This method is incomparably superior in the following features to other methods, for example, the fluorescence-excitation method, or the method using a crystal monochromator in the diffracted beam: (i) the Compton scattering is effectively eliminated at each s; that is, the fraction of Compton scattering which is included in $I_n$ is at most one percent, irrespective of the species of scattering atom, (ii) this elimination is made experimentally, irrespective of the value s; therefore, it is unnecessary for subtraction of the Compton contribution to use tabulated theoretical values, (iii) the scattered beam is detected with sufficiently strong intensity, (iv) at the same time the whole spectrum of the scattered beam is directly obtained; accordingly, unwanted fluorescent and scattered radiations can be effectively eliminated, and (v) the X-ray optical arrangement is simple, because a crystal monochromator is not used.

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References


An Immobile Dislocation Arrangement in As-Grown Copper Single Crystals Observed by X-ray Topography

BY MASAO KURIYAMA, JAMES G. EARLY AND HAROLD E. BURDETTE


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X-ray diffraction topography using transmission geometry has revealed an interesting array of extremely straight and narrow long-line images in sizeable copper single crystals grown under particular growth conditions by the Czochralski technique. These images are analyzed and elucidated by a model of Lomer-Cottrell dislocations. The formation of these sessile dislocations usually aids the growth of large copper crystals of high perfection. The high degree of perfection over the entire volume of the crystals accounts for macroscopic arrangements of Lomer–Cottrell dislocations which have not previously been observed by electron microscopic techniques.

1. Introduction

There have been several reports on growing metal single crystals containing regions which are totally dislocation-free (Howe & Elbaum, 1961; McFarlane & Elbaum, 1965). In particular, copper crystals of high perfection have been prepared and studied in detail by Young & Savage (1964) and Fehmer & Uelhoff (1969). More recently, Sworn & Brown (1972), followed by Tanner (1972), have demonstrated that copper crystals, although small in diameter, could be grown free of dislocations by initially narrowing the crystal diameter at one region of the boule.*

Even with these studies, however, the documentation of the growth conditions for the preparation of dislocation-free metal crystals still is far from complete, unlike the case of semiconducting crystals (Billig, 1956; Penning, 1958; Brice, 1968; Dash, 1959; Steinemann & Zimmerli, 1967). Continued efforts are still needed to establish reproducible growth conditions for the production of large, highly perfect metal crystals. As one such effort, Kuriyama, Early & Burdette (1974) have recently studied the relationship between fluid-flow conditions and the degree of crystal perfection during the growth of large, highly perfect copper crystals by the Czochralski technique. In this study, X-ray diffraction topography has revealed that one particular growth condition results in many extremely straight dislocation lines in the crystals. These lines run across almost the entire diameter of the crystal, and lie in a

* The reader should keep in mind always that the term 'dislocation free' is always dependent on the technique used to detect the dislocations.
crystallographic set of three possible slip planes for the face-centered cubic crystal. Interestingly, these lines can also be observed with good contrast in the topographs when this particular set of slip planes is chosen as diffracting planes. Consequently, these dislocation lines cannot be identified simply as ordinary edge or screw dislocations. The purpose of this paper deals with an identification of those extremely straight-line structures observed in these as-grown copper crystals.

2. Experimental procedures

The details of the crystal-growth procedures and the assessment of crystal perfection by X-ray dynamical diffraction have been described in a previous paper (Kuriyama, Early & Burdette, 1974). In this paper, only the experimental conditions relevant to the present work are described. Large copper single crystals were grown by the Czochralski technique from single-crystal seeds in a vacuum furnace. The pulling speed was between 0.013 and 0.100 cm min⁻¹. The melt and seed were rotated around a common axis in the same direction, with speeds ranging from 5 to 20 r.p.m.; the relative speed of rotation was 0.6 r.p.m. Copper of 99.999% purity was used as the melt charge. Crystal boules were grown with initial narrowing of the boule diameter at one region, thus forming a ‘bottle-neck’. The grown crystals were about 6 cm long with diameters between 1.5 and 3.0 cm and with a bottle-neck diameter of 0.5 mm. The boules were sliced into discs with an acid saw and the discs were polished on an acid polishing wheel in the manner of Young & Wilson (1961). The discs have (110) planes as their parallel faces, so that the four strongest diffracting planes, (111), (11̅1), (002) and (220), can be used in transmission geometry.

