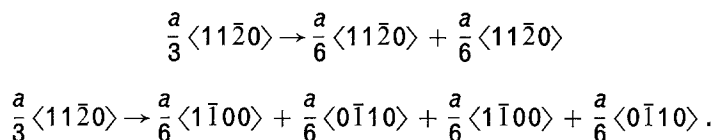


# Dislocations in $\beta$ -alumina electrolyte material

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$\beta$ -alumina obtained from a number of sources and manufactured by different techniques has been examined in the electron microscope. Dislocations have been observed on the basal plane and the Burgers vector determined as  $\mathbf{b} = a/3 \langle 11\bar{2}0 \rangle$ . The presence of this type of dislocation has been explained on the basis of the crystallographic structure of  $\beta$ -alumina. It is also predicted that the unit dislocation dissociates into two and four partials according to the energetically favourable reactions:



Experimental evidence has been obtained which shows the presence of dislocations separated into two and four partials in  $\beta$ -alumina. Microscopic deformation has been shown to occur in thin crystals of  $\beta$ -alumina in the electron microscope, by the passage of large numbers of dislocations along basal slip planes.

## 1. Introduction

A great deal of attention has been paid in recent years to the structure and properties of  $\beta$ - $\text{Al}_2\text{O}_3$  and only recently has the crystallography of the material been comprehensively reported. Interest in the material stems from the unusual electrical characteristics of the ceramic, in that it has very good ionic conductivity at relatively low temperatures. Such properties have found application for the material in connection with high temperature electrochemical cells. At the practical level such cells have been used to power an experimental road vehicle. In addition the material is electrically sensitive to changes in the surrounding chemical environment and hence, could find application as a chemical transducer.

The defect structure of solids is well known to influence a wide range of mechanical, electrical and physical properties. Characterization of a material would necessitate a thorough knowledge and understanding of any defects prior to explanation and experimental determination of their effect on properties. It is the purpose of this

publication to consider some of the possible defects, and report on those observed in  $\beta$ -alumina.

## 2. Structure of $\beta$ - $\text{Al}_2\text{O}_3$

Aluminium oxide generally occurs in the  $\alpha$  (corundum) form and also as alumina. Until 1931,  $\beta$ -alumina, formed during the purification of bauxite, was considered to be another such form. At the time its crystal structure was determined and the correct chemical formula suggested [1]. Structural investigations in greater detail have been carried out by later workers, significant work having been done by Peters *et al* [2].

The crystal structure of  $\beta$ -alumina ( $\text{Na-Al}_{11}\text{O}_{17}$ ), ( $P6_3/mmc$ ) consists of blocks of close packed oxygen ions with the metallic ion dispersed as in the spinel  $\text{MgAl}_2\text{O}_4$ . Between two such blocks of "spinel" a connecting layer of sodium and oxygen ions occur as shown in Fig. 1a. It is noticeable that the "spinel" blocks above and below the sodium-rich layer are mirror images. The unit cell then has the dimensions

