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Inclusions in Aluminium Crystals*

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Aluminium crystals, growing by recrystallization in fine-grained material, often do not consume some grains of the original material. They contain a number of inclusions, which do not vanish even after very long annealing. These reflect light simultaneously in the same direction. By means of (1) the etching method of Lacombe and Beaujard and (2) the X-ray method it is proved that these inclusions are deformed grains of the original material possessing spinel-twin relationship to the large surrounding crystal correct to within a few degrees. All four possible spinel-twin positions are represented.

The above is not valid when the 'inclusions' are larger than the average original grain size. In that case 'inclusions' have an undeformed lattice and possess no special orientation.

On the strength of these experiments it was expected that an aluminium crystal grown by recrystallization contains also inclusions with an orientation slightly different (by a few degrees) from its *own* orientation. The existence of such inclusions has been proved by X-ray methods.

By means of the etching-method it was possible to determine the orientation of inclusions with dimensions down to 30 μ; for the X-ray method the dimensions had to be of the order of 0·1 mm.

To account for the observations the assumption is made that a grain of the original material having approximately (within a few degrees) a spinel-twin orientation towards a growing crystal of aluminium is left by the latter as an unconsumed inclusion, whereas if the spinel-twin orientation is perfect to within a fraction of a degree that grain may grow in exact twin position by 'stimulation'.

Introduction

When a fine-grained aluminium test-piece is stretched several percent and then heated, large crystals can grow in it by so-called primary recrystallization. Under definite circumstances large crystals can also be prepared by submitting a fine-grained material, obtained by primary recrystallization, to a prolonged annealing. This phenomenon is called secondary recrystallization (exaggerated or discontinuous grain growth).

The large crystals obtained in these two ways often contain inclusions, with a grain size equal to that of the original material (0·03–0·2 mm.), which can be made visible by etching. The inclusions do not vanish even after a very long annealing, as for instance was found by Seumel (1936). Incident light reveals that many inclusions reflect in the same direction (Burgers & May, 1945) (see Fig. 3). This fact suggests that such inclusions have the same, or nearly the same, orientation. The question arises whether there exists a crystallographic relationship between the orientation of the surrounding crystal and the orientation of the inclusions, and, if so, what relationship. The purpose of the present investigation was to investigate the orientation, which we supposed to be a spinel-twin relationship.

Experimental part

In order to determine the orientations, two methods were used: (1) The etching method of Lacombe & Beaujard (1944, 1945, 1947). (2) The X-ray method.

The etching method

Mahl & Stranski (1942) observed that by etching aluminium with diluted strong acids, such as HCl or aqua regia, the cube planes are developed. This is apparently also the case when the etching method of Lacombe & Beaujard is used. In this method the specimen is first electro-polished, then etched with a mixture of 47 % fuming nitric acid, 50 % concentrated hydrochloric acid and 3 % concentrated hydrofluoric acid.

We have confirmed by X-rays that the etch pits, obtained in this way, are actually bounded by the cube planes. By means of a Busch Metaphot, a photograph (magnification 600 times) was made of an electro-polished and thereafter etched plate-shaped aluminium crystal. A Laue transmission photograph was made of the same crystal, from which the orientation of the crystal was determined by the method of Schiebold & Sachs (1926).

On the stereographic projection, obtained in this way, the plane of projection and the plane of the plate-shaped crystal coincide. On this projection the position of the traces of the cube planes on the surface of the test-piece was constructed. As the position of the crystal was fixed both on the metallurgical microscope and in the Laue camera, the stereographic projection could be superimposed on the photograph of the etched crystal in corresponding positions. The boundaries of the etch pits now coincided with the traces of the cube planes on the stereographic projection. From this it will be clear that the shape of the etch pits depends on the orientation of the crystal in the specimen, as was noticed already by Walton (1944).

* A preliminary account of this work has already appeared (May, Tiedema & Burgers, 1948).

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Fig. 4 shows this again for two contiguous crystals. As appeared from X-ray photographs, the left-hand crystal has a [111] direction, the right-hand crystal a [110] direction approximately perpendicular to the plane of the specimen.

