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1. Introduction. — In the present paper we review the efforts which have been made in our laboratory during the last few years to gain information about secondary grain boundary relaxations in cubic metals by electron microscopy. (Earlier work has been reviewed in the paper [1] given at the Yorktown Heights Conference in 1971.)

Our work has therefore been aimed at determining the extent to which ordered boundaries, possessing periodic structures of different possible types, exist. There has been much speculation that such boundaries are of relatively low energy and therefore should be stable under certain conditions. The following efforts will be described: [1] search for secondary grain boundary dislocation (GBD) relaxations in Coincidence Site Lattice (CSL) boundaries; [2] search for secondary GBD networks in Near-Coincidence (NC) boundaries; [3] detection of line structure due to secondary relaxations in Plane Matching (PM) boundaries; [4] studies of the faceting and the preferred orientations of grain boundaries during annealing.

Efforts [1] through [3] have involved attempts to observe fine structure directly, whereas [4] is related to the energy of the boundary as a function of its orientation, i.e., structure. Information of the latter type is of interest in any consideration of secondary relaxation models.

All of the experimental work has been carried out using thin-film gold specimens of the types shown in figure 1a and 1d containing boundaries of controlled geometry which were produced by welding epitaxially grown films together face-to-face and then annealing [1].

2. Search for secondary GBD relaxations in CSL boundaries. — It is now well established [1, 2] that...
boundaries may relax into a structure consisting of a grid of secondary GBD's embedded in a relatively high density CSL interface whenever the misorientation is sufficiently near the corresponding high density CSL misorientation. In general, the magnitude of the Burgers vector $|\mathbf{b}|$, of the secondary GBD's decreases as the CSL density decreases. Since there is only a limited number of high density CSL's, there is only a limited number of cases where the secondary GBD's have a relatively large $|\mathbf{b}|$. In addition, the secondary GBD grid spacing decreases as the deviation from the CSL orientation increases. At present there is no firm basis for deciding on the magnitude of the minimum $|\mathbf{b}|$ which is physically realistic or the minimum GBD spacing at which the model still holds. When the misorientation is far from a relatively low $\Sigma$ misorientation ($1/\Sigma = \text{fraction of atoms in coincidence sites}$) it seems quite possible that the mismatch may no longer be forced into discrete secondary GBD cores with small $|\mathbf{b}|$, since it is then no longer possible to produce patches of relatively high CSL density. In addition, it has been suggested [3] that the model breaks down, even for low $\Sigma$ cases, when the GBD spacing becomes comparable to the spacing between coincidence sites (i.e., the periodicity) in the boundary. By making certain assumptions about the magnitudes of the minimum allowable $|\mathbf{b}|$ and GBD spacing Warrington and Boon [4] have concluded that only as small percentage of random boundaries would be of CSL type.

In view of this situation it is necessary to investigate experimentally the question of how many boundaries are of this type. The problem is difficult, however, since our ability to resolve the secondary GBD network decreases as $|\mathbf{b}|$ and/or the network spacing decreases [5]. In earlier work it has been shown [5] that secondary GBD networks with $|\mathbf{b}|$ as small as 0.70 Å and spacings as small as ~60 Å can be resolved in $<001>$ twist boundaries ($\theta = 28.1^\circ$, $\Sigma = 17$) in gold. However, we were unable to detect any networks under similar conditions in $<001>$ twist boundaries near $\theta = 16.3^\circ$, $\Sigma = 25$ where the secondary GBD's would be expected to have $|\mathbf{b}|$ equal to 0.58 Å. More recently, Bollmann et al. [6] have apparently detected GBD's with $|\mathbf{b}|$ as small as 0.47 Å in a boundary with $\Sigma = 29$ in stainless steel. These GBD's were of the extra extrinsic type [1] and were widely dispersed in the boundary rather than closely spaced in regular arrays.