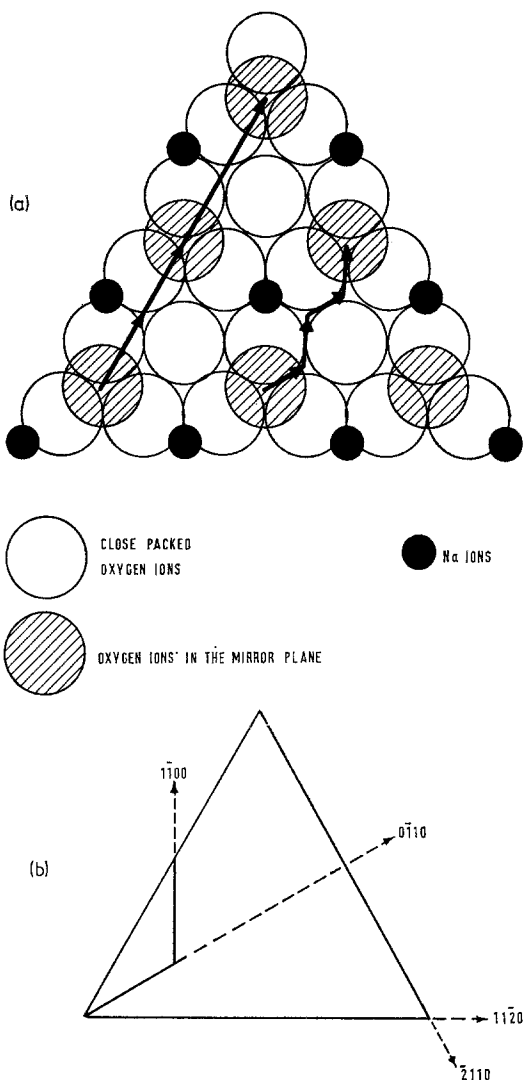


Figure 1 (a) Position of sodium ion on the mirror plane of  $\beta$ - $\text{Al}_2\text{O}_3$ . (b) Crystallographic directions.

$a_0 = 5.59 \text{ \AA}$  and  $c_0 = 22.6 \text{ \AA}$  and is made up of two of the "spinel blocks" and the connecting sodium-rich layer. Each of the sodium atoms in the mirror plane can take up one of two possible positions. Beevers and Ross considered the site where the sodium ion has six nearest neighbour oxygen ions to be more likely than the site having two (Fig. 1a). This view has been recently confirmed by the single crystal work of Bettman and Peters [3], who also measured a slight buckling of the oxygen layers to accommodate the structure. More recently it has been shown that some of the sodium ions can reside in an alternative position [2].

Phases richer in sodium than  $\beta$ - $\text{Al}_2\text{O}_3$  have been found and shown to be stable below  $1100^\circ\text{C}$ . Above this temperature they were thought to revert to  $\beta$ -alumina. Such a material with the composition  $\text{Na}_2\text{O}, 8\text{Al}_2\text{O}_3$  has been reported [4] having the same structure as  $\beta$ -alumina. Earlier works had suggested the presence of compounds with the formula  $\text{Na}_2\text{O}, 5\text{Al}_2\text{O}_3$  [5] and  $\text{Na}_2\text{O}, 6\text{Al}_2\text{O}_3$  [6].

The structure of  $\beta''$  is rhombohedral and has the space group  $R3m$ . Measurements of the lattice dimensions indicates values of the equivalent hexagonal cell dimensions of  $a_0 = 5.61 \text{ \AA}$  and  $C_0 = 33.9 \text{ \AA}$  and the crystal can be indexed assuming a repeat distance of  $11.3 \text{ \AA}$  or one third the unit cell length. Since this repeat distance is very nearly half of that of  $\beta$ -alumina ( $C_0 = 22.5 \text{ \AA}$ ), it has been suggested that three spinel blocks form the basic  $\beta''$  structure with interspaced "glide" planes. Such a structure can accommodate two sodium ions per unit cell in each "glide" plane and is consistent with the chemical formula  $\text{Na}_2\text{O}, 5\text{Al}_2\text{O}_3$ .

The spinel blocks are made up of oxygen ions in the close packed cubic structure, each block containing four oxygen layers. There are four possible ways in which these layers may be stacked in the unit cell. They are:

1. BC / A B C A / B C A B / C A B C / B A
2. A B / A B C A / C A B C / B C A B / A B
3. C A / A B C A / A B C A / A B C A / A B
4. C A / A B C A / A C B A / A B C A / A B

X-ray intensity calculations have been made by Whittington *et al* [7] which suggest that of the proposed models the second is the most likely, since good correlation was obtained with observed and calculated X-ray line intensities. Such a stacking sequence for the oxygen ion arrangement for the spinel blocks has recently received further support in the literature [8].

