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Chemical colouration of sodium beta-aluminas

L. C. DE JONGHE, A. BUECHELE
Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720, USA

A variety of experiments was performed on Na β-alumina single crystals and Na β''-alumina polycrystals of different microstructures, to clarify the nature of chemical colouration produced by contact with sodium. It was found that the colouration is due to a reduction of the electrolyte by sodium, introducing oxygen vacancies compensated by electrons. Colouration and bleaching kinetics have been determined. It was found that in polycrystals colouration proceeds along the grain boundaries. Water has no effect. The role of the colouration in electrolyte degradation is discussed.

1. Introduction

When sodium β- or β''-alumina solid electrolytes are in prolonged contact with molten sodium metal they discolour noticeably. The grey discolouration can be attributed to the chemical action of the molten sodium since the electrolyte darkens even if there is no current being passsd. The colouration develops as a layer from the sodium–electrolyte interface. Since slow degradation of the electrolyte can occur in Na/Na$_2$S$_x$ cells as a result of prolonged charge transfer [1], it is necessary to clarify the nature of the chemical darkening to determine its possible function. In this paper we describe a series of experiments on Na β-alumina single crystals and on Na β''-alumina polycrystals of differing microstructures, and we elucidate the nature of chemical colouration.

2. Experimental details

Sodium β-alumina single crystals* were packed in dried, coarse Na β-alumina powder† and annealed in air at 1500° C for two hours. This treatment healed most of the basal cleavage cracks that tend to develop in such large single single crystals, and eliminated absorbed and adsorbed water. Polycrystalline Na β''-alumina‡ with three different microstructures, A, B, C, was also used, The three different microstructures are shown in Fig. 1; the relevant data are listed in Table I.

The samples were dried for two hours at 800° C in air, and immediately immersed in molten sodium for up to 16 days. Temperatures were controlled to within ± 1° C, between 250 and 450° C. These experiments were performed in a glove box, under argon containing less than 5 ppm oxygen. Some oxidation of sodium appeared to be unavoidable, and the molten metal should therefore be considered to be saturated with oxygen. At 350° C this puts the oxygen fugacity at about 10^{-55} atm in the molten sodium.

After immersion the samples were sectioned. A discolouration was present in all samples. For one section of each specimen the discolouration could be strongly enhanced by silver exchange of the sodium in molten AgNO$_3$, at 300° C, for 20 min [2]. The colouration profiles of the polycrystalline specimens were then traced with a microdensitometer from micrographs of the silver-stained colouration layers. The profiles obtained were all normalized with respect to the photographic density at the Na/electrolyte interface. The rate of propagation of the colouration

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*Manufactured by Union Carbide, Linde Division, San Diego, California, USA.

†Alcoa X-B2 powder, Alcoa Company, Pittsburgh, Pennsylvania, USA.

‡Specially prepared by Ceramatec, Inc., Salt Lake City, Utah, USA. Nominal composition: 9.1 wt% Na$_2$O, 0.75 wt% Li, balance Al$_2$O$_3$.

