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Lutgard C. De Jonghe and Andrew Buechele

March 1981

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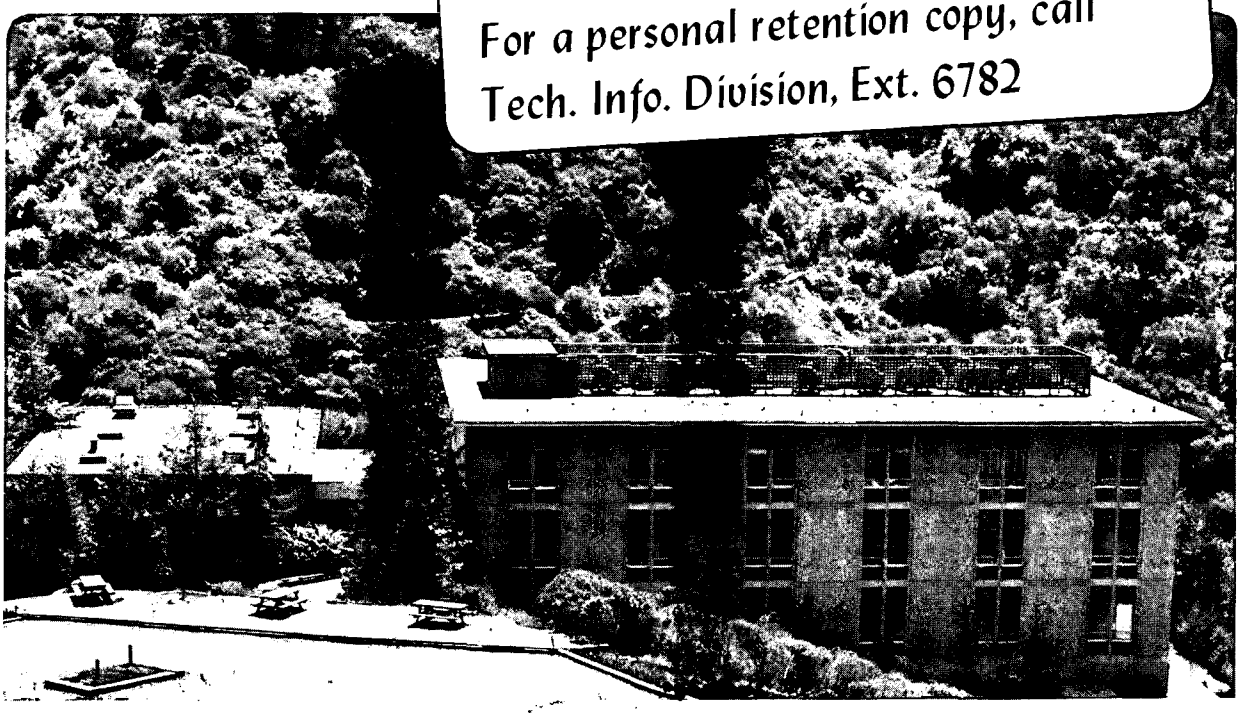

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This work was supported by the Electric Power Research Institute. Additional support was received from the Assistant Secretary for Conservation and Renewables Energy, Office of Advanced Conservation Technology, Electrochemical Systems Research Division of the U. S. Department of Energy under Contract No. W-7405-ENG-48.

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ABSTRACT

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

1. INTRODUCTION

When sodium-β or β" alumina solid electrolytes are in prolonged contact with molten sodium metal they discolor noticeably. The grey discoloration can be attributed to the chemical action of the molten sodium since the electrolyte darkens even if no current is passed through it. The coloration develops as a layer from the sodium/electrolyte interface. Since slow degradation of the electrolyte can occur in Na/Na_2S_x cells as a result of prolonged change 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 sodium-β alumina single crystals and on sodium β" polycrystals of differing microstructures, and we elucidate the nature of chemical coloration.

2. EXPERIMENTAL

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

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* Manufactured by Union Carbide, Linde Division, San Diego, California.
‡ Alcoa X-B2 powder, Alcoa Company, Pittsburgh, Pennsylvania.
‡ Specially prepared by Ceramatec, Inc., Salt Lake City, Utah.
Nominal Composition: 9.1 wt% Na_2O, 0.75 wt Li, balance Al_2O_3.