For the assessment of the perfection of sample crystals, two different X-ray optical arrangements were employed, namely, an asymmetrical crystal topographic camera and a high-resolution double-crystal scanning diffractometer. The first, which will be hereafter called asymmetrical crystal topography (ACT), is equipped with a monochromator made from a silicon crystal whose surface makes an angle of 13°5 arcmin with the (111) diffracting plane for Cu Kα radiation. The incident X-ray beam falls on the silicon crystal surface almost parallel to it, and the 111 diffracted beam appears with a size of 1.7 x 2.5 cm, sufficiently large to cover the entire area of the sample copper crystals. In the second arrangement, which will in the future be called the scanning diffractometer (SCAD), a scanning device is attached to a high-resolution double-crystal diffractometer so that the well collimated narrow beam can scan with high resolution the entire crystal. This enables one to obtain the profiles and widths of rocking curves at any location in the crystal. The quality of the beam in SCAD was checked with measurements of the rocking curves of a dislocation-free germanium crystal which was placed at the second crystal position.

The full width at half maximum (FWHM) of the 220 rocking curve from the germanium crystal was determined to be 12.8 arcmin in the Si (220) surface/Ge (220) surface mode and 15.5 arcmin in the Si (220) transmission/Ge (220) surface mode, with Cu Kα radiation. This silicon crystal was used as the first crystal or monochromator in either transmission or reflection geometry to obtain the rocking curves and scanning topographs from sample copper crystals.

The thickness of the copper discs was determined by the anomalous transmission effect (Kuriyama, Early
& Burdette, 1974) as shown in Fig. 1. The thickness can be geometrically related to the distance between the images $L_0$ and $L_v$. The thinnest disc was 0.1439 mm thick and the thickest was 0.8934 mm thick. The product of the ordinary linear absorption coefficient and thickness thus ranged from 7.93 to 49.24 for Cu $K\alpha$ radiation.

3. Rocking curve widths and topographs

The rocking curves were obtained from the copper discs for the 220 diffracted beam in the reflection geometry and the 111, $1\overline{1}T$, 11T, and 002 in the transmission geometry. For as-grown crystals, the peak intensity of the rocking curves varied up to 30% between different locations in the crystal. The width of the curves, however, did not vary as much. The values (FWHM) of the rocking-curve widths, averaged over the crystals, are $34''$ for the 220 surface reflection, and 14, 13 and $12''$ respectively for the 111 and $1\overline{1}T$, 11T and 002 reflections in the transmission geometry.* Typical profiles of the rocking curves are shown in Fig. 2 for these diffracting planes.

Fig. 3 shows a 220 reflection topograph† taken with the ACT. This represents the usual surface reflection topograph for the crystals grown under the conditions described in § 2. An example of the transmission topographs also taken with the ACT is shown in Fig. 4, where the 002 diffracted beam was used. The crystal used for this topograph was determined from the anomalous transmission effect to be 0.1439 mm thick. This topograph illustrates the common features in the transmission topographs from the crystals grown under the present growth condition. In this topograph, many lines run normal to the [111] direction, while another set of lines runs normal to the [111] direction. In addition, there appear black-and-white bands parallel to the [110] direction. As indicated in Fig. 4, the first set of lines is denoted by set I, the second by set II, and the set of bands by set III.

The transmission topographs obtained with the 111, 11T, 002 and 220 diffracted beams are reproduced in Fig. 5(a), (b), (c) and (d) respectively. It is observed in these topographs that the image contrast of the sets, I and II, depends on the diffracting planes used. The experimental results from these topographs can be summarized as follows:

(1) The lines in the sets, I and II, are extremely straight, narrow, and discontinuous, running almost across the entire crystal.

(2) The lines in set I lie in the (111) plane; when the images of these lines are projected on the (110) plane, the plane of the topographs, they run parallel to the [112] direction.

(3) The lines in set II lie in the (111) plane; when the images of these lines are projected on the (110) plane, the plane of the topographs, they run parallel to the [112] direction.

(4) In the 11T topograph, the lines in set I have better contrast than those in set II. In the 111 topograph, the relation of contrast is reversed. In the 002 and 220 topographs, both set I and set II appear to have equal contrast.

(5) Set III consists of black-and-white bands running in the [110] direction.

In this paper, we confine ourselves to the identification of sets I and II.

4. A sessile dislocation arrangement

In dynamical diffraction, the image contrast due to crystal imperfections is determined by the factor $\{1 - ^{(*)}$ The rocking-curve width in the transmission geometry varies as the crystal thickness changes. The values reported here are obtained from a crystal of $\mu L = 7.93$.