### 3. Experimental methods

Samples of  $\beta$ -alumina were obtained from a number of sources, usually commercial research laboratories, in the form of tubes or plates. In addition to the polycrystalline  $\beta$ -alumina, single crystal material was examined. This was obtained by cleaving large crystals from a brick of Monofrax, a type of fusion cast refractory brick used in the glass industry.

Thin sections of the ceramic were cut on a diamond impregnated wheel and mounted on a glass slide using Lakeside resin. The section was

then polished using a series of 200, 400 and 800 grit SiC powders until it was less than 50  $\mu\text{m}$  thick. Small sections of the  $\beta$ -alumina were then removed and glued on to single hole 3 mm copper discs using a solution of Lakeside resin in methanol. Further thinning was accomplished in an Edwards ion-beam thinning unit. An attack angle of 15 to 20° and voltage of 6 to 7 kV, at a current of 50 mA was found to give satisfactory thinning rates and suitable quality thin foils. The foils were examined in a Phillips EM200 electron microscope at 100 kV, equipped with single axis specimen tilting and electromagnetic dark field deflection facilities.

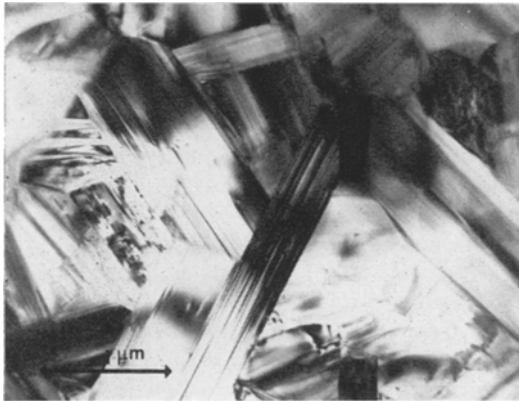


Figure 2 Linear defects lying in the basal plane.

#### 4. Dislocations in $\beta$ -alumina

In thin foils of all three types of materials examined, a high concentration of linear defects was observed, as is shown in Fig. 2. Such defects gave crystals the appearance of a banded structure. The bands are found to lie in the basal plane and are terminated either at a grain boundary or within a grain by dislocation. The bands can then be described as slip traces or stacking faults depending on the nature of the dislocation generating them, either a unit or partial dislocation, respectively.

The generation of defects on the basal plane may be explained on consideration of the crystallographic structure of  $\beta$ - and  $\beta''$ -alumina. The low density of bonding on the mirror planes allows the formation of low energy dislocations by the disruption of the minimum number of interatomic bonds. Their formation is also aided by the relatively large interatomic distances in the mirror plane. A  $(1\bar{2}10)$  section through the unit cell shows this in Fig. 3. The closest packing of the oxygen ions in the mirror plane is not shown in this particular plane, but would be visible in a  $(10\bar{1}0)$  section and have a separation of 5.6 Å. The spinel blocks are thus held together by widely separated Al—O—Al bonds together with the lower energy sodium ion to oxygen ion bonds. Thus from minimum energy considerations, dislocations would be expected

