Irradiation-Induced Defects in $\beta''''$-Alumina Examined by High-Resolution Electron Microscopy

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Abstract

Electron-induced defects in $\beta''''$-alumina, $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot 7\text{Al}_2\text{O}_3$, are examined by high-resolution electron microscopy. The phenomena can be reasonably explained in the same manner as previously done for the similar case in $\beta''$-alumina [Matsui & Horiuchi (1981). Acta Cryst. A37, 51-61]; two spinel-like blocks (each having six oxygen layers) on both sides of the lost conduction plane are directly combined to form cubic close packing of twelve oxygen layers through the minimum shift vectors. The arrangements of cations in a resultant defect block are slightly different from those in the spinel lamella of the same thickness.

Introduction

Characteristic phenomena of electron damage in $\beta''$-alumina, $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot 5\text{Al}_2\text{O}_3$, have so far been investigated widely (De Jonghe, 1977; Matsui & Horiuchi, 1977, 1981; Bovin, 1978, 1979). As is well known (Yamaguchi & Suzuki, 1968; Bettman & Peters, 1969), $\beta''$-alumina has rhombohedral symmetry ($R3m$, $a = 5.614$ and $c = 33.85$ Å) with a structure constructed by alternately stacked $\text{Na}_2\text{O}$ planes (or conduction planes) and so-called spinel-like blocks of four cubic-close-packed oxygen layers. Under electron irradiation, some of the conduction planes move out of the structure to create defect blocks by the direct contact of two spinel-like blocks on both sides of the lost conduction plane. Three different models have so far been proposed on the types of contact and the resultant defect structure. According to the first model of De Jonghe (1977), the defect blocks are essentially the spinel lamella of eight oxygen layers. Bovin (1979), on the other hand, found that his electron micrographs of defect blocks could not be explained by the spinel model and proposed a second one in which two spinel-like blocks are combined simply along the $c$ axis. The resultant defect block contains not only cubic but also hexagonal close packing of oxygen layers. This model, however, could not explain the images taken by De Jonghe (1977) and the other ($Q$ type) to that observed by Bovin (1979). Matsui & Horiuchi (1981), therefore, proposed a third model from which the appearances of the two types of defect images are reasonably and naturally expected. According to this new model, two spinel-like blocks are combined by one of the three, crystallographically equivalent, vectors (V$_1$ to V$_3$) including not only $z$ but also $x$, $y$ components in order to form cubic close packing of eight oxygen layers. Other sets of images ($P'$ and $Q'$) observed when the crystal was projected onto the (100) plane were also explained by this model.

Recently, similar phenomena of electron damage were also reported for $\beta''''$-alumina, $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot 7\text{Al}_2\text{O}_3$ (Matsui, Horiuchi & Ohta, 1980). As shown in Fig. 1(a) to (c), $\beta''''$-alumina also has rhombohedral symmetry ($R3m$, hexagonal unit-cell parameters are $a = 5.6$ and $c = 48$ Å) with a structure very similar to that of $\beta''$-alumina, except that each spinel-like block is composed not of four but of six close-packed oxygen layers (Weber & Venero, 1970). The separation between two conduction planes is about 16 Å. The oxygen layer sequence is described as

$$\ldots A_1 (BCABCA) B_1 (CABCAB) C_1 (BCABCA) A_1 \ldots,$$

while the corresponding sequence in $\beta''$-alumina is

$$\ldots A_1 (CBAC) B_1 (ACBA) C_1 (BACB) A_1 \ldots,$$

if both structures are described in the same setting for a rhombohedral lattice. The local atomic arrangements near the conduction planes are considered to be almost the same for both compounds. It is, therefore, expected that the process of defect formation in $\beta''''$-alumina will be the same as that in $\beta''$-alumina. The purpose of the present study is to confirm which one of the three models so far proposed for $\beta''$-alumina can be applied successfully to the phenomena in $\beta''''$-alumina.

Experimental

The sample crystal of $\beta''''$-alumina was prepared by the hot-press method (Matsui, Horiuchi & Ohta, 1980). The sintered block was gently crushed in CCl$_4$ and then dispersed on a holey carbon film. Electron microscope observations were made by a Hitachi H-1250 type instrument operated at 1 MV. High-magnification images were taken from two directions normal to the...
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(110) and the (100) planes. Direct magnification was about $2 \times 10^5$ times. Through-focus series of images were taken with an objective aperture of 0.56 Å$^{-1}$ in reciprocal space. The images obtained near the Scherzer focus (1085 Å underfocus for our 1 MV electron microscope with spherical aberration coefficient 10 mm) were selected for subsequent analyses because, under such conditions, the images reflect approximately the projected potentials of thin crystals (Scherzer, 1949; Cowley & Iijima, 1972).