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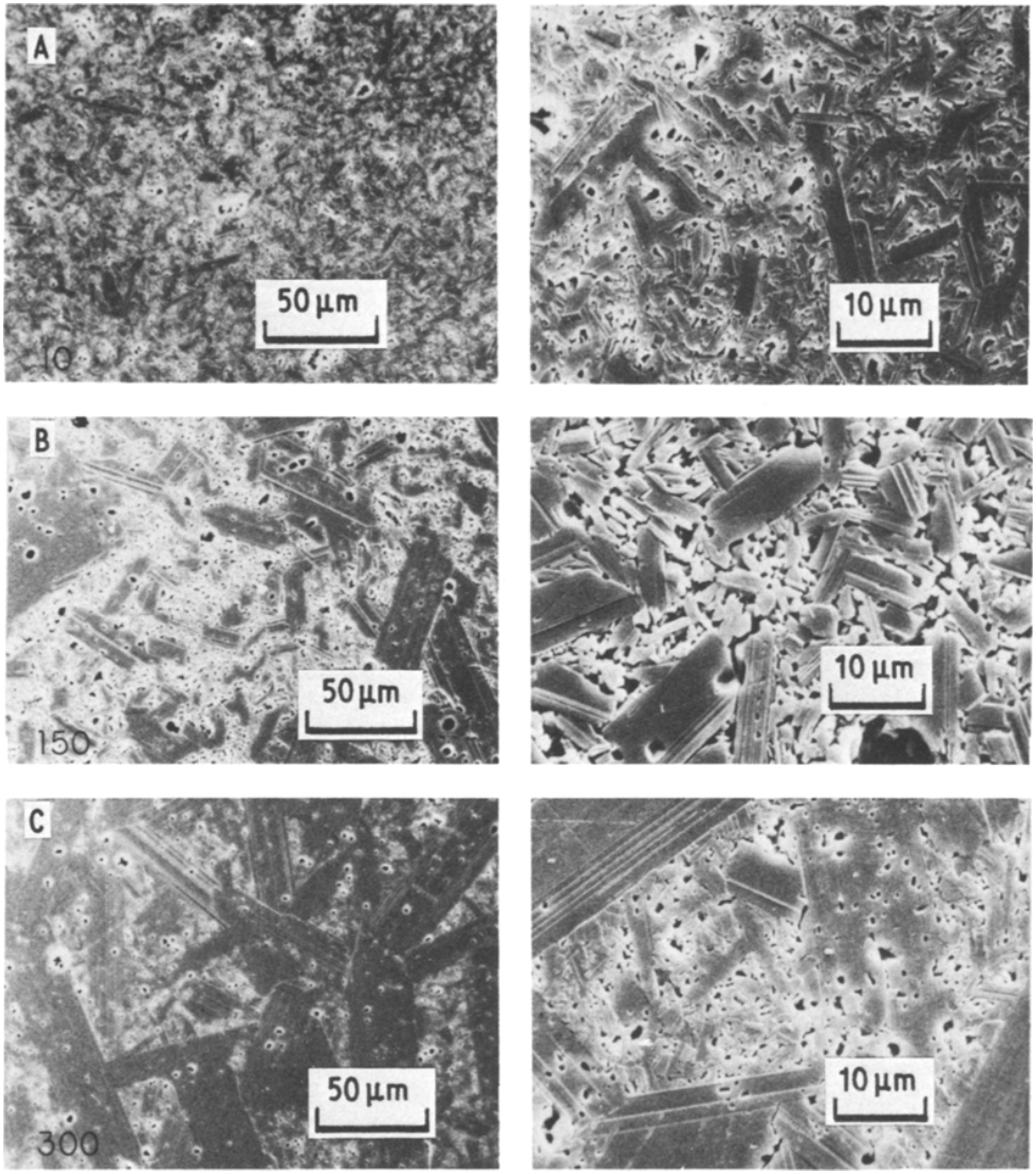

Figure 1 Microstructures of Na β''-electrolytes A, B and C.

was determined from the distances, x, in the profiles, where erf $[x/2\,(Dt)^{1/2}] = 0.5$. For simple diffusion control this criterion would give $D = x^2/0.92t$ [3] provided the densitometer trace corresponded quantitatively to the concentration profile. It was not possible to verify the exact relationship between optical density and concentration of the colouration defect; however, a qualitative correspondence should exist, thus permitting fairly reliable determination of colouration defect diffusion rates.

The colouration of the single crystals appeared to occur in a more discrete layer and their colouration propagation rate could be measured directly from the layer thickness after staining one part of each specimen. The other part of these single-crystal specimen sections was reheated in air at temperatures between 200 and 600° C. This led to a bleaching that proceeded from the surface, again as a discrete layer. The thickness of the bleached layer could be measured optically after silver staining.

TABLE I Microstructural data for the three microstructures, A, B and C

Parameter	A	B	C
Average grain size (μm)	1.1	5.4	5.2
Large-grain (> 10 μm) volume-fraction	< 0.01	0.59	0.83
Average large-grain size (μm)	2.4	15	20
Average largest-grain dimension (nm)	–	38	54
Small-grain volume-fraction	~ 1	0.41	0.17
Average small-grain size (μm)	1.1	2.8	1.1

To verify the effect of the adsorbed surface water on the bleaching rate, some single-crystal samples were partly bleached after exposure to air at 20° C and 50% humidity for 10 h, cooled, re-exposed to the moist air and bleached again. Other crystals were partly exchanged in 9 M H_2SO_4, to replace some Na^+ with H_3O^+.