This property was used to determine the orientations of the inclusions with respect to the surrounding crystal. A crystal with inclusions, obtained by primary recrystallization, was electro-polished and etched. Photographs were made of these inclusions with a magnification of 300 or 600 times. Fig. 5 shows an example. From the large crystal a Laue transmission photograph was made and the orientation determined in the way mentioned before. Stereographic projections of the four possible twin positions on the {111} planes were constructed. On each of the stereographic projections so obtained the traces of the cube planes were indicated.

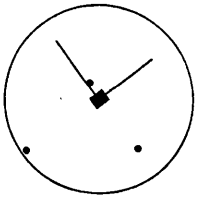

Fig. 1. Stereographic projection of crystal A (cube poles).

If now a projection is placed on a photograph so that the traces of the cube planes of the large crystal coincide with the boundaries of the etch pits of that crystal, the boundaries of the etch pits of the inclusion always coincide with the traces of the cube planes of one of the possible spinel-twin positions within a deviation of about 5°. For a particular crystal this appears from Figs. 1, 2 and 6.

Fig. 6 (*a–d*) shows four areas on the same aluminium crystal A (magnification 600 times), as can be seen from the similar position of the etch pits. Each photograph contains an inclusion B, in which the shape of the etch pits demonstrates the different orientation from that of the matrix.

Fig. 1 gives the stereographic projection (cube poles) of the large crystal A, whereas in Fig. 2 (*a–d*) the cube poles of the four possible spinel twins with regard to A are indicated. The traces of the cube planes with the plane of the test-piece are indicated by short lines through the centre of every projection. Comparing the directions of these traces with those of the boundaries of the etch pits (drawn schematically in the centre of the projections), these directions are seen to be approximately parallel in all four cases. *It follows that an approximate spinel-twin relationship can be assigned to every inclusion. All four spinel-twin positions are represented.*

The above is not valid for inclusions which are larger than the average grain size of the original material. As will be shown in the next section, these inclusions give Laue photographs with sharp spots. It therefore seems probable that they represent special grains of the original material which, on stretching the test-piece, underwent but a very slight deformation, so that, as regards energy, they remained practically equivalent to the growing crystal, which left them unconsumed.*

A similar investigation was carried out on crystals of an aluminium–manganese alloy (1·1 % Mn) obtained by *secondary* recrystallization by Beck, Holzworth & Sperry (1948) and kindly put at our disposal by Prof. Beck. These crystals contain also small (primary) grains, as shown by Beck *et al.* The same approximate spinel-twin relationship between large crystal and unabsorbed grains was found to exist in this case.

With the method described, it was possible to determine the orientation of inclusions with dimensions down to about 30 μ.

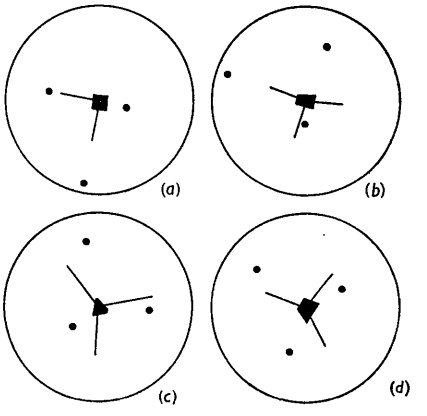

Fig. 2. Stereographic projections of the four spinel twins B with respect to crystal A. The short lines through the centre indicate the traces of the cube planes on the surface of the crystal; they are approximately parallel to the sides of the etch pits in the photographs of Fig. 6 (*a–d*). Compare with figures in centre of projections.

The X-ray method

In order to obtain a confirmation of the results of the optical investigation, Laue photographs were made of a number of larger inclusions. Tungsten radiation and a diaphragm of diameter 0·15 mm. and length 100 mm. were used. In this way it was still possible to photograph inclusions with a dimension of $\pm 0{\cdot}1$ mm. Laue transmission photographs were made from the primary recrystallized material. On the photographs the patterns of the large crystal and of the inclusion always appear superimposed. If these two are *exact* spinel twins, some definite spots must coincide.† On

* The possibility, however, must be kept in mind that these inclusions are themselves new crystals, also formed by the recrystallization process, in the same way as the large crystals with a smaller growing velocity: in that case these latter crystals will grow around them (Burgers, 1947*a*).