† Several of the topograph enlargements are composites as a result of microscope limitations during enlargement.
exp \{i\mathbf{H} \cdot \mathbf{u}(r)\}\), where \(\mathbf{H}\) is a reciprocal-lattice vector in a reference perfect crystal and \(\mathbf{u}(r)\) is an atomic displacement vector at a position \(r\) inside the crystal (Kuriyama, 1967; 1969). In the first-order approximation for almost perfect crystals, this factor may be replaced by \(\frac{\partial \{i\mathbf{H} \cdot \mathbf{u}(r)\}}{\partial \mathbf{K}}\), where \(\mathbf{K}\) is a coordinate along the X-ray propagation direction (Kuriyama, 1970; 1972; 1973). There are two propagation directions in a single Bragg diffraction; one is the transmitted direction \((\mathbf{K} = 0)\) and the other the Bragg-diffracted direction \((\mathbf{K} = \mathbf{H})\). In X-ray diffraction topography, the principal concern is not with quantitative information on the imperfections, but rather, the qualitative visual impact given by the imperfections through such information as their locations, shapes and distributions. In a crude approximation which is suitable for qualitative topography, the local contrast condition may be replaced by a simpler factor \(\mathbf{H} \cdot \mathbf{u}(r)\) or \(\mathbf{H} \cdot \mathbf{b}\), where \(\mathbf{b}\) is the Burgers vector of a dislocation. It should, of course, be noted even in this crude approximation that \(\mathbf{u}(r)\) is not parallel to \(\mathbf{b}\). However, the crude contrast factor, \(\mathbf{H} \cdot \mathbf{b}\), is convenient for practical purposes.

This contrast condition eliminates at once the possibility that the lines in sets I and II are glissile dislocations of a pure screw or pure edge character. Such dislocations lie in a slip plane, and their Burgers vectors also lie in this plane. When this slip plane is parallel to the diffracting planes, there will not be image contrast for these dislocations. In contrast with this prediction, the lines are clearly visible in the topographs under these particular diffraction conditions, as the summarized results indicate. Results 2 and 3 state that these lines lie in the \((111)\) slip planes and the \((11\bar{1})\) slip planes, respectively, for set II and set I. Let us first assume that these line images are caused by dislocations. The formation of the clear images under the particular diffraction conditions implies that the Burgers vectors, or more correctly those significant atomic displacements associated with the dislocations, do not lie in the dislocation slip planes.

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Fig. 5. ACT transmission topographs obtained from different diffracting planes (a) 111; (b) 11\bar{1}; (c) 002; (d) 220. The line images of set II are shown in the vertical direction.
Fig. 6. SCAD topograph taken in the reflection geometry. This magnified 220 topograph of the surface shows the images of dislocations terminating on the surface. Although short in length, they are aligned in the same direction as observed in Fig. 4.

Along with result 1, this strongly suggests that the dislocations observed in the topographs could be dislocations interacting with each other to form immobile lines of dislocations, i.e. Lomer–Cottrell locks (Lomer, 1951; Cottrell, 1952).

In a face-centered cubic crystal, the possible interactions of dislocations on two intersecting slip planes have been studied extensively (for example, Cottrell, 1964; Hirth & Lothe, 1968). Consider set II as an example. Result 3 demands that the lines of dislocations should be either in the [01] direction or in the [10] direction. The possible lock direction [10] would not be visible in the topographs, because this direction is perpendicular to the [112] direction in which the observed line images of set II run in the plane of the topographic images. In order to produce the locks in the direction of [01], the two intersecting slip planes have to be (11) and (11). For the locks in the direction of [01], the (11) and (11) planes are involved. There are three possible directions of the Burgers vectors in each slip plane. These three dislocations in a slip plane can therefore interact with three possible dislocations in the other intersecting slip plane. After consideration of (i) which pairs of dislocations can be energetically stable, (ii) which of the stable pairs can glide afterwards, and (iii) which form annihilated screw dislocations, only two pairs are found which can form a sessile dislocation line that runs parallel to a given locking direction. Both pairs result in the same Burgers vector which lies in neither of the original slip planes. For the [01] locking direction, the resultant Burgers vector is (1/2) [01]. We denote this Lomer–Cottrell lock as type IA. For the dislocation locked in the [01] direction, the resultant Burgers vector is given by (1/2) [01]. This lock is denoted as type IB. In a similar fashion, for set I the following Lomer–Cottrell locks were found: IA runs parallel to the [01] direction with the Burgers vector (1/2) [01], and IB runs in the [01] direction with the Burgers vector (1/2) [01].

