# Surface layers in polycrystalline sodium ß-alumina

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X-ray powder diffractometry using $CrK\alpha$ radiation has revealed the existence of surface layers 5 µm deep in samples of high-density polycrystalline sodium $\beta$-alumina. The surface layer is prominent by virtue of its crystal lattice distortion in which the $c$-axis is elongated by 1%. Its presence is due to ion exchange between $Na^+$ and $H_3O^+$ that occurs on exposure to air.

## 1. Introduction

Sintered $\beta$-alumina tubes of composition $(1 + x)$ $Na_2O \cdot 11Al_2O_3$ are used as solid electrolytes in electrochemical cells because of their high ionic conductivity. Two phases are normally present in the material: $\beta$ $(x \simeq 0.25)$ and $\beta''$ $(x \simeq 1)$, the second being stabilized by a small quantity of MgO and/or $Li_2O$. An X-ray diffraction (XRD) study of samples cut from the tube has shown the presence of a surface layer in which a lattice expansion is evident in both phases.

## 2. Experimental method

In examining surface layers by diffractometry the need to use a flat specimen caused some difficulty as the $\beta$-alumina ceramic is manufactured in the form a cylindrical tubes of external diameter 33 mm. Specimens were prepared by cutting axially a number of 2 mm wide strips from the tube, laying them on a flat surface and mounting them in Lakeside 70 resin. The imperfect flatness of the sample caused some line-broadening but this did not complicate interpretation of the results.

For detection of surface layers, low-angle diffraction with $CrK\alpha$ radiation is desirable since the X-ray beam does not penetrate deeply. Sensitivity to lattice-parameter changes would normally be greatest at high angles ($\partial\theta/\partial d \to \infty$ for $2\theta \to \pi$) but, at high angles, beam penetration is increased and the diffraction pattern becomes dominated by bulk rather than surface effects. In this investigation most changes in the $CrK\alpha$ XRD pattern were found in the range $2\theta$ from 20° to 75°.

## 3. Results

### 3.1. Lattice expansion

The unit cells of $\beta$- and $\beta''$-alumina are, respectively, hexagonal and rhombohedral [1]; both are conventionally indexed according to a hexagonal unit-cell. Typical lattice constants are $a(\beta) = a(\beta'') = 0.561$ nm, $c(\beta) = 2.234$ nm and $c(\beta'') = 3.352$ nm.

Fig. 1a shows part of the diffraction pattern for a sample of ceramic which had been ground flat to remove the tube surfaces; Fig. 1b shows the corresponding pattern for the outer surface of the tube. A comparison of Fig. 1a and b shows that the 0 0 4/0 0 6 line has become displaced and that extra lines have appeared to the right of the $\beta$-lines (1 0 7), (0 0 10) and (2 0 6) and the $\beta''$ lines (1 0 10), (1 0 11) and (2 0 10). A similar pattern to that of Fig. 1b was obtained from the inner surface of the tube.

Fig. 1b indicates that most of the lines in this region of the diffraction pattern are being displaced to a lower $2\theta$-position. Lines with a high $l$ index are particularly sensitive to changes in the $c$-parameter, and the change from Fig. 1a to b indicates a lattice expansion from $c(\beta) = 2.234$ to 2.257 nm, and from $c(\beta'') = 3.352$ to 3.366 nm. Evidence concerning possible changes in the $a$ parameter is more difficult to obtain owing to the absence of reflections with a high $h$ or $k$ index.