† Viz. one (111), three (110), three (211), six (210), six (311) and others. The (100) spots from one partner coincide with (221) spots from the other one, and the three remaining (111) spots with (511) spots. The latter lie in the three coinciding [110] zones, while the coinciding (110), (210) and (311) spots lie on the three coinciding [211] zones. The (211) spots, together with the (110) spots, lie on the coinciding [111] zones.

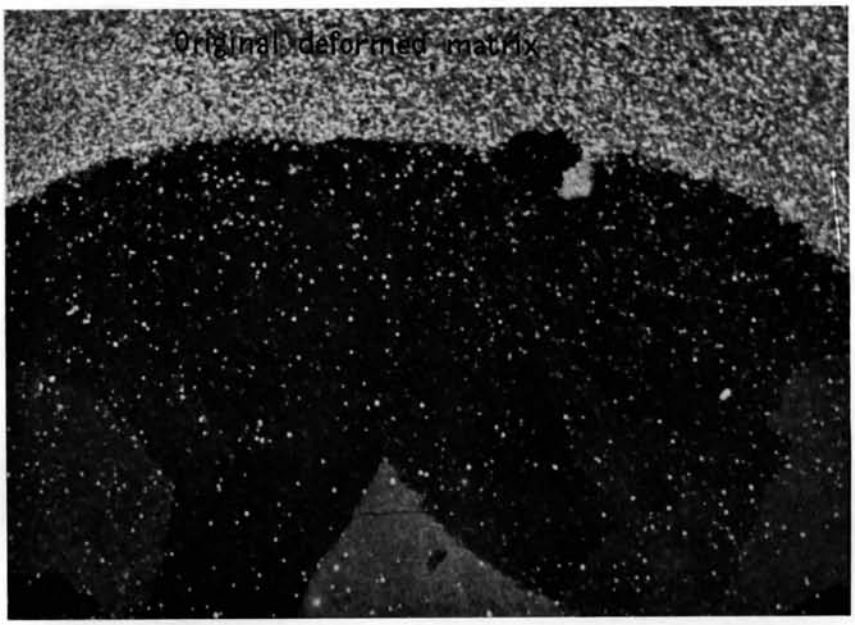

Fig. 3. Large aluminium crystal with inclusions (~natural size).

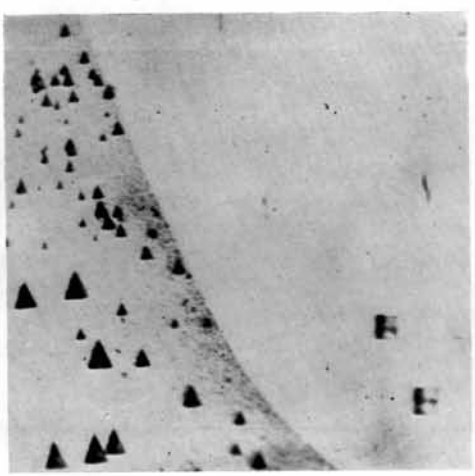

Fig. 4. Etch pits of two differently orientated crystals (×300). Left: [111] approximately ⊥ surface; right: [110] approximately ⊥ surface.

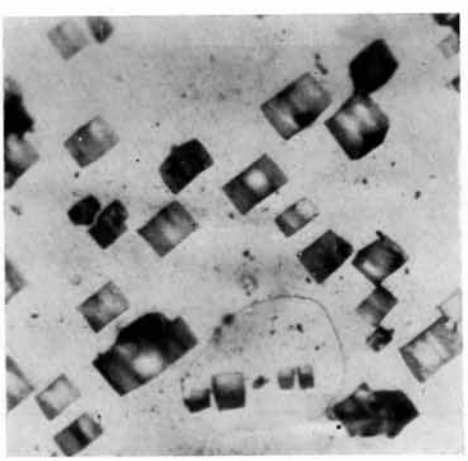

Fig. 5. Aluminium crystal with unconsumed inclusion (×300).