We therefore decided to make a further effort to detect GBD networks in the $\theta = 16.3^\circ$ ($\Sigma = 25$) twist boundaries. For this purpose we employed a newly acquired Siemens 102 electron microscope with a high intensity single crystal pointed filament electron gun and a high resolution tilting stage. A considerable number of boundaries with $\theta$ near 16.3° ($\Sigma = 25$) were prepared from especially thin (150-200 Å thick) gold films possessing the best obtainable surface quality. These specimens were annealed in order to achieve maximum equilibration, and were then examined under optimum diffraction conditions. In order to avoid local bending and achieve simple diffraction conditions the specimens were supported on 1 000 mesh grids. Despite all of these efforts, no clear evidence was obtained for the existence of secondary GBD networks in any specimens. This negative result indicates that either: [1] networks were present but they were not detected because of their low contrast, or [2] relaxations into an array of secondary GBD's did not occur.

The former possibility is probably not inconsistent with the observation of Bollmann et al. [6] that GBD's with $|\mathbf{b}|$ as small as 0.47 Å can be detected. The latter GBD's were widely separated, whereas the presumed GBD's in the present work would have been arranged in arrays where their long range strain fields cancelled and where they would have been more difficult to image. In any case it appears that more powerful techniques will be required to reveal possible intrinsic secondary GBD arrays in CSL boundaries with $\Sigma$ values $\approx 25$.

3. Search for secondary GBD networks in NC boundaries. — In NC boundaries suitable atomic nets exist on the crystal faces adjoining the boundary which almost match in size and shape. Exact coincidence is then obtained by applying stresses which can then be cancelled by a network of suitable GBD's. Descriptions of boundaries of this type have been given elsewhere [2, 3, 7].

So far, no boundaries of this type, i.e., exhibiting GBD networks, have been shown to exist in cubic crystals. Weins and Weins [8], however, have found macroscopic facets in non-CSL [001] tilt boundaries in silver which appeared to have a preference for orientations corresponding to NC segments of relatively short periodicity. We, therefore, have made a strong effort to observe GBD networks in two such boundaries using techniques similar to those used in our search for the $\Sigma = 25$ CSL boundary (section 2).

The first boundary was the [001] twist boundary ($\theta = 31.0^\circ$, $\Sigma = 17$) described previously by Balluffi and Tan (see Fig. 3 of [3]). This boundary requires a mismatch strain of 0.028 which can be accommodated by a square network of edge GBD's with $|\mathbf{b}| = 0.68$ Å. The second boundary was the [110] twist boundary ($\theta = 90.0^\circ$, $\Sigma = 35$) which can be produced in the ABFE plane of figure 2 by applying a mismatch strain of 0.01 which can be accommodated by a network of edge GBD's with $|\mathbf{b}| = 0.58$ Å. Twist misorientations from the exact NC condition, which are inevitable in these boundaries, can be accommodated by grids of screw
GBD’s with the previous b’s. Despite considerable effort, no evidence for the existence of any GBD networks in these boundaries was found.

The negative result for the (001) twist boundary is evidence that this boundary probably does not exist, since it is known that GBD networks with $|b| = 0.7$ Å can be detected (section 2). On the other hand, the negative result for the second boundary is probably not definitive, since GBD networks with $|b| = 0.58$ Å may have been present while at the same time escaping detection (section 2).

4. Secondary relaxations in PM boundaries. — In many cases secondary boundary relaxations have been observed which appear as single sets of parallel lines under the microscope. In these cases stacks of identical and relatively low \{hkl\} planes in each of the two crystals adjoining the boundary intersect the boundary in sets of traces which almost match in spacing and direction. The subsequent relaxations then cause as much matching of the planes across the boundary as possible. The mismatch is forced into narrow bands (lines) which bear a close relationship to the Moiré pattern produced by the unrelaxed planar traces as pointed out by Pumphrey [9]. Such boundaries have been frequently interpreted in terms of PM models which have been described and discussed by a number of investigators [2, 4, 9-12]. In most PM models the detailed atomic arrangement within each matching plane is ignored, and it is considered sufficient to match the structureless planar sheets across the boundary without regard to atom matching along the planar edges. The resulting boundary structure is therefore assumed to be ordered (periodic) in one dimension but random (disordered) in a second dimension.