Results

An example of a low-magnification photograph of $\beta''''$-alumina which suffered from electron damage is shown in Fig. 2. The defects were created from the inner region as shown by arrows and then extended towards the crystal edge. The 1 MV high-magnification image of such defect blocks projected onto the (110) plane is shown in Fig. 3. Two kinds of defect images, tentatively named as $R$ and $S$ types, are visible in this micrograph. The arrows connecting nearest white dots on both sides of the defect blocks are slightly inclined to the right for $S$, and to the left for $R$. The amount of inclination for $R$ is slightly larger than that for $S$. These observations of two types of image may be related to the case in $\beta''''$-

Fig. 1. Crystal structure of $\beta''''$-alumina. The projections onto the (110) and the (100) planes are shown in (a) and (b), respectively. One-third of the $c$ axis is shown because the crystal has rhombohedral symmetry. Squares are sodium atoms in the conduction planes. Open and solid circles are Al (partly Mg) atoms in the spinel-like blocks. The solid circles indicate cations which are arrayed twice as densely compared to those indicated by open circles. The stacking of oxygen layers is indicated at the left-hand side of (a). The sign $A$ means that the positions $A_1$ to $A_4$ shown in (c) are all occupied.

Fig. 2. Low-magnification image of $\beta''''$-alumina projected along the [110] direction. Arrows show the points where the irradiation-induced defects start to extend towards the crystal edge.

Fig. 3. High-magnification electron micrograph of $\beta''''$-alumina projected normal to the (110) plane. Two types of defect images, $R$ and $S$, are observed. The width of each defect block is about 30 Å.
Interpretations and discussions

(1) Interpretations of images

As pointed out before (Matsui, Horiuchi & Ohta, 1980), the images of \( \beta''' \)-alumina may be reasonably interpreted considering the results of the image calculations for \( \beta'' \)-alumina (Matsui & Horiuchi, 1981) because both compounds have almost the same crystal structure except for the thickness of each spinel-like block. It is, therefore, considered that the white and gray dots in Fig. 3 may correspond to the sites \( W \) and \( G \) in Fig. 1(a). Similarly, white and gray dots in Fig. 4 may correspond to the sites \( W \) and \( G \) in Fig. 1(b).

Image contrasts of the defect blocks in Figs. 3 and 4 can then be interpreted in the same manner as that given by Matsui & Horiuchi (1981) for \( \beta'' \)-alumina. The oxygen layer sequence in an original \( \beta''' \)-alumina is, as mentioned before,

\[
\text{(lower region)} \quad \ldots B_1 (CABCAB) C_1 (ABCABC) A_1 \ldots
\]
\[
\text{(upper region)}
\]

where conduction plane \( C_1 \) is assumed to be eliminated upon irradiation. According to the principles deduced by Matsui & Horiuchi (1981) from the study on \( \beta'' \)-alumina, upper and lower parts of the lost conduction plane must be combined so that 'cubic' close packing of twelve oxygen layers is attained in the resultant defect block. As was the case for \( \beta'' \)-alumina, there are three vectors \( V_1 \) to \( V_3 \) by which relative movements of the upper region with respect to the lower one are described. The schematic drawings of these three vectors are given in Fig. 5. They are also expressed as

\[
\begin{align*}
V_1 &= -\frac{1}{2}a_1 - \frac{1}{3}a_2 + V_c \\
V_2 &= \frac{1}{3}a_1 + \frac{1}{3}a_2 + V_c \\
V_3 &= -\frac{1}{2}a_1 + \frac{1}{3}a_2 + V_c \quad (V_c \approx -2.4c)
\end{align*}
\]

where \( a_1, a_2 \) and \( c \) are the lattice vectors of \( \beta''' \)-alumina. The absolute value of \( V_c \) is about 2.3 Å, corresponding to the distance between two close-packed oxygen layers. The \( x, y \) components of these three vectors have opposite signs compared to those for \( \beta'' \)-alumina (Matsui & Horiuchi, 1981). This is because the oxygen layer sequences in both compounds are mutually

![Fig. 4](image-url)

**Fig. 6.** Schematic representations of how the positions of white dots change to give several types of defect image in electron micrographs. The origin of the \( R \) and \( S \) types of image in Fig. 3 is shown in (a) and that of the \( R' \) and \( S' \) images in Fig. 4 in (b). The solid squares stand for the white dots in EM images before the crystal suffers from electron damage, while the circles stand for those after electron damage.
opposite; i.e. $A \rightarrow B \rightarrow C \rightarrow A$ for $\beta''$-alumina and $A \rightarrow C \rightarrow B \rightarrow A$ for $\beta'$-alumina, if both are expressed in the same setting for a rhombohedral lattice. The oxygen layer sequence in the defect blocks thus created in $\beta'''$-alumina is

$$\ldots B_1 [(CABCAB)(CABCAB)] C_j \ldots,$$

where $j$ is 2, 3 or 4 depending on which one of $V_1$, $V_2$ and $V_3$ was actually employed to create each defect block. The corresponding sequence for the defect block in $\beta'$-alumina was

$$\ldots B_1 [(ACBA)(CBAC)] B_j \ldots,$$

where $j$ is also 2, 3 or 4 (Matsui & Horiuchi, 1981).