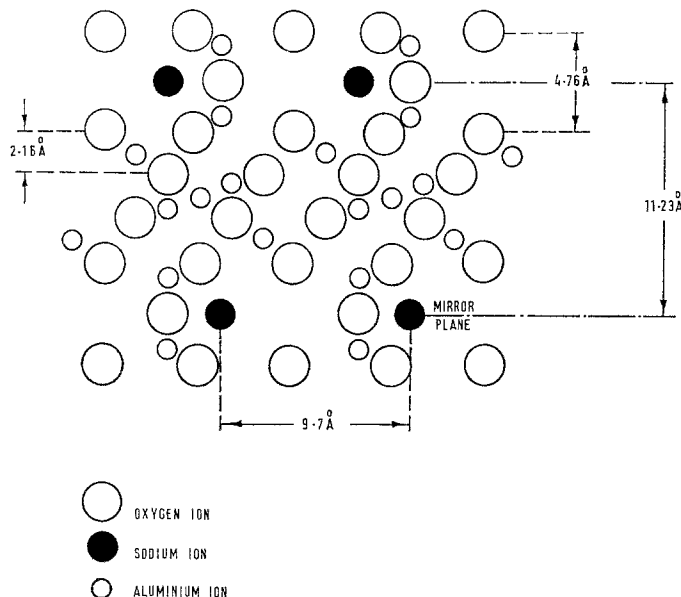
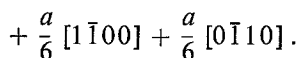
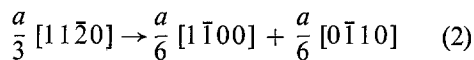
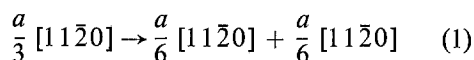
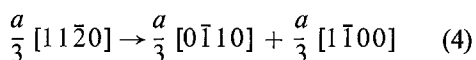
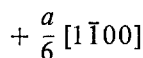
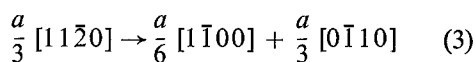


Figure 3 Position of atoms in the unit cell parallel to  $c_0$  direction  $(1\bar{2}10)$  plane.

to occur in and move on the mirror planes. The configuration of oxygen and sodium ions in the mirror plane of a stoichiometric crystal is shown in Fig. 1a. Also shown is the Burgers vector of the unit dislocation, together with two of the possible movement paths of the dislocation. The crystallography of the possible movements is shown in Fig. 1b, and the mechanisms are:



There are two further possibilities:



The reactions above are chosen on the basis of a reasonable co-ordination of the oxygen bond in the mirror plane, with the possible sites of the aluminium bond on the tetrahedral site between three oxygen ions forming the surface of the adjacent spinel block.

For the stoichiometric two block composition, the mechanisms of Equations 3 and 4 show a decrease in elastic energy on dissociation and are considered unlikely to occur since they are subject to geometric constraint. However, Equation 4 indicates a mechanism whereby the  $\beta$ - $\text{Al}_2\text{O}_3$  (2 block) may be transformed to a region of  $\beta''$  (3 block) by the movement of the  $a/3$   $[0\bar{1}10]$  partial dislocation. Although this reaction may not be the most energetically favourable, an excess of sodium in the mirror plane could alter the situation, stabilizing the reaction by effectively lowering the stacking fault energy.

The magnitude of the Burgers vector in terms of the lattice parameter has been given by Partridge [9].

$$b = a [3(u^2 + uv + v^2) + (c/a)^2w]^{\frac{1}{2}}$$

where  $u$ ,  $v$  and  $w$  are the three index Miller-Bravais indices, and  $c$  and  $a$  are the lattice parameters. On the assumption that the energy

of a dislocation is proportional to the magnitude of the square of the Burgers vector, then the most likely dissociation mechanism may be calculated. The results for the dislocations used in Equations 1 to 4 are given below.

Dislocation	$b$	$b^2$
$a/3$ 1120	$a$	$a^2$
$a/6$ 1120	$a/2$	$a^2/4$
$a/6$ 1100	$\frac{a\sqrt{3}}{6}$	$a^2/12$
$a/6$ 0110	$\frac{a\sqrt{3}}{6}$	$a^2/12$
$a/3$ 0110	$\frac{a\sqrt{3}}{3}$	$a^2/3$

Summation of the relative dislocation energies of Equations 1 and 2 indicates that both dissociations result in a lowering of energy, there being a nett energy reduction in favour of separation into two partials (Equation 1), of  $ka^2/2$  and into four partials, of  $2ka^2/3$ , where  $k$  is an arbitrary constant. Thus on an elastic energy basis, dissociation into four partials would be expected (Equation 2). However, the occurrence and width of separation in a dislocation dissociation would depend on the respective energies of the stacking faults generated by splitting into two or four partials.

