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Stacking Faults in γ-Alumina

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Extra spots and line segments observed in single-crystal electron-diffraction patterns of γ-alumina are interpreted in terms of faults in the cubic close-packed stacking of the oxygen atoms. Near the fault planes some aluminium atom sites are 'unfavourable' in that they are nearer than usual to other aluminium sites. It is suggested that the vacant aluminium sites in γ-alumina occur preferentially at such 'unfavourable' positions along fault planes.

Electron-diffraction patterns from films formed by heating thin aluminium foil to about 600° C. usually consist of rings, arcs and spots due to γ-alumina, which has a cubic, spinel-type lattice with $a_0 = 7{\cdot}9$ Å. If a fine electron beam is used, cross-grating patterns from individual single crystals may sometimes be observed.

Good single-crystal patterns have been obtained from films formed by heating thick aluminium foil and then dissolving away the remaining aluminium by floating the foil on caustic soda solution.

In such single-crystal patterns extra spots and faint continuous lines may usually be detected. In particular, in the hexagonal [111] pattern obtained with the electron beam along [111], extra spots and segments of lines through some of the stronger spots occur as illustrated in Fig. 1. With the beam along [1$\bar{1}$0], faint continuous lines join the spots with indices $4h,4h,4l$, excepting the origin (Fig. 2). Such lines and spots are exactly those which might be expected from the occurrence of faults in the stacking of the layers in the face-centred cubic close-packed arrangement of oxygen atoms in the lattice.

The diffraction effects to be expected from a disordered stacking of close-packed layers have been calculated by Hendricks & Teller (1942) and by Méring (1949). They found that there are continuous lines in the reciprocal lattice perpendicular to the planes of the layers and passing through the points with indices $h-k \neq 3n$, referred to the basic hexagonal cell of the layers. If the stacking sequence approximates to that for hexagonal close-packing, $A\,B\,A\,B\,A\,B\,A\,B\,\ldots$, these continuous lines have maxima of intensity near the positions of the normal reciprocal-lattice points for the hexagonal cell. This case has been observed by Edwards & Lipson (1942) to occur in hexagonal cobalt having about one fault per fourteen layers.

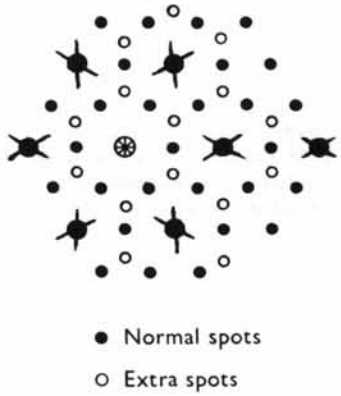

Fig. 1. The arrangement of extra spots and line segments observed in the [111] electron diffraction pattern of γ-alumina.

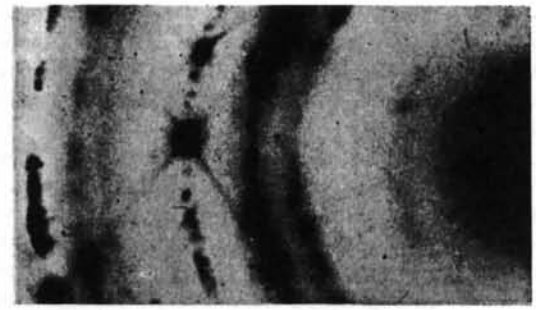

Fig. 2. Continuous lines through a 004 spot forming part of an imperfect [1$\bar{1}$0] electron-diffraction pattern of γ-alumina.

Faults occurring in a cubic close-packed sequence, $A\,B\,C\,A\,B\,C\,A\,B\,C\,\ldots$, such as that of the oxygen layers in γ-alumina, will give continuous lines with maxima of intensity around the positions of those strong reflexions, lying on the lines, to which the oxygen atoms contribute. There will be four sets of parallel lines corresponding to the four equivalent sets of parallel planes of oxygen atoms in the lattice. The extra spots in the [111] pattern are given by the intersection of one set of lines with the almost-plane Ewald sphere. The maximum intensity regions of lines from two such sets of lines form the cross at the 004 reflexion in Fig. 2. The angle between the lines is that between two [111] directions, namely 70·5°.