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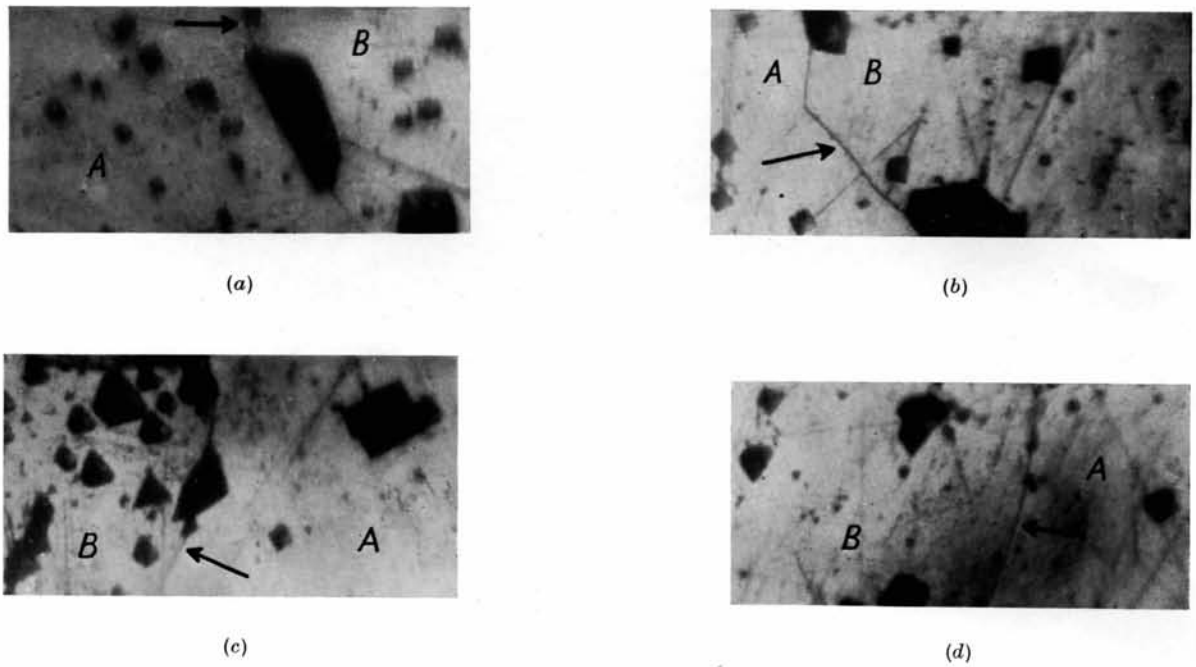

Fig. 6. Etched surface of a crystal A and of four inclusions B ($\times 600$). Boundary between A and B indicated by arrow.

Fig. 7.

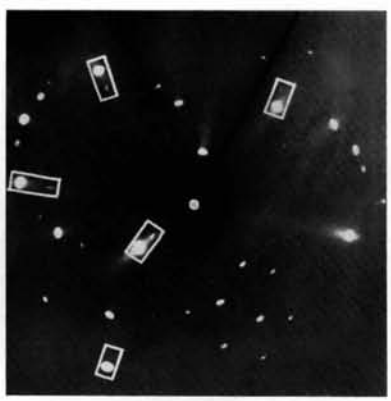

Fig. 8.

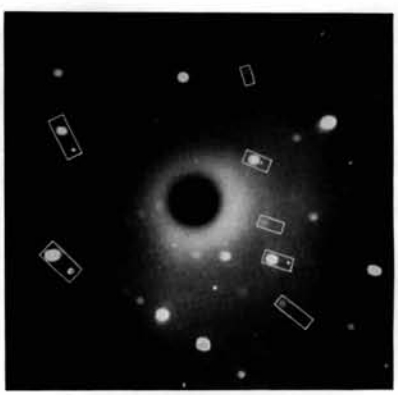

Fig. 9.

Fig. 7. Superimposed transmission Laue patterns of a large aluminium crystal (sharp spots) and of an unconsumed inclusion of the original deformed matrix (slightly elongated spots). Pairs of spots enclosed in frames would coincide if the orientation relationship between crystal and inclusion was exactly that of a spinel twin.