It has been shown that when covalent bonds can be regarded as spatially directed, mechanically stiff and, for the purpose of dislocation generation and movement, to be brittle, then it is possible to draw models of the atom positions in the core of dislocations [10]. In the  $\beta$ - and  $\beta''$ -alumina structures and mirror planes are bonded by means of aluminium-oxygen and sodium-oxygen bonds. The sodium ion can move with relative ease along the mirror plane, and the spinel blocks can, therefore, be considered to be connected solely by means of the aluminium-oxygen bonds for the purpose of dislocation studies.

Aluminium-oxygen bonds in  $\alpha$ -alumina are considered to be mainly covalent in character [11]. Some modification would be appropriate for the bond in the region of sodium ions, the different symmetry and the longer bond length in the mirror plane of  $\beta$ -alumina. Models of the dislocation core and the extended dislocation are shown in Fig. 4a to d, the dislocation reactions being given by Equations 1 and 2.

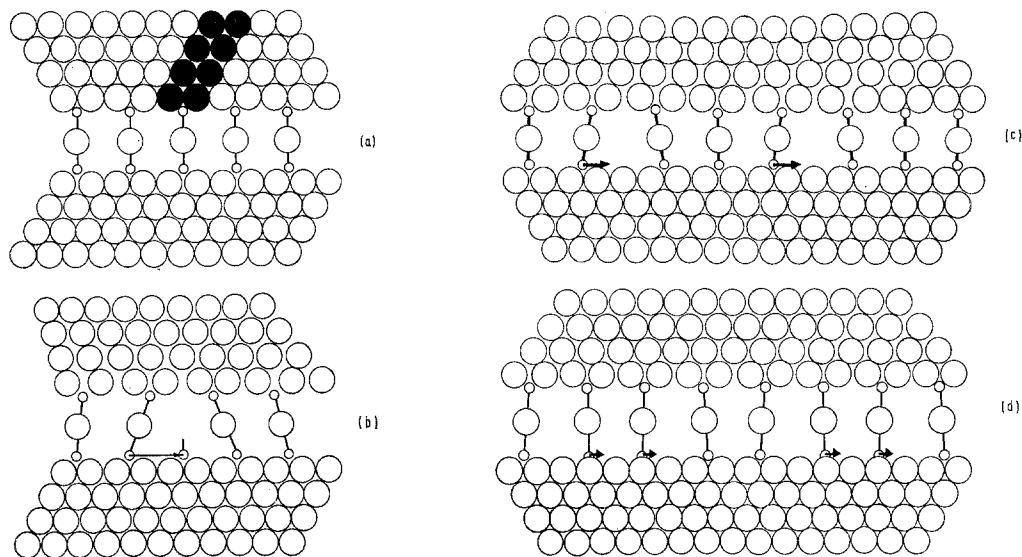
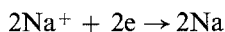


Figure 4 Atomic distribution at the core of unit and partial dislocation in the mirror planes. (a) Perfect crystals of close packed oxygen ions about a mirror plane. (b) Removal of two layers of oxygen ions [shaded in (a)] forms the unit dislocation with  $b = a/3 [11\bar{2}0]$ . (c) Separation of the unit dislocation into two partials. The Burgers vectors are indicated by the arrows. (d) Further separation of the dislocation into four partials. The Burgers vectors of the partial dislocations do not lie in the plane of the paper, but alternately above and below at  $30^\circ$ .

An electronic charge on the dangling bond at the core of the dislocation can be generated with each dislocation movement or growth. In reality, for each Al—O bond broken by dislocation generation movement, an Na—O bond would also be separated. Since these would be adjacent and lie along the line of dislocation, any charge imbalance would be confined to the dislocation core. Neutralization of the charge imbalance could occur by impurity precipitation along the core effectively pinning the dislocation. A possible mechanism in a material containing an excess of sodium ions would be the reaction of the ions with the negatively charged bonds to form sodium atoms.