To investigate the role of oxygen in the bleaching phenomenon, coloured samples were heated in an evacuated quartz ampoule. The ampoule also contained a vanadium foil. The vanadium was heated separately to about 700° C to remove oxygen. This provided an atmosphere where the oxygen partial pressure was below about 10^{-38} atm.

Single crystals were also coated with a sealing glass* such that a small section of a cleaved 00.1 surface was left exposed (Fig. 6a). This sealed crystal was immersed in sodium at 350° C for about 48 h. After this immersion, the crystal was sectioned and stained by silver exchange and the colouration pattern examined. The staining pattern would give information on possible colouration anisotropies or colouration defect diffusion paths.

Polycrystals of Na β''-alumina and of silver-exchanged β''-alumina were partly masked and irradiated for 1 min with an intense ultra-violet (u.v.) beam. The cut-off wavelength corresponded to a photon energy of about 10 eV. These specimens were then examined for discolouration. This experiment could give an indication of the role of free electrons and holes in the colouration process. Ionic conductivities of polycrystalline specimens before colouration, after colouration and after bleaching were measured with an a.c. dispersive method. The details of this method have been described elsewhere [4].

3. Results and discussion

Detailed transmission electron microscope observations of chemically discoloured Na β''-alumina failed to reveal any features that could be attributed to the discolouration. This strongly suggested that the chemical colouration involved the formation of point defects rather than second phases. During colouration, the single crystals also maintained their integrity, again indicating that second-phase formation was not occurring; for example, sodium metal precipitation would be difficult to accommodate in the β or β'' lattice without causing considerable strain, leading to fracture. The results of the experiments have therefore been interpreted in terms of point defects.

From the time scale involved in the formation of the colouration zones [5], the published evidence of Na^+ diffusion through the spinel blocks [4], the expected diffusivity of the aluminium ions and the approximate electron transport rates [6], it was concluded that the chemical colouration could involve only transport of electrons or holes, of sodium, or of oxygen either by oxygen vacancies or by hydronium ions.

3.1. Single-crystal experiments

The chemical colouration of the single crystals appeared to proceed approximately isotropically.

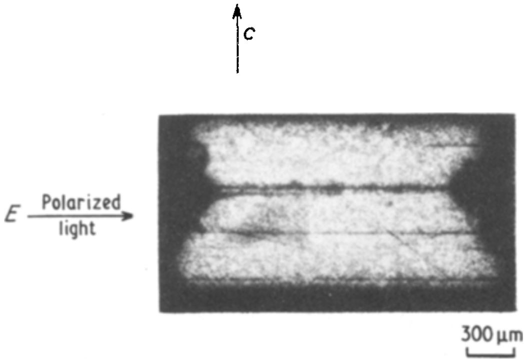

Figure 2 Isotropic colouration of Na β-alumina single crystal, immersed for 6 days at 350° C. The uneven colouration along the basal plane direction is due to sodium filling of cleavage cracks that had not healed in the 1500° C anneal.

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*IN-3 package sealant, Owens-Illinois Electronic Materials Center, Toledo, Ohio, USA.

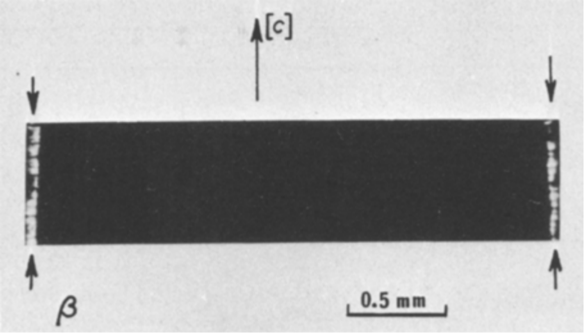

Figure 3 Anisotropic bleaching of chemically coloured crystal, heated for 15 h at 300° C in air.

This is illustrated in Fig. 2 for a crystal immersed for about 6 days at 350° C. The uneven penetration along the basal planes is due to the presence of partial cleavage cracks that could not be healed in the 1500° C anneal prior to immersion. This phenomenon also showed that Na β-aluminas are readily wetted by molten sodium; when such crystals were removed from the sodium bath a mirror could be observed where the metal had penetrated into the partial cracks.