### 3.2. Surface layer depth

Although the diffraction pattern in Fig. 1b is consistent with the appearance of a surface lattice expansion, an alternative possibility is that the
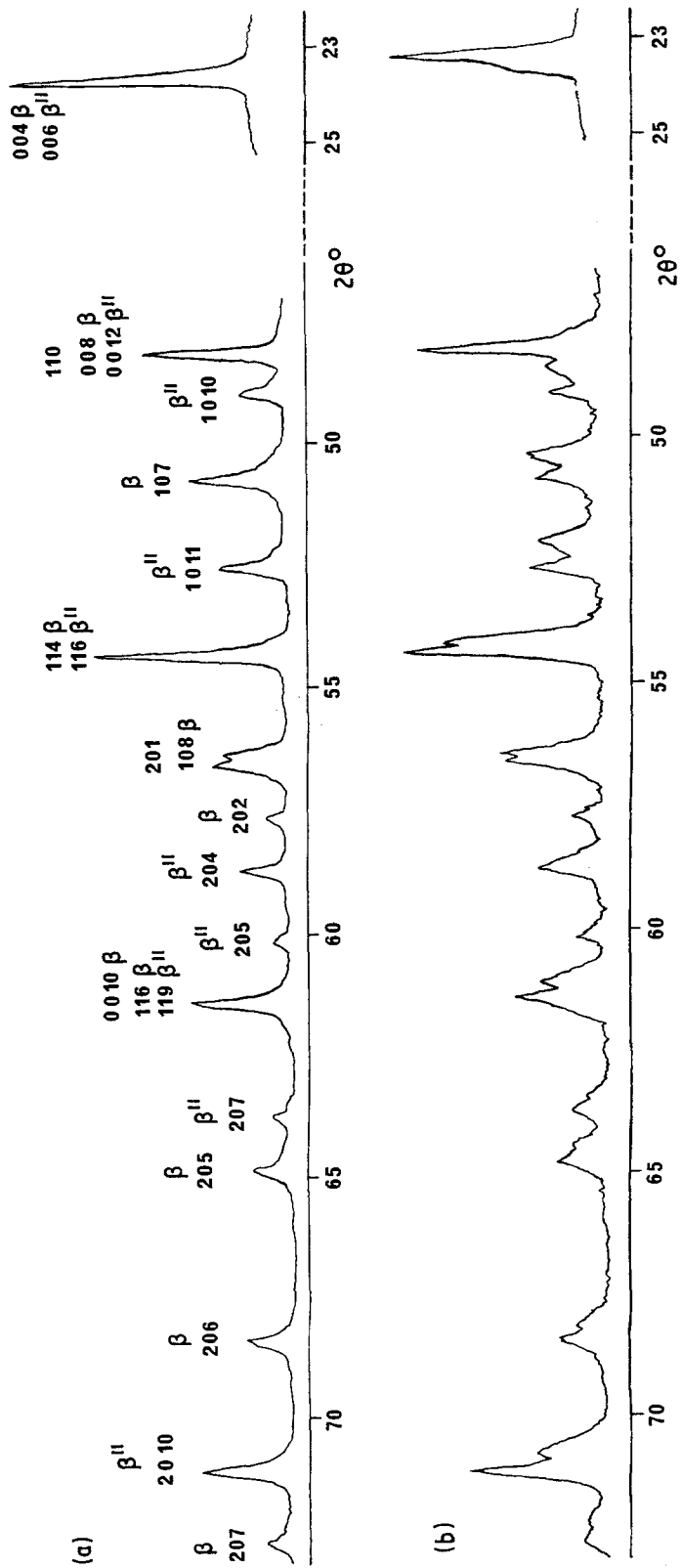
*Figure 1* (a) XRD pattern of a ground slab of $\beta$-alumina; (b) XRD pattern of the outer surface of a $\beta$-alumina tube.

line displacement is caused by a proportion of defective grains distributed through the bulk. The evidence suggests, however, that the lattice expansion is concentrated at the surface. Apart from the observation that $CrK\alpha$ radiation revealed the lattice parameter change far more clearly than $CuK\alpha$, it was apparent that the displaced lines were more intense at low angles, while at high angles there was no change in the XRD pattern.