## 5. Observations of dislocations

Transmission electron microscopy showed the majority of dislocations to lie in the basal plane. Such dislocations were readily observed in polycrystalline  $\beta$ - $\text{Al}_2\text{O}_3$  of all types, but were best seen in single crystal material, obtained by cleaving thin plates from large cast blocks of Monofrax (fused  $\beta$ - $\text{Al}_2\text{O}_3$ ). The plates were mechanically polished and ion beam thinned in the usual way.

As would be expected in single crystal material, the dislocation density was extremely low, several foils being dislocation free, whilst all others examined had a low dislocation density. The dislocations present in the thin films were usually long and straight, indicative of their "grown-in" origin. Occasionally a dislocation occurred in a non-equilibrium configuration (Fig. 5). The loop which is being emitted by a Frank-Reed source is visible for  $\mathbf{g} = [\bar{1}010]$  and  $[\bar{1}2\bar{1}0]$  and invisible for  $\mathbf{g} = [0\bar{1}10]$  and  $[01\bar{1}0]$ . The dislocation arrangement with the loop visible is shown in bright and dark field in Fig. 5a and b and the loop is out of contrast in Fig. 5c. The invisibility condition  $\mathbf{g} \cdot \mathbf{b} = 0$  [12], where  $\mathbf{g}$  is the diffraction vector and  $\mathbf{b}$  is the Burgers vector of the dislocation, is valid for defects on the basal plane of hexagonal crystals. The direction of the Burgers vector of the dislocation loop is thus  $\mathbf{b} = [\bar{2}110]$ , as predicted. The shortest repeat distance of atoms in the unit cell allows the vector  $\mathbf{b} = (a/3) [\bar{2}110]$  to be assigned to be unit dislocation.

Partial dislocations are most easily identified when the foil plane is other than basal, when the ends of the dislocation can be located in the foil surface. Pairs of partial dislocations can then often be seen to be in the same slip plane, and to

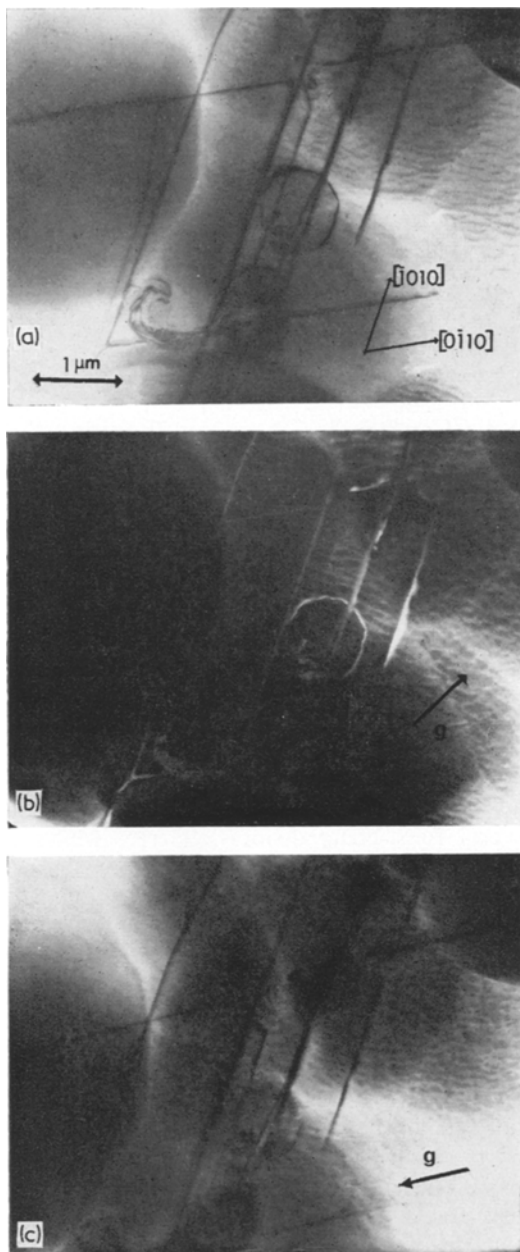


Figure 5 (a) Dislocations in Monofrax, showing long straight dislocations and the loop at A in contrast. (b) The same area as (a) in dark field  $g = [12\bar{1}0]$ . (c) Bright field image of the same area with the dislocation loop out of contrast.