Fig. 8. Superimposed patterns of a large aluminium crystal (large spots) and of an unconsumed grain of the original deformed matrix (small spots) which possesses nearly the same orientation as the large crystal. Specimen–film distance: 4·5 cm. but reproduction is two-thirds of original size.

Fig. 9. Superimposed back-reflexion Laue patterns of a crystal obtained by exaggerated grain growth of an Al–Mn alloy (1·1 % Mn) and an unconsumed inclusion of the original primary recrystallized matrix (small spots). Spots which would coincide in the case of an exact spinel-twin relationship are enclosed in frames. Notice that the spots of the inclusion are sharp.

a photograph showing the superimposed patterns one may thus expect several coincidences. We observed no exact coincidences; the spots which should coincide lie, however, close to each other. On Fig. 7 such pairs of spots are shown enclosed. The inclusion is therefore only *approximately* a spinel twin with regard to the large crystal. At the same time it is seen on Fig. 7 that the spots of the inclusion show asterism. *This means that the inclusion consists of deformed material.*

Inclusions larger than the original grain size, with dimensions of about 0·5 mm., gave *sharp* Laue spots. This fact leads to the conclusion stated at the end of the previous section.

On the strength of the foregoing it was assumed that grains of the original material, which possess nearly the same orientation as the large crystal, may also not be consumed. Indeed, it was possible to find such grains by investigating a crystal with spinel-twin inclusions by X-rays. Fig. 8 shows an example of a Laue photograph showing spots of both large crystal and inclusion. The orientation of the inclusion is similar to that of the large crystal, the difference being again a few degrees.* These inclusions cannot be made visible by etching.

Laue back-reflexion photographs were made in the case of the secondary crystals. From these photographs the orientation was determined in some cases by a method using a standard projection, in other cases by the method of Greninger (1935). Here too we obtained the same result (see Fig. 9). As might be expected, the spots of the inclusions are sharp since they consist of undeformed material.

Discussion

The experimental part shows that crystals growing by primary as well as by secondary recrystallization cannot absorb grains which are approximately in spinel-twin position with regard to them or which possess nearly their own orientation. The spinel-twin case, observed here for aluminium, may also hold for iron and nickel–iron, judging from papers of O'Neill (1928) and Custers & Rathenau (1941). We should like to draw attention to the *Z-Körner* in the last-mentioned paper, which deviate about 8° from the twin position with regard to the surrounding cube texture. That in aluminium the unabsorbed grains really are grains of the original material seems to follow from the fact that the Laue spots of the inclusions, embedded in crystals formed by primary recrystallization, show asterism (see Figs. 7 and 8).

The assumption that a growing crystal can hardly consume a grain which possesses a spinel-twin position with regard to it was made also by other authors (for example Petersen (1947)).

It seems improbable that the inclusions originate from impurities in the original material, as they appear also in pure aluminium (99·998 %).* From the work of Lacombe & Beaujard (1947) and of Lacombe & Yannaquis (1948), on the attack by etching of the boundaries between two contiguous crystals, it is evident that even in very pure aluminium (99·9986 %) differences occur in the intensity of the attack between two different crystals, as well as along one definite boundary at points where it undergoes a change in direction. On account of the very high purity of the material used, it is very probable that the intensity of the attack depends on the relative *orientation* of both crystals and not on the presence of impurities. We suppose, therefore, that the presence of the inclusions is caused by the particular orientation of the growing crystal with respect to the surrounding material.

A related phenomenon, which occurs rather often in aluminium, is the appearance of 'stimulated' crystals (Sandee, 1942; Burgers, 1947*b*). These are crystals which started growing from a nucleus when another crystal, already growing, had approached the nucleus very closely. X-ray photographs showed that 'stimulating' and 'stimulated' crystals are always *exact* spinel twins (Burgers & May, 1945). Later experiments indicate that the difference of orientation does not exceed 10′.