When coloured crystals were heated in air, the bleaching surprisingly occured only in the direction of the conduction planes, as shown in Fig. 3 for a chemically coloured crystal heated in air, at 300° C for about 15 h. The bleaching proceeded as a well-defined layer at this temperature. Chemically coloured single crystals heated for 24 h at 400° C in the evacuated quartz ampoule ($P_{O_2} \simeq 10^{-35}$ atm) did not show any signs of bleaching, as is evident from Fig. 4.

These results compellingly establish that the colouration involves removal of oxygen from the Na β-aluminas, while bleaching in air involves a reoxidation. The colouration appears as a broad optical absorption indicating that electrons are involved as well. Additionally, it was found by Weber [7] that chemical colouration at high temperatures appears to lead to a measurable increase in electronic conductivity. It is therefore concluded that the colouration of Na β-aluminas by molten sodium metal is a reduction of the electrolyte in which the oxygen vacancies that are produced are charge compensated by electrons. The detailed nature of the defect causing the light absorption is not known at present. Possibly, a local sodium-ion redistribution may be associated with it which, together with the oxygen vacancy and a weakly bound electron, would give the rather broad optical absorption.

The remarkable asymmetry in the colouration/bleaching reaction needs to be explained. It is believed that the answer may be in differences in the dependence on the oxygen fugacity if the $V_O^{\cdot\cdot}$ (oxygen vacancy) diffusion rate in the spinel block compared to the conduction planes of the crys-

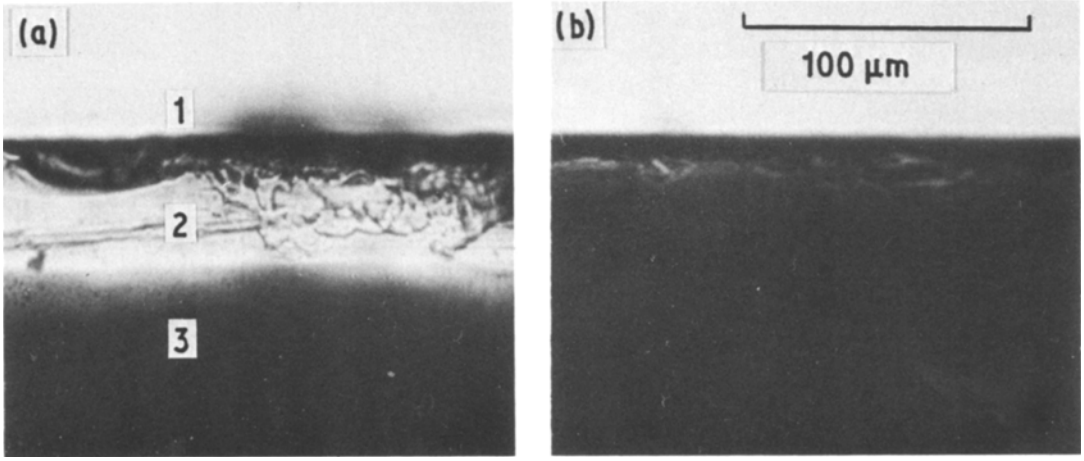

Figure 4 Comparison of bleaching of chemically coloured crystals heated for 48 h at 400° C (a) in air, (b) in low P_{O_2}. No bleaching occurs at low P_{O_2}.

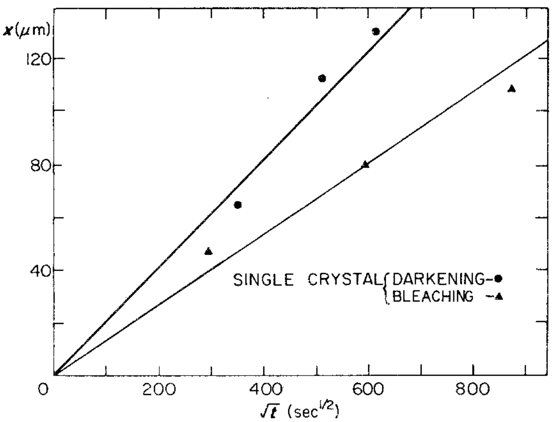

Figure 5 Bleaching and colouration rates of single crystals at 350° C. The bleaching proceeds more slowly than the colouration.