The approximate contrast conditions for these possible locks were next applied to the diffraction conditions used. The results are shown in Table 1. As mentioned previously, the contrast condition resulting in $H \cdot b = 0$ simply means that the image contrast under such a diffraction condition is inferior to the contrast under different diffraction conditions. These results are in a good agreement with the observed results 3 and 4. Since all the dislocation lines of these locks make an angle of about $30^\circ$ with the (10) plane, they should terminate on the crystal surface. To confirm this, high-resolution 220 reflection topographs were taken with the SCAD. As can be observed in Fig. 6, the dislocation images on the surface topograph are indeed aligned, though short in their length, in exactly the way predicted. In Fig. 6, the images of the terminating dislocations of set II run in the vertical direction perpendicular to the [11] direction.

Table 1. Contrast factor for possible Lomer–Cottrell locks

<table>
<thead>
<tr>
<th>Type of locks</th>
<th>Line vector</th>
<th>Contrast factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>[01]</td>
<td>111 111 002 220</td>
</tr>
<tr>
<td>1B</td>
<td>[01]</td>
<td>1/2 1/2 1/2 1/2</td>
</tr>
<tr>
<td>II A</td>
<td>[01]</td>
<td>1/2 1/2 1/2 1/2</td>
</tr>
<tr>
<td>II B</td>
<td>[01]</td>
<td>1/2 1/2 1/2 1/2</td>
</tr>
</tbody>
</table>

In addition, the high-resolution 111, 111 and 002 transmission topographs were taken with the SCAD. As shown in Fig. 7, the line images of sets I and II...
were indeed very narrow. It is therefore concluded that the assumption of Lomer–Cottrell locks elucidates all the results listed in § 3 with the exception of result 5.

5. Discussion

Lomer–Cottrell dislocations have been found in face-centered cubic crystals with electron transmission microscopy (Whelan, 1958; Mader, Seeger & Thieringer, 1963). They appear, however, as rather isolated local events in the entire crystal. The length of the dislocations are short. Unlike the observations with electron transmission microscopy, the Lomer–Cottrell dislocations observed in the present paper have occurred almost throughout the entire crystal, and their length is on a macroscopic scale. The difference between the electron microscopic and the X-ray topographic observations can be attributed to the following facts. First, the crystals used for X-ray topography are bulky (1.5 cm in diameter and almost 1 mm thick) compared with the thin films used for electron transmission microscopy. Next, because of the overall high degree of perfection in the bulk crystals (judged from their display of the prominent Borrmann anomalous transmission effect), all the regions in the interior of the crystals are likely to have similar properties with respect to each other. If the formation of a Lomer–Cottrell dislocation is energetically favorable at one place, there is no doubt that dislocations of a similar type would occur everywhere inside the crystal. This phenomenon is very unlikely to occur in thin films, since the perfection of these thin films is not as high over the entire film as it is in these crystals used for X-ray anomalous transmission topography. The simultaneous use of X-ray topography with a simple metal crystal of high perfection has, for the first time, made it possible to observe the extensive arrays of Lomer–Cottrell dislocations on a macroscopic scale over the entire volume of the crystals.

There are a few additional comments worthy of note concerning the growing of sizable perfect copper single crystals. When a slice of the as-grown crystal showed the arrangements of Lomer–Cottrell dislocations over its entire volume, as shown above, the degree of crystal perfection was equally high for any part of the crystal boule of about 6 cm long. In contrast, some as-grown crystals grown under different growth conditions frequently showed a high degree of perfection in one portion of the boule, but not necessarily the same quality of perfection in other parts of the boule. Most of these crystals tended to develop low-angle grain boundaries somewhere along the length of the boule.

This may indicate that a particular growth condition aids dislocation interactions to form immobile Lomer–Cottrell locks. When this phenomenon takes place, the resultant crystal becomes highly perfect. If widespread slip occurs or if many dislocations form randomly, as in the case of the other growth conditions, then the locking would not take place and the dislocations would still be mobile and affect the subsequently grown part of the crystal, resulting in a less perfect crystal.

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References

New York: Gordon & Breach.
Phys. 34, 3376–3386.
Solids, Suppl. 1, 81–87.
32, 559–561.