square fringe pattern was detected up to twist angles of 22° . Actually micrographs showing very faint 0-lattice fringe patterns were obtained at angles up to 25° . We further note that the bubbles show a single fringe pattern running at 45° to the square grid, with a spacing $1/\sqrt{2}$ that of the square grid. Thus, referring back to Section 3, we conclude that the fringes within the bubbles are f.c.c. Moiré fringes. Since the square fringe pattern does not occur within the bubble region it must result from scattering from the periodic structure of the grain boundary region. In Fig. 4 the square fringe spacings measured from micrographs such as in Fig. 3 are plotted versus θ , and we see that there is excellent agreement with Eq. 8, Part I, which gives the 0-lattice spacing.

We would now like to decide whether the 0-lattice images in Fig. 3 are due to diffraction strain contrast or interference strain contrast. In general we expect both contrast mechanisms to be present. However, we would like to decide which is predominant, particularly at small periodicities. In order to do this we first note that the depth of field in the electron micro-

scope, D_f , is given by the expression $D_f = \delta/\beta$, where δ is the lateral distance to be resolved and β is the angle that the image forming rays make after leaving the specimen. For the case of diffraction strain contrast β is the angular divergence of either the incident or diffracted beams, which is typically 10^{-3} radians. For the case of interference strain contrast and Moiré fringes the two imaging beams usually make an angle much greater than the angular divergence of a single beam, typically 10^{-2} radians. Assuming that only Moiré fringes are present in the bubble regions consider now the behavior of images formed by diffraction contrast and interference contrast when the focus of the objective lens is changed continuously. In the case where diffraction strain contrast is the main mechanism the 0-lattice image from the grain boundary region should go in and out of focus more slowly than the Moiré fringe pattern in the bubble regions. This occurs because the depth of field of the image formed by diffraction contrast is greater than that of the image formed by interference contrast. On the other hand, when interference strain contrast is the main mechanism, the 0-lattice image should go in and out of focus at about the same rate as the Moiré fringe pattern since the depth of field of the two images is about the same.

Figures 5a-1 show a through-focus series taken for a $\theta=4.5^\circ$ boundary where the 0-lattice spacing is $34\text{\AA}$. It is evident that the 0-lattice image in the grain boundary region has a considerably greater depth of field than the Moiré fringes in the bubbles indicating that diffraction strain contrast is the main imaging mechanism.

Figures 6a-1 show a through-focus series taken for a $\theta=10^\circ$ boundary where the dislocation spacing is $16\text{\AA}$. In this case the depths of field of the two images are about the same indicating that interference strain contrast is the main imaging mechanism.

Upon comparison of Figures 3e,f,g,h we see that as d_0 decreases, the dislocation network becomes progressively more difficult to separate out from the Moiré pattern in qualitative agreement with Thölén's calculations. However, it is quite evident from Figure 5 that dislocation networks with spacings less than $0.3\xi_g$ can still be imaged by diffraction contrast which does not agree with Thölén's experimental conclusion. Evidently, Thölén has underestimated the strength of the diffraction strain contrast when d_0 becomes small (i.e. $<0.3\xi_g$).

4.2 Imaging of Secondary GBD's

Secondary GBD's were detected in the vicinities of the $\Sigma=5$, 13 and 17 misorientations over ranges of $\Delta\theta$ (Eqn. 6, Part I), which were appreciably wider than those observed by Schober and Balluffi (1970). Figures 7 a-c show secondary GBD's in the vicinity of the $\Sigma=5$ misorientation at $\theta=36.87^\circ$. The measurements of secondary GBD spacing are plotted versus $\Delta\theta$ in Figure 4 and we see that there is good agreement with eqn. 6, Part I. Examples of secondary GBD's detected in the vicinity of the $\Sigma=13$ and 17 misorientations are presented in Figure 8a,b. In these cases experimental errors in the measurement of d_s and $\Delta\theta$ preclude any meaningful test of the validity of eqn. 6, Part I.

5. DISCUSSION

The present results involving the imaging of the 0-lattice in the electron microscope are completely consistent with the observed diffraction effects due to the 0-lattice reported in Part I. At low angles the observed 0-lattice grid (Figure 3a) can be correctly interpreted as a network of discrete screw dislocations whose spacing obeys the Frank formula (Eqn. 8, Part I) and which is imaged mainly by means of diffraction strain contrast. As the angle is increased and the network spacing decreased in the range beyond $\theta \approx 10^\circ$ and $d_0 \approx 16\text{\AA}$ the discrete dislocation description becomes increasingly unrealistic. Also the 0-lattice is then imaged mainly by means of interference strain contrast. As pointed out in Part I, the details of the displacement field in the grain boundary in this region are unknown. Thus, even though the images in Figure 3e,f,g,h give the appearance of square dislocation networks, all that can be said at present is that they are due to an interference effect which results from the displacement field associated with the 0-lattice. The observation that the square grid does not penetrate into the bubble regions is further confirmation of the conclusion reached in Section 3.2 (Part I) that the 0-reflections result from the periodic structure of the boundary, and not from double diffraction between the upper and lower f.c.c. crystals.

It was not possible to obtain 0-lattice images for $\theta > 25^\circ$, $d_0 < 7\text{\AA}$. It is believed that our ability to detect finer spacings was limited by low image contrast rather than insufficient microscope resolution, since $7\text{\AA}$ is well above the $2\text{\AA}$ line resolution of the Siemens 102 microscope. The structure factor of grain

boundary reflections is known to decrease with increasing θ (Guan and Sass (1973a)), which, of course, leads to decreasing image contrast.