tals. The $V_{\mathrm{O}}^{\cdot\cdot}$ diffusion rate in the spinel blocks would have to depend much more strongly on the oxygen partial pressure than in the conduction planes: in oxidizing conditions the $V_{\mathrm{O}}^{\cdot\cdot}$ concentration in the spinel block would have to be so low that $V_{\mathrm{O}}^{\cdot\cdot}$ transport would be strongly suppressed, while the more open structure of the conduction planes would not be so strongly affected. The fact that colouration is observed to proceed in a layer-like fashion supports this type of explanation. Indeed, a strong dependence on oxygen partial pressure of the $V_{\mathrm{O}}^{\cdot\cdot}$ diffusion rate would lead to a fairly abrupt change in concentration profile. The explanation for the asymmetry in the colouration/bleaching reaction requires that bleaching occurs more slowly than colouration. This was indeed the case, as follows from a comparison of colouration and bleaching rates, shown in Fig. 5. To demonstrate that $V_{\mathrm{O}}^{\cdot\cdot}$ injection could occur through the spinel blocks, a single crystal was partly covered with sealing glass, as described in Section 2, and as shown in Fig. 6a. Contact of the molten sodium was such that no reduction along conduction planes could occur. The darkening pattern after immersion, Fig. 6b, clearly indicates that the colouration proceeded through the spinel blocks.

Some further elucidation of the nature of the colouration defect followed from the u.v. irradiation of Na and Ag β''-aluminas. The u.v. photons produced darkening in the Ag β''-aluminas, as is evident in Fig. 7. The photon energies ranged up to 10 eV so that electron–hole pairs could be created directly. The darkening produced by u.v. irradiation should then be analogous to the photographic imprinting effect where silver ions capture the electrons to form small metallic silver clusters leaving an electron hole. Photodarkening could not be produced in the Na β''- or β-alumina. This indicated that the sodium ions do not readily trap electrons, further corroborating the fact that colouration cannot be attributed simply to a sodium ion–electron pair.

The rate of propagation of the colouration in the single crystals was determined at 300° C and 350° C. The results are shown in Fig. 8. Only a limited set of data could be collected due to the limited supply of large crystals. From the time dependence of the coloured-layer thickness, the scaling constant, K, could be found from $K = x^2/2t$, where x is the layer thickness after time t. This gave at 300 and 350° C, $K_{300} = 1.1 \times 10^{-10}$ cm^2 sec^{-1} and $K_{350} = 3.4 \times 10^{-10}$ cm^2 sec^{-1}, respectively. The activation energy calculated from these two values for the colouration defect propagation rate is about 16 kcal mol^{-1}. This is approximately half of the activation energy for electron transport determined for Na β-alumina [6]. The value of the activation energy thus indicates that the $V_{\mathrm{O}}^{\cdot\cdot}$ diffusion is rate-controlling.

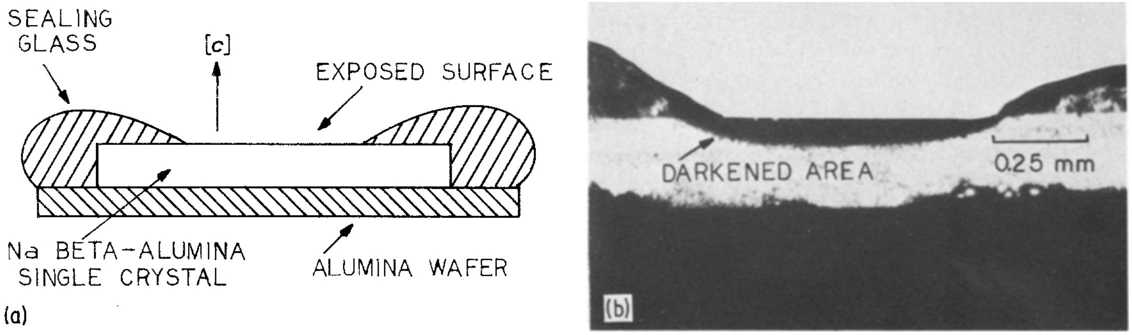

Figure 6 (a) Sketch of single crystal coated with sealing glass; (b) colouration pattern after exposure to molten sodium at 350° C for 34 h.