The schematic representations on how the white dots on either side of the lost conduction plane move to give several kinds of defect images are shown in Fig. 6(a) and (b) for projections normal to the (110) and the (100) planes, respectively. From Fig. 6(a), for example, it is understood that the defect blocks formed by $V_1$ or $V_2$ may be imaged as $S$ type and those formed by $V_3$ as $R$ type when they are projected onto the (110) plane. Similarly, from Fig. 6(b), the defect blocks formed by $V_1$ or $V_3$ may be imaged as $S'$ type and those formed by $V_2$ as $R'$ type when projected onto the (100) plane. The real observations in Figs. 3 and 4 are thus reasonably understood.

The three slide vectors $V_1$ to $V_3$ are mutually related by 120° rotations around the $c$ axis and, therefore, they are crystallographically equivalent, because the original $\beta'''$-alumina had a threefold rotational symmetry. The three defect blocks derived by these vectors must then be structurally identical except for their orientations with respect to the host rhombohedral lattice of $\beta'''$-alumina.Appearances of two different types of defect image are then interpreted as due to the loss of the threefold rotational symmetry in the defect blocks. How the defect blocks are expected to be imaged in electron micrographs is summarized in Table 1(a) and (b), where (a) shows the cases of projection onto the \{110\} plane and (b) onto the \{100\} plane. It is expected from this table, for example, that the defect blocks formed by $V_3$ will be imaged as $R$ type when projected onto the (110) plane but as $S$ type when projected onto the (210) or (120) planes, although such experiments are impossible due to the limitations of the tilting angle of the goniometer ($\pm 30°$).

### Table 1. The classification of the types of EM images of the irradiation-induced defects in $\beta'''$-alumina in terms of the slide vectors $V_1$ to $V_3$ employed in creating each defect block and the projection planes \{110\} in (a) and \{100\} in (b)

<table>
<thead>
<tr>
<th>(a) Projection plane {110}</th>
<th>(b) Projection plane {100}</th>
</tr>
</thead>
<tbody>
<tr>
<td>{110} {120} {210}</td>
<td>{100} {010} {110}</td>
</tr>
<tr>
<td>$V_1$ $S$ $S$ $R$</td>
<td>$V_1$ $S'$ $R'$ $S'$</td>
</tr>
<tr>
<td>$V_2$ $S$ $R$ $S$</td>
<td>$V_2$ $R$ $S'$ $S'$</td>
</tr>
<tr>
<td>$V_3$ $R$ $S$ $S$</td>
<td>$V_3$ $S'$ $S'$ $R'$</td>
</tr>
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(2) Possible structure model of the defect block in $\beta'''$-alumina

The results obtained so far on the defect formation mechanism in $\beta'''$-alumina are schematically summarized in Fig. 7(a) to (c). The created defect blocks contain twelve cubic-close-packed oxygen layers but the arrangements of cations in them are different from those in the spinel lamella of the same thickness.

One minor problem, which we encountered in $\beta'$-alumina (Matsui & Horiuchi, 1981), must be mentioned concerning the arrangements of Al atoms in the central part of the defect block. These Al atoms were originally
facing the conduction planes forming Al–O–Al bridges by the corner-sharing of two AlO₄ tetrahedra. When the mutual shifts by V₁, V₂ or V₃ are applied, the edge sharing of tetrahedra must be created in the central part of the defect block. Such a polyhedral relation is, however, considered to be unstable (Pauling, 1960). In the case of β‴-alumina, Matsui & Horiuchi (1981) suggested that some of such tetrahedral Al atoms may move further into the neighbouring octahedral vacant positions. According to the image calculations of the defect blocks, the probability of such movements was estimated to be roughly 30–50%. Probably, similar movements of Al atoms may occur also in the defect blocks in β‴-alumina, as shown by arrows in the central parts of Fig. 7(b) and (c).

(3) Applicability of other models

If the defect blocks in β‴-alumina are essentially the spinel lamella, as De Jonghe (1977) postulated for the case of β‴-alumina, the layer sequence of oxygens may be

... B₁ [(CABCAB)(ABCABC)] A₁ ...

indicating that the defect image of type R must always be observed when the crystal is projected onto the (110) plane, because the positions C₁ and C₄ cannot be distinguished for this projection. The observations of the S type of defect image in Fig. 3, on the contrary, cannot be explained by this model. Similarly, the observations of the S′ type of image in Fig. 4 are inconsistent with this model. In this way, the two models proposed for the phenomena in β‴-alumina by De Jonghe (1977) and Bovin (1979) cannot be applied to those in β‴-alumina.

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References