To account for these facts we should like to make the following assumption. When a growing crystal meets grains of the original material which are in an *approximate* spinel-twin position it cannot consume them. When, however, it meets grains which are either *exactly* in spinel-twin position, or deviating so very little from this position that they can be 'pushed' into it, 'stimulation' occurs. This case will not occur as often as that in which the grains deviate some degrees from the exact twin position. Therefore inclusions are usually far more numerous than 'stimulated' crystals.

Note added in proof. In a recent paper Lacombe & Berghezan (1949) describe results closely related to those obtained by us.

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* We should like to point out that this photograph is quite different from an apparently similar photograph obtained by Lacombe (1948, p. 91, Fig. 3). From his photograph it follows that the difference in orientation between the two contiguous crystal parts is about 10′. It can be derived from our photograph that the difference between large crystal and inclusion amounts to several degrees, *whereas the spots of the inclusion show asterism.*

* This aluminium was kindly put at our disposal by Prof. Lacombe.

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The Accuracy of Atomic Co-ordinates Derived by Least-Squares or Fourier Methods

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Recent work by Cruickshank on the accuracy of atomic co-ordinates obtained in Fourier syntheses is here related to that of Cochran on the connexions between the least-squares and Fourier methods. Except when the atomic peaks are not resolved, it is shown that the same co-ordinates and estimated errors are obtained by the method of least squares and by appropriately weighted Fourier series (corrected for finite summation). An expression is obtained for the relative accuracies of the weighted and unweighted Fourier methods.

1. Introduction

The purpose of this paper is to relate and extend two of the approaches which have recently been made to the problem of the determination of atomic co-ordinates and their accuracy. In one approach (Cox & Cruickshank, 1948; Cruickshank, 1949) it has been shown how to estimate the standard deviations of co-ordinates derived by the Fourier method, when corrected for finite summation. In the other approach (Cochran, 1948*a*, *b*) relationships have been obtained between the Fourier and least-squares methods.

According to the former approach the standard deviation of an atomic co-ordinate (in an orthogonal cell) derived from a Fourier series, after correction for finite summation by Booth's (1946) method, is

$$\sigma(x_{rj})=\frac{1}{V}\frac{2\pi}{a_j}\left\{\sum_3 h_j^2\Delta F^2\right\}^{\frac{1}{2}}\Big/\left|\frac{\partial^2\rho}{\partial x_j^2}\right|, \qquad (1\cdot1)$$

where x_{rj} is the jth co-ordinate of the rth atom ($j=1$, 2, or 3), a_j the cell side, h_j the plane indices, $\Delta F=F_o-F_c$, $\partial^2\rho/\partial x_j^2$ is the curvature of the peak in the x_j direction, and $\sum_3$ denotes summation over all planes included in the series. This estimate and the finite-series correction are valid assuming

(1) the ΔF's may be treated as independent;

(2) the shapes of the observed and calculated peaks near the maxima are the same; and

(3) the peaks are resolved and the finite-series corrections small.

It has since been realized that (1·1) is incorrect for certain positions in the unit cell in systems with symmetry relations which permute the plane indices, e.g. if $F_{hkl}=F_{lhk}=F_{klh}$. The correct formula in this case is given in § 4.

2. Determination of atomic co-ordinates

Cochran's relationships between the Fourier and least-squares methods may be obtained in the following way.

Let u be the total number of independent planes observed, and let $\sum_u$ denote a summation over those u planes, a summation which must be distinguished from $\sum_3$, which includes all planes dependent on these u planes.

In Hughes's (1941) application of least squares the required atomic co-ordinates are those for which $\sum_u w(F_o-F_c)^2$ is a minimum, w being the weight given to one independent 'observation'. This expression may be rewritten $\sum_3 w_1(F_o-F_c)^2$, where, if s is the multiplicity of a plane, $w=w_1 s$. The co-ordinates x_{rj} satisfy

$$\sum_3 w_1(F_o-F_c)\frac{\partial F_c}{\partial x_{rj}}=0, \qquad (2\cdot1)$$

$\partial F_c/\partial x_{rj}$ denoting differentiation of the calculated structure factor with respect to one of the atomic parameters, so that, if t atomic co-ordinates are determined by symmetry from this one parameter, $\partial F_c/\partial x_{rj}$