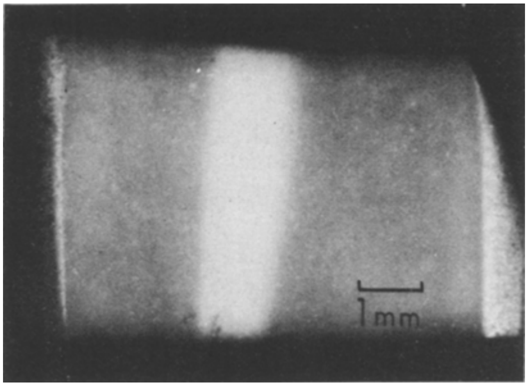

Figure 7 Ag β''-alumina masked in centre and exposed to u.v. light. The u.v. light produced a photochemical darkening in the exposed electrolyte.

3.2. Effect of adsorbed water or H_3O^+ substitution

No effects on appearance or kinetics were detected for either the colouration or the bleaching for those crystals that had experienced repeated water absorption and bleaching, or that contained some substituted H_3O^+. This indicates that the colouration cannot be attributed to effects of water.

3.3. Alternating current dispersive measurements

No significant differences could be detected in the a.c. conductivity behaviour of untreated, coloured or bleached polycrystals up to 200° C. Above 200° C measurements could not be made as bleaching could not be avoided, since our conductivity measurements were carried out in air.

3.4. Polycrystal experiments

Some normalized plots of the colouration profiles of electrolytes with microstructures A and B (Fig. 1) are shown in Fig. 9a and b. The colouration profiles for electrolyte C could not be determined accurately, since they were too diffuse. Initially, the profiles appeared to follow a simple error function solution, but at long immersion times they tended towards a step function. This may again be seen as an indication of a concentration-dependent defect diffusivity.

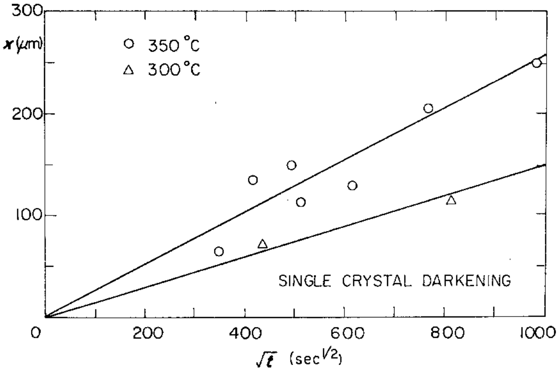

Figure 8 Chemical colouration kinetics at 300 and 350° C for Na β-alumina single crystals.

The results of the chemical colouration experiments at 350° C on the polycrystalline electrolytes are shown in Fig. 10. The rate of colouration propagation is substantially faster in the electrolyte with small grain size. This establishes that the grain boundaries act as rapid transport paths for the colouration-producing defects. The data permit an evaluation of the approximate bulk and grain-boundary transport rates by using the Hart analysis [8]. This analysis can be applied if the mean penetration distance is much larger than the grain size, a condition which was satisfied here. The effective diffusion coefficient, D^{eff}, can then be related to the lattice diffusion coefficient, D_L, and to the grain-boundary diffusion coefficient, D_B:

$$D^{\text{eff}} = D_L + B\,\delta\,D_B/s, \qquad (1)$$

where B is a geometric parameter approximately equal to 1, δ is the grain-boundary thickness, which is of the order of 1 nm, and s is the average grain size. The data are summerized in Table II and lead to the following results at 350° C.

For Na β''-alumina:

$$D_L \leqslant 1 \times 10^{-10}\,\text{cm}^2\,\text{sec}^{-1}$$

$$D_B = 9.8 \times 10^{-7}\,\text{cm}^2\,\text{sec}^{-1}$$

$$(B = 1; \quad \delta = 10^{-7}\,\text{cm});$$

For Na β-alumina:

TABLE II Colouration kinetics at 350° C

Material	D^{eff} (cm² sec⁻¹)	Average grain size (μm)
β''-polycrystal, A	9.8×10^{-10}	1.1
β''-polycrystal, B	3.0×10^{-10}	5.4
Single crystal β	4.5×10^{-10}	—