The observations of secondary GBD's are consistent with the previous work of Schober and Balluffi (1970), but cover a greater range of $\Delta\theta$. It is believed that it was possible to resolve finer dislocation networks in this study because of the availability of a superior electron microscope from the standpoint of resolution and image contrast.

Since diffraction effects from secondary GBD's were not observed in Part I, it is reasonable to inquire whether the observed secondary GBD networks resulted from interference effects involving reflections which were present as a result of double diffraction. As demonstrated in Section 3.4 (Part I) secondary GBD reflections which resulted from double diffraction were present (see, for example, Figure 9d, Part I). An interference pattern produced by combining these reflections with f.c.c. reflections would exhibit the periodicity of the secondary GBD array. Since the secondary GBD network is not seen within the bubble region, see for example Figure 7, we may conclude that these images do correspond to a real grain boundary structure and do not result from interference effects involving double diffraction reflections.

It is interesting to consider why the secondary GBD's were detected by direct imaging, but not by diffraction techniques. Several explanations can be suggested. It is possible that secondary GBD reflections were actually present but were either too weak to detect or else were difficult to distinguish because of double

diffraction. In this respect we note from Figure 7 and 8 that the secondary GBD periodicity was imperfect, which should make associated effects in the diffraction pattern quite weak and, therefore, difficult to detect. Furthermore, since the GBD spacings that were detected are relatively large ($30-40\text{\AA}$), the dominant imaging mechanism could very well be diffraction strain contrast, which of course, does not require interference effects involving extra reflections to produce the image. Thus, the observation of imperfectly periodic secondary GBD networks by diffraction contrast would not be inconsistent with the negative conclusion of the diffraction study in Part I.

Attempts were made to look for secondary GBD arrays in the vicinity of other relatively low Σ orientations, such as $\theta=16.26^\circ$ ($\Sigma=25$) as well as between the low Σ orientations shown in Figure 4. These attempts were not successful. Figure 4 summarizes the complete results of Part I and II.

6. CONCLUSIONS

1. The 0-lattice of $\langle 001 \rangle$ twist boundaries was imaged down to spacings as small as $7\text{\AA}$ (corresponding to $\theta=25^\circ$). The results again demonstrated the periodic nature of high angle twist boundaries (as in Part I) and were completely consistent with the conclusions reached on the basis of the diffraction experiments described in Part I.

2. An experimental method was devised for determining whether the 0-lattice was imaged by conventional diffraction strain contrast or by interference strain contrast which arises from the interference between f.c.c. and 0-reflections (see Part I). It was demonstrated that spacings down to about $34\text{\AA}$ were imaged mainly by means of diffraction strain contrast, while networks

with spacings of about $16\text{\AA}$ or less were imaged mainly by means of interference strain contrast.

3. Secondary grain boundary dislocation networks were observed in the vicinity of $\Sigma=5$, 13 and 17 misorientations. The range of $\Delta\theta$ over which these observations were made was larger than that of the previous study by Schober and Balluffi (1970).

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FIGURE CAPTIONS

- Figure 1. Edge view of bicrystal thin film specimen showing bubble in grain boundary.
- Figure 2. (a) Illustration of the conditions used to image the 0-lattice. The arrows indicate how the extra reflections around 000 are produced by double diffraction.
- (b) Bright field image formed using reflections in the vicinity of 000 in (a). $\theta=12^\circ$, $d_0=14\text{\AA}$
- Figure 3. 0-lattice grids observed in boundaries with $\theta=7^\circ$ (a), 11.5° (b), 13° (c) and 15° (d). 16.5° (e), 18° (f), 20° (g) and 22° (h). Directions indicated are average directions for Crystals 1 and 2 (see Figure 1).
- Figure 4. Observed 0-lattice spacings, d_0 , and secondary GBD spacings, d_s , as a function of θ .
- Figure 5. (a)-(l) Through-focus series for a $\theta=4.5^\circ$ boundary with $d_0=34\text{\AA}$. In (a), (b) and (l) we see that the Moiré fringes in the bubble have disappeared while the 0-lattice image from the boundary still remains. The defocus is negative at the start of the series.
- Figure 6. (a)-(l) Through-focus series for a $\theta=10^\circ$ boundary with $d_0=16\text{\AA}$. By comparing (b) and (c) we see that the Moiré fringes in the bubble and the 0-lattice image from the boundary both disappear at approximately the same value of defocus. The defocus is negative at the start of the series.
- Figure 7. Secondary GBD networks observed in boundaries in the vicinity of $\theta=36.87^\circ$ ($\Sigma=5$) with $|\Delta\theta|$ of (a) $\sim 0.1^\circ$ (b) $\sim 1^\circ$ (c) $\sim 2.5^\circ$. The smallest spacing observed, which is in (c), is $35\text{\AA}$.
- Figure 8. Secondary GBD networks observed in boundaries in the vicinity of (a) $\theta=22.62^\circ$ ($\Sigma=13$) (b) $\theta=28.07^\circ$ ($\Sigma=17$).

Figure 1

Figure 2

Figure 3

Figure 3 (continued)

- Δ Observed by microscopy (present work)
 $\circ$ Observed by diffraction (see Part I)
 — $d_o = b_o / 2 \sin (\theta / 2)$
 - - - $d_s = b_s / 2 \sin (\Delta \theta / 2)$

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8