However, many of the observed line structures can be satisfactorily described in terms of the CSL model in which the DSC-lattice [13] is highly elongated [10, 14]. In such cases the boundary is, of course, ordered in two dimensions and possesses a 2-dimensional secondary GBD network. However, the GBD’s in the network possess b’s of widely differing magnitudes because of the large eccentricity of the DSC-Lattice. If the small $|b|$ of one set is sufficiently small it may not be resolved, and the network will then appear as a single set of parallel lines. It is therefore of interest to establish whether some of these observed boundaries are PM boundaries which are disordered in one dimension or whether they are merely CSL boundaries with highly elongated DSC-Lattices.

Pumphrey [11] has presented evidence for the existence of a boundary in which one component of the GBD network was evidently missing and which he therefore classified as a PM boundary. However, the boundary was a low angle boundary with $\theta = 10.4^\circ$. Such boundaries are well understood in terms of discrete lattice GBD’s (O-Lattice model), and this result is therefore surprising and rather difficult to understand. We have therefore continued to investigate the possible existence of high angle PM boundaries.

In our work we have found at least one type of boundary which appears to be of the PM type. Crystal 1 was first rotated with respect to Crystal 2 by 90$^\circ$ around [110] (Fig. 2) and the boundary was located in the plane ABCD (Fig. 2 : Above). The traces of stacks of (220) planes in the two crystals then exactly matched across the boundary while the atoms along the planar edges were mismatched. Finally, twist components, $\Delta \theta$, as large as 8$^\circ$ were added by rotating Crystal 2 around [001]. Subsequent microscopy revealed single sets of parallel lines running parallel to the common \{110\}, direction (Fig. 2 : Above) at a spacing obeying

$$d = \frac{a_0/2\sqrt{2}}{2 \sin \left(\frac{\Delta \theta}{2}\right)}$$

(see Fig. 3). The lines therefore possessed a $|b|$ strength in the plane of the boundary equal to the (220) interplanar spacing and a spacing corresponding to the Moiré pattern produced by the (220) planar traces which were mismatched across the boundary by $\Delta \theta$.

Despite all efforts we were unable to detect any other line structure in the boundaries. As shown
below, a satisfactory boundary model which is ordered in two dimensions cannot be obtained using either the CSL or NC approach, and we therefore conclude that these boundaries must have been PM boundaries which were ordered in the direction $\overrightarrow{AC}$ but disordered in the direction $\overrightarrow{AB}$.

The configuration in figure 2 is relatively near a $\Sigma = 17$ CSL condition which could be obtained by a $3.4^\circ$ rotation around $[\overline{1}10]_{1,2}$ bringing G into H. However, this CSL would require a periodicity in the boundary in the direction $\overrightarrow{AB}$ at least as large as the diagonal of the CSL which is $\sim 20$ Å. Since the observed spacing in this direction between the GBD’s was $< 20$ Å (Fig. 3), we conclude that this is an unreasonable model. (Furthermore, no evidence was found for the edge dislocations which would be required in the $[\overline{1}10]_{1,2}$ direction.) A similar argument may be used to reject a NC model. The two lattices may be brought into exact coincidence at A and C and D and B (Fig. 2: Above) by applying a 0.01 strain to Crystal 2. However, the periodicity in the direction $\overrightarrow{AB}$ would again be $\sim 20$ Å, and this model is therefore also unsatisfactory.