exhibit a characteristic waviness. Partial dislocations were observed in all types of  $\beta$ -alumina examined, as would be expected on a minimum energy basis (Equation 1), usually the unit dislocation having split into a pair of

partials (Fig. 6). Such pairs of partial dislocations were particularly prevalent in the larger grains of the polycrystalline material where they could have been generated by a stress relief mechanism, during the ion-beam thinning process.

Occasionally, particularly in thicker regions of

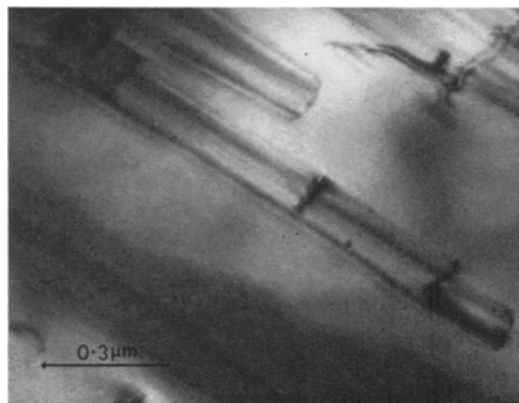


Figure 6 Pairs of partial dislocations in a thin foil of  $\beta$ -alumina.

the foils of polycrystalline material, the dislocations were seen to have dissociated into four partials (Fig. 7) as would be expected if Equation 2 were operative. It is noticeable even in this case that although the dislocation is widely dissociated ( $\sim 0.4 \mu\text{m}$ ), the pairs of partials 1 and 2, and 3 and 4 are not widely separated indicating that the stacking fault energy of a fault generated by the first partial  $b = (a/6)[1\bar{1}00]$  is higher than the stacking fault energy of the fault generated by the first two partials of

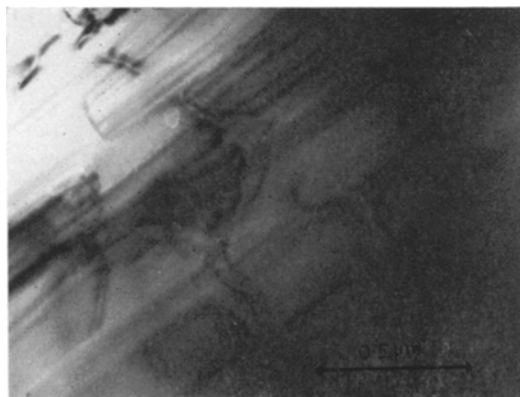


Figure 7 Four partial dislocations formed by dissociation of a unit dislocation, occurring in a thicker section of the same foil.

Equation 2 or the first partial of Equation 1. As can be readily seen this is consistent since:

$$\frac{a}{6} [11\bar{2}0] = \frac{a}{6} [1\bar{1}00] + \frac{a}{6} [0\bar{1}10].$$

Identification of the Burgers vector of a partial dislocation is sometimes difficult and not always possible, since the invisibility criteria  $\mathbf{g} \cdot \mathbf{b} = 0$  is not conclusive. For a precise determination of the Burgers vector further criteria need to be utilized [12]. In the present investigation it was not possible due to limitations of tilting facilities and charging of the specimens. However, the dislocations partials examined were seen to be in the basal plane, and extended in a close packed direction of the basal plane.

## 6. Dislocation mobility and deformation

Homogeneous deformation of a solid crystalline material requires two different criteria to be satisfied. Von Mises [13] recognizes that five independent slip systems are necessary, an independent slip system being defined as one which cannot be replaced by two or more alternative systems. A further condition is that the Peierls stress for dislocation movement on all active slip planes should be less than the resolved fracture stress of the material. It can be readily seen that provided dislocation motion occurs only on the basal plane of  $\beta$ - $\text{Al}_2\text{O}_3$ , then only two independent slip systems are operative, and homogeneous deformation is not possible. The material is therefore brittle at low temperatures.