Since the diffraction pattern shows lines from both surface layer and bulk simultaneously, it is possible to obtain an estimate of the layer depth. If $\mu$ is the linear absorption coefficient ($9\,\text{mm}^{-1}$ for $CrK\alpha$ in $\beta$-alumina), $\theta$ is the angle of reflection and $I_0$ is the intensity of the incident beam, the diffracted intensity from a volume element of thickness $dx$ is given by

$$dI = \frac{I_0}{\sin\theta} \exp\left(\frac{-2\mu x}{\sin\theta}\right) dx, \qquad (1)$$

where $x$ is the distance from the surface. If $s$ is the surface-layer depth, $I_1$ is the intensity of the displaced (surface-layer) line and $I_b$ is the intensity of the undisplaced (bulk) line, integration of Equation 1 between 0 and $s$ yields $I_1$ and integration between $s$ and $\infty$ yields $I_b$. The layer depth can then be expressed as

$$s = \frac{\sin\theta}{2\mu} \ln\left(1 + \frac{I_1}{I_b}\right). \qquad (2)$$

By measuring the relative intensities of displaced and undisplaced lines for a series of reflections, $s$ can be calculated from the slope of cosec $\theta$ against $\ln(1 + I_1/I_b)$. Most surfaces examined have shown layers of the order $5\,\mu\text{m}$ in depth.

## 3.3. Origin of the surface layer

A number of possible explanations for the surface layer lattice expansion can be envisaged:

(a) Strain relaxation at a free surface.

(b) Soda depletion at the surface (the problem of soda loss during sintering of $\beta$-alumina is well known). The increased $c$-value for the $\beta$-phase ($2.257\,\text{nm}$) in the surface layer corresponds approximately to that of Monofrax H (single-crystal $\beta$-alumina) [2], which has a lower $Na_2O$ content ($6.3\,\text{wt}\%$) than that of the sintered ceramic (about $8.5\,\text{wt}\%$).

(c) Ion exchange between $Na^+$ and $H_3O^+$ from moisture absorption on exposure to air, or diffusion of molecular $H_2O$ into the conduction planes. Ion exchange with $H_3O^+$ would be expected to cause an expansion of the $c$-axis [3].

The possibility of residual strain in the sintered tubes was investigated by measuring the bulk lattice constant of a mechanically-polished slab of the ceramic, grinding the slab to a fine powder and remeasuring the lattice constant. Measurements before and after grinding were identical to within 0.03%, indicating that there was no significant residual lattice strain in the sintered tubes.

To determine whether the surface layer was due to soda depletion (i.e. a stoichiometric change) or to interaction with atmospheric moisture, a number of experiments were carried out on mechanically-polished slabs of the ceramic. Slabs that had recently been polished showed no surface layer, as in Fig. 1a, but after etching in concentrated phosphoric acid, or after exposure to air for several weeks, surface layers appeared, as in Fig. 1b. The layer could be removed either by repolishing or by heating the specimen to $1000^\circ$ C. These observations suggested that the layer development was due to moisture, but they were not conclusive. Exposure of specimens to water for several days did not produce significant layer growth, while storage of specimens in vacuum did not suppress the lattice expansion entirely. Exposure to concentrated phosphoric acid did produce a surface layer but thus could indicate either ion exchange with $H_3O^+$ or leaching-out of $Na_2O$ from the $\beta$-alumina by the acid.

The experimental arrangement, shown schematically in Fig. 2, was devised in order to distinguish between the two possibilities. The polished $\beta$-alumina slab was forcibly ion-exchanged with $H_3O^+$ by an electric field in such a way that any layer development could be attributed only to ion exchange. The positive electrode (water)
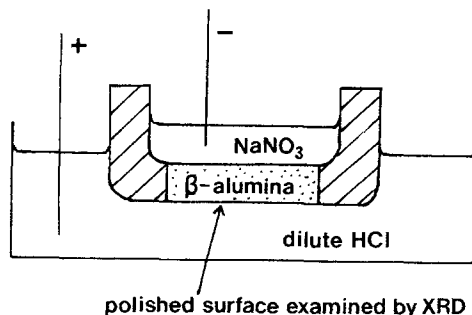