5. Studies of the faceting and preferred orientation of boundaries during annealing. — Efforts are in progress to obtain information about the variation of boundary energy with boundary orientation under conditions where $\theta$ across the boundary is held constant. Polycrystalline specimens possessing columnar grains of only two crystal orientations as in figure 1d have been useful for this purpose. Such a specimen can be obtained by annealing the thin-film bicrystal shown in figure 1a to a relatively high temperature (see figure caption for details). The boundary geometry in figure 1d is clearly only metastable, since every boundary forms a closed loop enclosing a crystal island (Fig. 4): there are no boundary triple points and therefore no linked networks of boundaries. Further annealing should therefore result in the shrinkage of each island until all boundaries have been eliminated. However, the driving force for this process is rather small, and the island system is frequently stable to $600^\circ$ C or above. Consequently, there is a large temperature range in which it is possible to observe boundary islands of mean diameters from a few hundred Å to several micrometers.

We have made an extensive study of the orientations which the numerous transverse boun-
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...daries in the columnar polycrystals tend to adopt after annealing. In general, we would expect a tendency for boundary segments to adopt low energy orientations, and in a few cases extensive faceting has been observed. If the island grains could be ideally equilibrated under a condition of constant volume the island shape should reflect the appropriate section of a γ-Wulff plot. However, the situation can be perturbed in the present specimens by the following factors:

5.1 Pinning of the boundary at bubbles lying in the original horizontal boundary. — However, this is not expected to be a very strong effect [15].

5.2 Anisotropy of the migration rate of the boundary while it is between stages a and b (Fig. 1). — There is considerable evidence from recrystallization studies that such an anisotropy exists, with the slowest moving (and hence most prominent) face of a growing grain being {111} [16, 17]. On this basis the prominent faces of our islands should have been parallel to a {111} plane of the outer grain. However, in all specimens so far the {111} planes made a considerable angle with the film normal, and boundaries in this orientation were unlikely to survive without rotating towards the film normal (Fig. 1, b to c).

5.3 Surface drag. — It has been reported [18] that boundary mobility is reduced at small specimen thicknesses, and the effect has been attributed to a surface drag. This could conceivably result from thermal grooving (Fig. 1e), the presence of pinholes in either Crystal 1 or 2, or other surface defects in the present thin specimens.

5.4 History. — It is quite possible that the migration to the surface of the original horizontal boundary does not occur randomly. Although we have no direct evidence of a preferred orientation for breakthrough, because of the other pinning effects described above, it conceivably could be a significant determinant of the preferred boundary direction after annealing.

To date we have studied high angle CSL tilt boundaries close to Σ = 3, 5, 9, 11, 13, 17a, 19a and 19b, a number of non-CSL orientations and a number of low angle boundaries. In the high angle boundaries well developed faceting has only been observed in the Σ = 3 and 11 systems. The {111} and {211} twins in the Σ = 3 system are extremely prominent (Fig. 4b) and the {311} twin in the Σ = 11 system is clearly visible in figure 4c. There is considerable evidence (e.g., Fig. 4a) that low angle <001> tilt boundaries frequently tend to facet. The example shown has well defined facets which lie parallel to the average <110> directions of the two crystals in the boundary plane. A more extensive computer-assisted survey of the statistically most frequent boundary orientations in both low and high angle random and ordered <001> tilt boundaries shows that the most frequently occuring boundary plane lies along the average <110> crystal direction.

6. Discussion and Conclusions. — 6.1 No substantial progress has been made in the detection of secondary GBD relaxations in CSL boundaries (section 2). Progress has been hindered by our inability to detect GBD networks of fine spacing and small |b|. The Σ = 29 boundary (with |b| = 0.47) studied by Bollmann et al. [6] appears to possess the weakest secondary CSL type relaxation yet identified.

6.2 Little progress has been made in the study of possible secondary GBD relaxations in NC boundaries in cubic metals (section 3). No GBD networks of this type have yet been observed, and the only indication that NC boundaries may exist is the single faceting experiment of Weins and Weins [8].

6.3 A clear example of a PM boundary which is ordered (periodic) in one dimension and disordered in the other has evidently been found (section 4). As shown by Warrington and Boon [4], the geometrical conditions for the formation of such boundaries should be quite common, and further study of their occurrence and detailed structure should therefore be undertaken.