Under certain conditions Von Mises criteria need not apply. This occurs when there is no

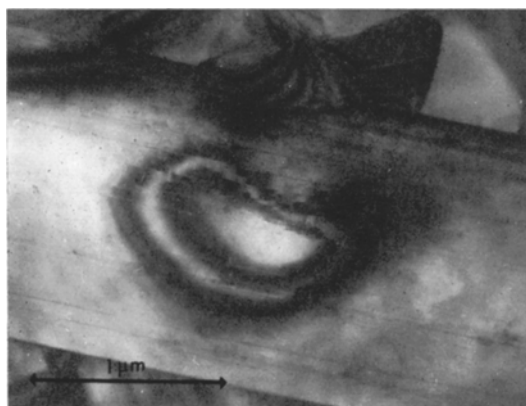


Figure 8 Microscopic plastic strain in a large grain of  $\beta$ -alumina is evident, due to the relative displacement of material in the vicinity of the thickness contours.

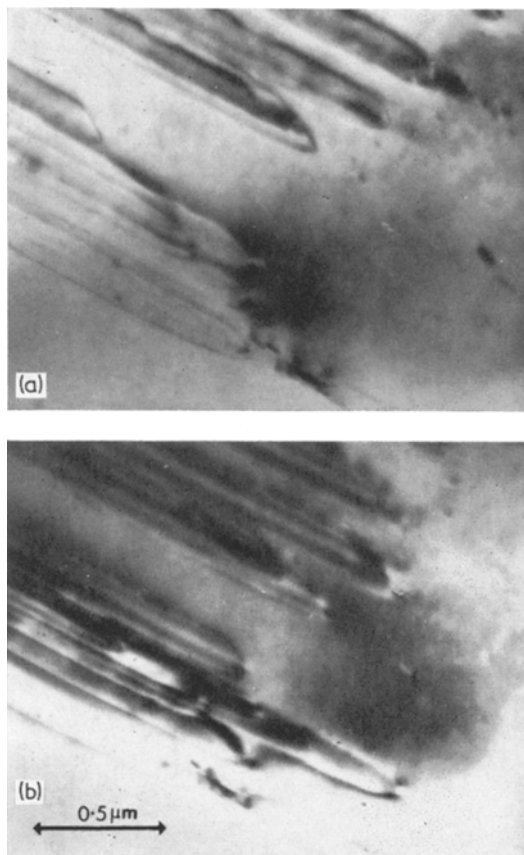


Figure 9 Dislocation movement in a basal slip plane in the electron microscope: (a) shows dislocations which in (b) can be seen to have moved. Each microphotograph was taken with 0.5 sec exposure at an interval of 5 sec.

constraint on the crystal surfaces. Such conditions often occur in the thin foils used in transmission electron microscopy where a single crystal surface forms both the upper and lower surfaces of the thin foil. A typical example is shown in Fig. 8. The points of interest are the thickness contours in the centre of the large grain. It is apparent that sections have been displaced relative to each other and that movement must have taken place after thinning of the foil had ceased. The largest slip distance is of the order of 4000 Å indicating that a large number of dislocation ( $\sim 10^3$ ) has passed along that particular basal slip plane. Some of the dislocations are visible as are traces of their movement in the slip planes. The ease of movement of dislocations in this orientation is readily demonstrated by examination of Fig. 9a and b. Both micrographs were taken of the same

area of foil at an interval of approximately 5 sec. The dislocations can be seen to have moved. It would, therefore, appear that the Peierls stress on the basal plane is not a limiting factor in obtaining plasticity in  $\beta$ -Al<sub>2</sub>O<sub>3</sub>.

### Acknowledgements

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