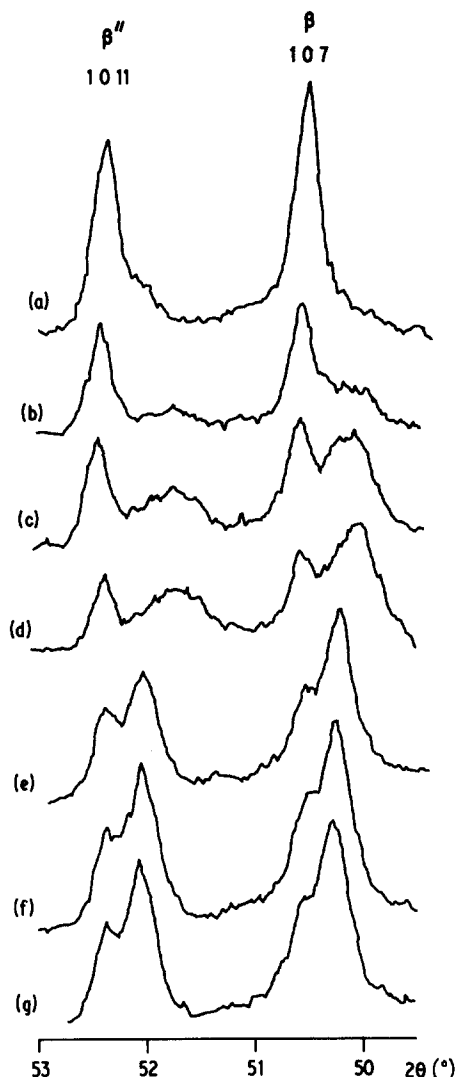Figure 2 Field-assisted ion exchange with $H_3O^+$.

Figure 3 Surface-layer development and removal in the field-assisted ion exchange experiment. Total charge passed: (a) 0, (b) 0.05 A h, (c) 0.25 A h, (d) 0.4 A h, (e) − 0.15 A h, (f) − 0.25 A h and (g) − 0.45 A h.

contained a small quantity of hydrochloric acid to promote electrical conduction; the acid caused slight etching of the $\beta$-alumina, but much less so than in the case of concentrated $H_3PO_4$. After passage of current the polished surface was re-examined by XRD. The results are shown in Fig. 3, in which the progressive changes in the $\beta(1\,0\,7)$ and $\beta''$ $(1\,0\,11)$ lines are shown. In the freshly-polished slab no surface layer is present (Fig. 3a); after passage of current, line displacement pro-gressively appears (Fig. 3b to d), the surface layer attaining a depth of $10\,\mu m$ after 0.4 A h (Fig. 3d).

Both electrodes were then replaced by $NaNO_3$

solution and current passed in the reverse direction, upon which the layer was progressively removed (Fig. 3e to g). Fracture of the $\beta$-alumina slab prevented complete restoration of the original XRD pattern in Fig. 3a, but it is clear that the layer development and removal can be attributed to ion exchange. Fig. 3 reveals a difference in charac-ter between the growth and the removal of the surface layer. When the layer grows the displaced lines remain at the same angle of reflection, $2\theta$, while their intensities increase, whereas, on removal, the displaced lines remain at the same intensity while the lines sharpen and the displacement, $\delta 2\theta$, is progressively reduced. Physically, this indicates that when the layer develops to a depth, $s_0$, it does so as an advancing front behind which complete ion exchange $Na^+ \to H_3O^+$ occurs, whereas, on removal of the layer, the layer thickness remains at $s_0$ and, within the layer, partial re-exchange of $H_3O^+$ by $Na^+$ occurs. This is probably a conse-quence of the lower mobility of $H_3O^+$ in $\beta$-alumina relative to tht of $Na^+$ [4].

## 4. Conclusions

$\beta$-alumina specimens exposed to air develop a sur-face layer several micrometres in depth in which the $c$-axis expands by 1%. The lattice expansion is the result of ion exchange between $Na^+$ and $H_3O^+$. On surfaces exposed to air, a thin film of moisture builds up, following which ion exchange occurs by diffusion

$$Na^+ + 2H_2O \rightleftarrows H_3O^+ + NaOH. \qquad (3)$$
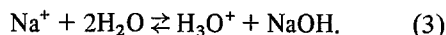
Heating the specimen drives the equilibrium to the left, while etching in acid drives the equilibrim to the right. In a recent paper Dunn [5] has reported the development of a resistive surface layer in $\beta$-alumina tubes exposed to air; this can be attributed to ion exchange, as observed here. This phenomenon is likely to occur in all $Na^+$-conducting solid and vitreous electrolytes.

## Acknowledgements

## References
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