6.4 The results in section 5 indicate that energy minima exist for {111} and {211} twins (Σ = 3) and {311} twins (Σ = 11) which are deep enough not to have been overridden by the kinetic factors which have already been discussed. The result that the {111} and {311} twins are of unusually low energy agrees with the calculations and measurements described by Hasson et al. [19] for aluminum and appears to be consistent also with observations of Herrmann et al. [20] for copper and silver. The case of the {211} twin is more controversial, but there is evidence [21] that this is indeed a low energy interface in gold.

The above boundaries all have relatively high values of the planar density of coincidence sites (PDCS). However, other boundaries of comparable PDCS did not appear during annealing, and we therefore did not find a simple relationship between the frequency of occurrence of particular boundary orientations and either the PDCS or Σ. For example, the three facets which we observed had values of the PDCS, ρ = Γ/a)^2, corresponding to Γ_{111} = 2.31, Γ_{311} = 1.21 and Γ_{211} = 0.82. However, other boundary systems which have equally high or higher PDCS in which faceting was not observed include the {331} twin in Σ = 19a with the PDCS corresponding to Γ = 0.92 and the {210} twin in Σ = 5 with Γ = 0.89.

The long-standing and intuitive idea [22] that boundaries with a high PDCS are particularly low
energy boundaries therefore does not seem to be generally true. In agreement with Herrmann et al. [20], we conclude that factors other than the periodicity of the geometrical structure are often important in determining the energy. Additional evidence which supports this conclusion are observations that the energies of similar types of twins in different metals vary widely.

Our preliminary observations suggest that in cases of fixed crystal misorientation the boundary orientations of relatively low energy correspond to planes with high densities of O-Lattice elements. The low energy boundary orientation in \( <001 > \) tilt boundaries was found to be parallel to the average \( <110 > \) direction. This plane in every case possessed the highest density of O-Lattice elements. In addition, the observed facets in the \( \Sigma = 3 \) and \( 11 \) systems corresponded to planes of high O-lattice element density. It seems possible that relaxations associated with the O-Lattice may be responsible for the relatively low energy.

Finally, we comment on the possibility of a simple criterion for low boundary energy. As seen above, the simple PDCS criterion is clearly inadequate. The pair potential calculations of Hasson et al. [19] predict the unusually low energies of the \{111\} and \{311\} twins but not of the \{211\} twin. A simple geometrical interpretation of this result is not obvious, and in general, it seems unlikely that criteria based on simple geometrical arguments of an a priori nature will be successful. The detailed nature of the interatomic potentials must be considered, and it is also likely that conduction electron effects and the matching of wave functions across the boundary are of importance in determining the energy and the configuration of the boundary.

References


DISCUSSION

W. BOLLMANN: Comment on «plane matching».

The structure of crystalline interfaces can be understood on the basis of the tendency of the crystals to conserve in the boundary as much of their structure as is possible. The first stage is the conservation of the crystal structure itself, deviations from the perfect crystal structure itself, deviations from the perfect crystal structure are corrected by subgrain boundaries (or phase boundaries of two closely resembling phases). The common structure is conserved in the areas between the dislocations. The next best possibility is the conservation of a common substructure, such as a coincidence site lattice or a close coincidence site lattice (Bonnet, Durand, ...) (proceedings). The deviations from these configurations are corrected by DSC-dislocations. If the deviation from a coincidence orientation becomes too large (e.g. 32° rotation around the 001 axis in f. c. c.) there may still be the orientation of the common axis to be conserved and deviation from that orientation lead to parallel dislocation lines which are the same as those predicted by the plane matching approximation (Pumphrey [1]). In a final stage boundaries may exist, where apparently no order at all can be conserved. Such a boundary should be able to «dissolve» extrinsic dislocations completely as was observed by Pumphrey (proceedings). To summarise, it can be said that, if the crystals find a possibility to conserve some order in an interface, they will do so, and the structure of the interface can be determined based on this assumption.