Table I. The samples were dried for 2 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 discoloration was present in all samples. For one section of each specimen the discoloration could be strongly enhanced by silver exchange of the sodium in molten $AgNO_3$, at 300°C, for 20 min (2). The coloration profiles of the polycrystalline specimens were then traced with a microdensitometer from micrographs of the silver stained coloration layers. The obtained profiles were all normalized with respect to the photographic density at the Na/electrolyte interface. The rate of propagation of the coloration was determined from the distances, x, in the profiles where erf $(x/2\sqrt{Dt}) = 0.5$. For simple diffusion control this criteria 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 coloration defect; however, a qualitative correspondence should exist permitting determination of coloration defect diffusion rates that are fairly reliable.

The coloration of the single crystals appeared to occur in a more discrete layer and their coloration 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.

To verify the effect of the adsorbed surface water on the bleaching rate, some single crystalline samples were partly bleached after exposure to air at 20°C containing 50 percent H_2O, cooled, reexposed to the moist air and bleached again. Other crystals were partly exchanged in H_2SO_4, to replace some Na^+ with H_3O^+.

To investigate the role of oxygen in the bleaching phenomenon, colored samples were heated in an evacuated quartz ampule. The ampule 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 Na at 350°C for about 48 hours. After this immersion, the crystal was sectioned and stained by silver exchange, and the coloration pattern was examined. The staining pattern would give information on possible coloration anisotropies or coloration defect diffusion paths.

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* IN-3 Package Sealant, Owens-Illinois Electronic Materials Center, Toledo, Ohio.

Polycrystals of sodium-beta" alumina and of silver exchanged beta" alumina were partly masked and irradiated for 1 min with an intense U.V. beam. The cutoff wavelength corresponded to a photon energy of about 10 eV. These specimens were then examined for discoloration. This experiment could give an indication of the role of free electrons and holes in the coloration process. Ionic conductivities of polycrystalline specimens before coloration, after coloration, and after bleaching were measured by 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 discolored Na-β" alumina failed to reveal any features that could be attributed to the discoloration. This strongly suggested that the chemical coloration involved the formation of point defects rather than second phases. During coloration, the single crystals also maintained their integrity, again indicating that second phase formation was not occurring; for example, Na metal precipitation would be difficult to accommodate in the beta or beta" 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 that was involved in the formation of the coloration zones (5), the published evidence of Na^+ diffusion through the spinel blocks (4), the expected diffusivity of the aluminum ions and the approximate electron transport rates (6), it was concluded that the chemical coloration 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 coloration of the single crystals appeared to proceed approximately isotropically. 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 sodium-beta aluminas are readily wetted by molten sodium; when such crystals were removed from the Na bath a sodium mirror could be observed where the metal had penetrated into the partial cracks.

When colored crystals were heated in air, the bleaching surprisingly occurred only in the direction of the conduction planes, as is shown in Fig. 3 for a chemically colored crystal heated in air, at 300°C, for about 15 hours. The bleaching proceeded as a well defined layer at this temperature.

Chemically colored single crystals heated up to 24 hrs at 400°C in the evacuated quartz ampule ($P_{O_2} \simeq 10^{-35}$ atm) did not show any sings of bleaching, as is evident from Fig. 4.

These results compellingly establish that the coloration involves removal of oxygen from the sodium-beta aluminas, while bleaching in air involves a re-oxidation. The coloration appears as a broad optical absorption indicating that electrons are involved as well. Additionally, it was found by Weber (7) that chemical coloration at high temperatures appears to lead to a measurable increase in electronic conductivity. It is therefore concluded that the coloration of sodium-beta aluminas by molten sodium metal is a reduction of the electrolyte

in which the oxygen vacancies that are introduced 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 coloration/bleaching reaction needs to be explained. It is believed that the answer may be in differences in the dependence on the oxygen fugacity of the $V_O^{\cdot\cdot}$ diffusion rate in the spinel block compared to the conduction planes of the crystals. The $V_O^{\cdot\cdot}$ 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 $V_O^{\cdot\cdot}$ concentration in the spinel block would have to be so low that $V_O^{\cdot\cdot}$ transport would be strongly suppressed, while the more open structure of the conduction planes would not be so strongly affected. The fact that coloration is observed to proceed in a layer-like fashion supports this type of explanation. Indeed, a strong oxygen partial pressure dependence of the V_O diffusion rate would lead to a fairly abrupt concentration profile change. The explanation for the asymmetry in the coloration/bleaching reaction requires that bleaching would occur more slowly than coloration. This was indeed the case, as follows from a comparison of coloration and bleaching rates in Fig. 5. To demonstrate that $V_O^{\cdot\cdot}$ injection could occur through the spinel blocks, a single crystal was partly covered with sealing glass as described in the experimental

section 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 coloration proceeded through the spinel blocks.

