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Low-angle tilt boundaries and inhomogeneous current densities in sodium beta alumina

L. C. DE JONGHE
Department of Materials Science and Engineering, Cornell University, Ithaca, New York, USA

Observation of [$h\,k$.0] low-angle tilt boundaries in sodium beta alumina is reported. The boundaries have a habit plane close to the (0 0.1) planes, and are evidence for the existence of dislocations with a Burgers vector component in the [0 0.1] direction. The indications are that these dislocations dissociate according to

$$c_0\,[00.1] \rightarrow \tfrac{1}{2}c_0\,[00.1] + \tfrac{1}{2}c_0\,[00.1].$$

Such tilt boundaries can cause micro-inhomogeneities in sodium ion current flow and both enhancement and decrease of conduction plane current density seems possible.

1. Introduction

Sodium beta alumina is a hexagonal crystal which can be described as sodium conduction planes separated by spinel blocks [1, 2]. It is well established that Na^+ ion conduction normal to the ion conducting basal plane, i.e. through the spinel blocks, is many orders of magnitude slower than in the conduction plane [3]. This high anisotropy should present special problems for ion conduction in a polycrystalline or defect containing electrolyte. Point defects such as those described by Roth [4], dislocations in the basal plane discussed by Stevens [5], and complex faults normal to the basal planes observed by De Jonghe [6], all are expected to affect the rapid, homogeneous flow of sodium ions during d.c. conduction. In this paper we report on the observation of [$h\,k$.0] low-angle tilt boundaries that can be found in sodium beta alumina solid electrolyte, and we comment on how such boundaries can cause microscopic inhomogeneities in sodium ion current.

2. Experimental procedure

Polycrystalline sodium beta alumina solid electrolyte was prepared from Alcoa XB-2 "superground" powder. Sintering was carried out under argon, with the samples packed in sodium beta alumina to prevent soda loss. Sintering times and temperatures were approximately 1 h at ~1750° C. Thin foils were prepared by ion milling, and observed in a Siemens 102 transmission electron microscope.

3. Observations

Low-angle titlt boundaries can frequently be found inside the large sodium beta alumina grains. An example of such tilt boundaries is shown in Fig. 1. We note that the trace of the tilt boundary is very nearly along the basal planes. The selected area diffraction pattern shows that the tilt components are of the order of 1°, but no information on the twist component of such boundaries is available: the geometry of the diffraction patterns and the correspondence in intensities of the related reflections indicate that if there is a twist component it must be very small. The tilt axis is clearly contained in the basal plane, making it possible to observe the subgrains simultaneously by direct lattice imaging with 00.1 type reflections. Depending on the diffraction conditions, the fringe spacing is either 11.3 Å ($c_0/2$) or 22.6 Å (c_0), as was discussed by Bevan *et al.* [7]. Part of an [$h\,k$.0] tilt boundary (~1° misorientation) is shown in Fig. 2 with 11.3 Å fringes. Each fringe

Figure 1 Low-angle [$h\,k.0$] tilt boundaries in sodium beta alumina. The tilt boundaries are normal to [0 0.1].

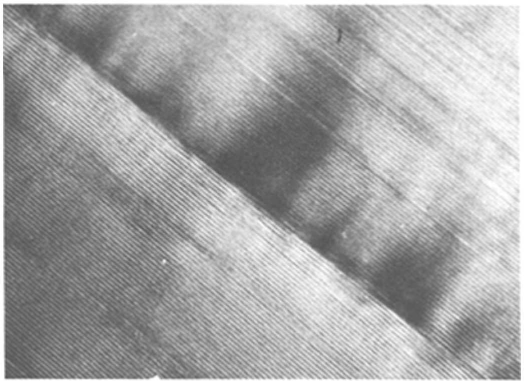

Figure 2 [$h\,k.0$] tilt boundary imaged with lattice fringes. The fringe spacing is 11.3 Å.

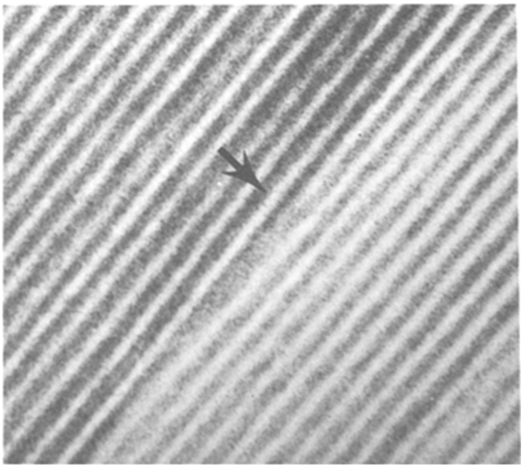

Figure 3 11.3 Å lattice fringe image showing the magnitude of the [0 0.1] component of the Burgers vector.