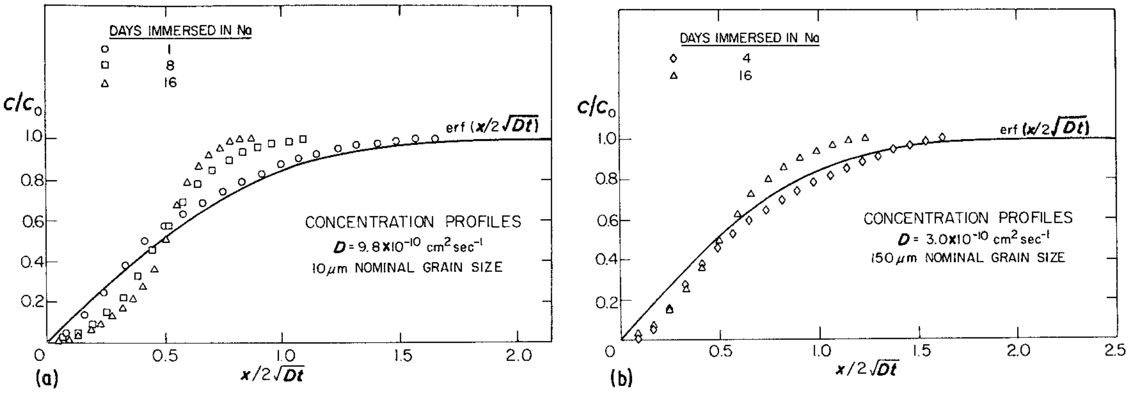

Figure 9 Normalized colouration profiles determined from micrographs of stained polycrystalline specimens. (a) Electrolyte with microstructure A; (b) electrolyte with microstructure B.

$$D_L = 4.5 \times 10^{-10} \mathrm{cm}^2 \mathrm{sec}^{-1}.$$

The ratio of the grain-boundary to the bulk diffusion rates, D_B/D_L, for the β'' polycrystals examined here is about 10^4. This is a lower limit, since only an upper limit to D_L could be determined. Clearly, grain-boundary diffusion dominates the kinetics of chemical colouration in polycrystalline β'' electrolytes. It should thus be expected that the partial electronic conductivity associated with chemical colouration develops first along grain boundaries. The presence of a gradient in the electronic/ionic transport number ratio can lead to internal deposition of sodium, i.e., the Mode II degradation discussed in detail in [1, 9]. This should cause grain boundaries to be active sites for initiation of Mode II degradation [1], possibly leading to Mode I initiation.

A rough estimate of the time needed for complete homogenization of an electrolyte, with a 2 mm wall thickness in contact with sodium at 350° C, would be about 0.5 years. It should be emphasized, however, that the sulphur-electrode side of the electrolyte in a Na/Na_2S_x battery is not the same oxygen chemical potential as the sodium side. The oxygen fugacity in the sulphur electrode is not known, but it is likely to be higher than in the sodium electrolyte. A gradient in the electronic/ionic transport number ratio should therefore persist indefinitely through a Na β- or β''-alumina solid electrolyte in an Na/Na_2S_x cell. Charge transfer through such an inhomogeneity could lead to Mode II degradation, as discussed in [1].

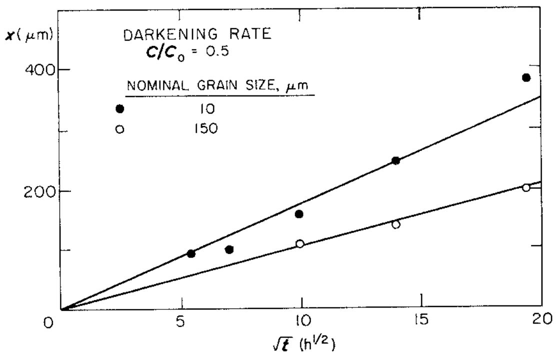

Figure 10 Colouration kinetics of Na β''-alumina polycrystals of microstructure A and B, at 350° C.

4. Summary and conclusions

(a) Chemical colouration of Na β-alumina electrolytes is due to reduction of the electrolytes by the sodium metal.

(b) The colouration is due to $V_O^{\cdot\cdot}$ injection compensated by electrons.

(c) The colouration proceeds mainly through the spinel blocks in single crystals. Bleaching, or reoxidation, proceeds through the conduction planes.

(d) Water has no effect on the colouration or bleaching reaction.

(e) In polycrystals, colouration proceeds preferentially along grain boundaries.

(f) The chemical colouration introduces gradients in the electron/ion transport number ratio that can lead to a Mode II degradation in electrolytes used in Na/Na_2S_x cells.

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