The aluminium atoms in the lattice complicate the

situation slightly. In the γ-alumina structure, two types of aluminium layer alternate in the spaces between oxygen layers. In one, all aluminium atoms are in octahedral holes (an O layer), and in the other, one-third of the aluminium atoms are in octahedral holes, and two-thirds are in tetrahedral holes (a T layer) (Verwey, 1935; Wells, 1945, p. 333). Hence the structure repeats after every six layers. Not all the aluminium sites are filled. In the cubic unit cell $21\frac{1}{3}$ aluminium atoms are distributed among the 24 aluminium sites. Verwey concluded from a consideration of X-ray powder pattern intensities that the vacant sites are probably octahedral holes.

When a fault occurs in the stacking sequence of the oxygen layers, the arrangement of the aluminium atoms is upset. The aluminium atoms adjacent to the stacking fault may be arranged in one of several possible ways, but in each case some of the aluminium sites will be closer to neighbouring aluminium sites than in the normal lattice. It seems probable that such unfavourable sites will be vacant in preference to the sites with normal surroundings. Two of the possible arrangements of aluminium atoms about a stacking fault are illustrated in Fig. 3. The diagrams represent sections of the lattice perpendicular to the close-packed planes. In Fig. 3(a) a simple fault of the type ... $A\,B\,C\,A\,B\,A\,B\,C$ ... occurs about an O layer of aluminium atoms. Half the aluminium atoms in tetrahedral positions in the neighbouring T layers are then in unfavourable positions. Two such unfavourable sites occur for every three aluminium atoms in the O layer. In Fig. 3(b) a similar fault occurs about a T layer of aluminium atoms. If the T layer is arranged as shown, only the aluminium atoms in the octahedral holes, that is one-third of the atoms in the T layer, are in unfavourable positions. Similarly other possible arrangements of aluminium atoms about a fault plane contain a number of unfavourable sites equal to one-third, or, more commonly, two-thirds of the number of aluminium atoms in a layer. This applies also to cases where the sequence of alternating T and O layers of aluminium atoms is upset.

If all such unfavourable sites created by stacking faults were vacant, approximately one stacking fault such as that of Fig. 3(a) in every 32 layers in each of the four equivalent directions, or one stacking fault such as that of Fig. 3(b) in every 16 layers in each of the four equivalent directions, would reduce the ratio of Al to O sites from $\frac{3}{4}$ to $\frac{2}{3}$ to correspond to the formula Al_2O_3.

Rough estimates of the frequency of stacking faults, based on the relative intensities of the extra and normal spots of the [111] pattern, indicate that faults occur at something of the order of one for every ten layers. Thus the number of unfavourable aluminium sites in the structure should be sufficient to allow all or most of the vacant aluminium sites to occur along fault planes.

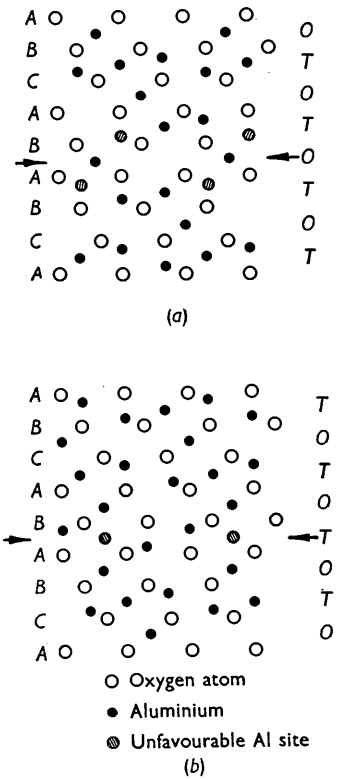

Fig. 3. Two possible arrangements of aluminium atoms around a stacking fault in the layers of oxygen in γ-alumina, showing unfavourable sites.

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