then can be thought of as corresponding to a spinel block. Close examination of the lattice images indicated that the fringe dislocation images have a Burgers vector of $\frac{1}{2}$ [c_0], or 11.3 Å. The fringe contrast right at the boundary is, however, somewhat obscured due to the superposition of the dislocation strain contrast, and it is difficult to get convincing images. In Fig. 3 we show an enlargement of what corresponds to such a $\frac{1}{2}$ [c_0] dislocation in a low-angle tilt boundary. A Burgers vector with a component of $\frac{1}{2}$ [c_0] should bring the spinel blocks back into registry, except for a stacking fault, and provide continuity of the sodium ion conduction planes. This would then indicate that total dislocation would dissociate according to:

$$c_0\,[0\,0.1] \rightarrow \tfrac{1}{2}c_0\,[0\,0.1] + \tfrac{1}{2}c_0\,[0\,0.1]\,.$$

When the two partial dislocations are both contained in the subboundary, then a stacking fault of the type ABAB/BABAB should exist between the pair. Here A and B represent the two spinel blocks of the perfect beta alumina crystal structure.

4. Current inhomogeneities due to low-angle boundaries

The presence of the [$h\,k.0$] low-angle tilt boundaries described here will have an effect on the microscopic distribution of the sodium ion current during d.c. conduction. Indeed, if we consider the Na^+ ion flow in a simplified two dimensional model of such a boundary (Fig. 4a), we note that for the current direction indicated the ion flow

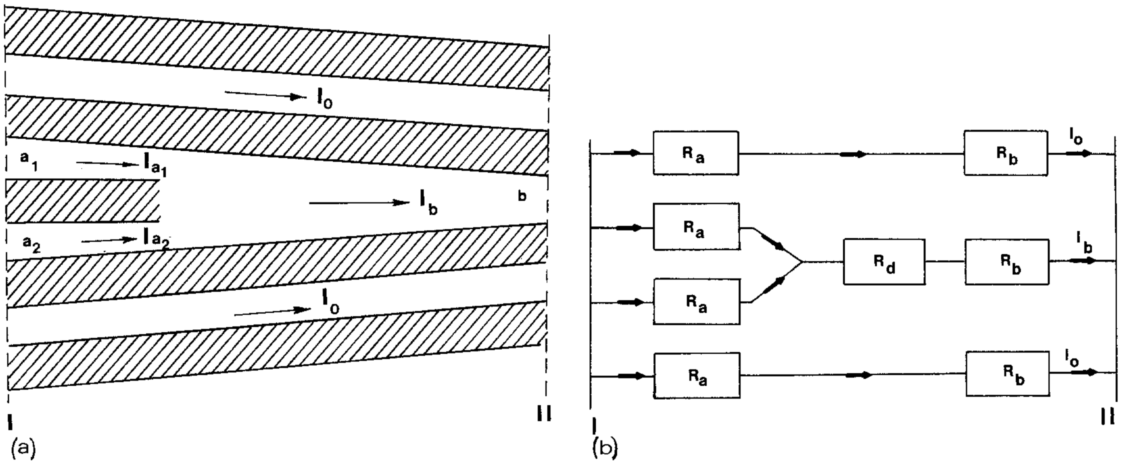

Figure 4 (a) Two-dimensional model of part of a dislocation in a $[h\,k.0]$ tilt boundary. (b) Schematic electrical analogue of (a).

from two conduction planes, marked a_1 and a_2, has to converge into one conduction plane, marked b. This pecularity is solely due to the near impermeability of the spinel blocks to Na^+ flow, inhibiting current redistribution in the $[c]$ direction. A simplified electrical analogue is shown in Fig. 4b. Here we have assigned equal ohmic resistances, R_a and R_b, to plane segments of the same length. We symbolize the fixed dislocation "core" resistance (if any) by R_d. If we assume that boundaries I and II of the crystal in Fig. 4b are maintained at some uniform potentials ψ_I and ψ_{II}, then the requirement that no accumulation or depletion of sodium ions or electrolysis occurs leads to a sodium ion current in the plane segments a_1, a_2 and b that differs from the other segments. One finds for the sodium current I_b in the segment b

$$I_b = I_0 \frac{R_a + R_b}{(R_a/2) + R_d + R_b}$$

where I_0 is the Na^+ current as indicated in Fig. 4a. Clearly, if $R_d < (R_a/2)$ a sodium current enhancement will occur in the plane segment b. Conversely, if $R_d > (R_a/2)$ then the sodium current density is lowered in plane segment b. It is not clear at present if such micro-inhomogeneities could lead to eventual failure of the electrolyte, although it is plausible that localized heating or initiation of electrolysis at subboundaries may be contributing to the breakdown of the solid electrolyte.

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