Some further elucidation of the nature of the coloration defect followed from the U.V. irradiation of Na- and Ag-beta" aluminas. The U.V. photons produced darkening in the silver-beta" 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-beta" or beta-alumina. This indicated that the sodium ions do not readily trap electrons, further corroborating that coloration cannot be attributed simply to a sodium-electron pair.

The rate of propagation of the coloration 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 colored layer thickness, the scaling constant, K, could be found from $K = X^2/2t$, when 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 and $K_{350} = 3.4 \times 10^{-10}$ cm^2/sec, respectively. The activation energy calculated from these two values for the coloration defect propagation rate is about 16 kcal/mole. This

is approximately half of the activation energy for electron transport determined on Na-beta alumina (6). The value of the activation energy thus indicates that the $V_O^{\cdot\cdot}$ diffusion is rate controlling.

3.2 Effect of Adsorbed Water or H_3O^+ Substitution.

No effects on appearance or kinetics were detected for either the coloration 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 coloration cannot be attributed to effects of water.

3.3 A.C. Dispersive Measurements

No significant differences could be detected in the A.C. conductivity behavior of untreated, colored or bleached crystals 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 coloration profiles of electrolytes with the microstructures A and B (Fig. 1), are shown in Fig. 9a and 9b. The coloration profiles for the electrolyte C could not be determined accurately, since they appeared 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 dependence defect diffusivity.

The results of the chemical coloration experiments at 350°C, on the polycrystalline electrolytes are shown in Fig. 10. The rate of coloration propagation is substantially faster in the small grain size electrolyte. This establishes that the grain boundaries act as rapid transport paths for the coloration 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:

$$D^{eff} = D_L + B\,\delta\,D_B/s$$

where B is a geometric parameter about equal to 1, δ is the grain boundary thickness which is on the order of 10 Å, and s is the average grain size. The data are summarized in Table II and lead to the following results at 350°C:

for Na-β" alumina: $D_L = 1 \times 10^{-10}$ cm^2/sec

$D_B = 9.8 \times 10^{-7}$ cm^2/sec

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

for Na-β alumina; $D_B = 4.5 \times 10^{-10}$ cm^2/sec.

It can be observed that 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. Clearly, grain boundary diffusion dominates the kinetics of chemical coloration in polycrystalline electrolytes. It should thus be expected that the partial electronic conductivity associated with chemical coloration develops first along grain boundaries. This should cause grain boundaries to be active sites for a Mode II degradation initiation (1), possibly leading to a 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 Na at 350°C, would be about 0.5 years. It should be emphasized, however, that the sulfur electrode side of the electrolyte in a Na/Na_2S_x battery is not at the same oxygen chemical potential as the sodium side. The oxygen fugacity in the sulfur electrode is not known, but is likely to be substantially higher than in the sodium electrolyte. An electronic/ion transport number ratio gradient should therefore persist indefinitely through a Na-beta or beta" alumina solid electrolyte in a Na/Na_2S_x cell. Charge transfer through such an inhomogeneity could lead to Mode II degradation, as discussed in Ref. 1.

4. SUMMARY AND CONCLUSIONS

(1) Chemical coloration of sodium-beta alumina electrolytes is due to reduction of the electrolytes by the sodium metal.

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

(3) The coloration proceeds mainly through the spinel blocks in single crystals. Bleaching, or re-oxidation, proceeds through the conduction planes.

(4) Water has no effect on the coloration or bleaching reaction.

(5) In polycrystals, coloration proceeds preferentially along grain boundaries.

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

5. ACKNOWLEDGEMENTS

This work was supported by the Electric Power Research Institute. Additional support was received from the Assistant Secretary for Conservation and Renewables Energy, Office of Advanced Conservation Technology, Electrochemical Systems Research Division of the U.S. Department of Energy under contract No. W-7405-ENG-48.

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FIGURE CAPTIONS

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

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

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

Figure 4. Comparison of bleaching of chemically colored crystals, heated for 48 hrs at 400°C in air (A) or in low P_{O_2} (B). No bleaching occurs at low P_{O_2}.

Figure 5. Bleaching and coloration rates of single crystals at 350°C. The bleaching proceeds slower than the coloration.

Figure 6. A. Sketch of single crystal coated with sealing glass
B. Coloration pattern after exposure to molten sodium at 350°C for 34 hrs.

Figure 7. Ag-β" alumina masked in center and exposed to U.V. The U.V. produced a photochemical darkening in the exposed electrolyte.

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

Figure 9. Normalized coloration profiles determined from micrographs of stained polycrystalline specimens. A. Electrolyte with microstructure A; B. Electrolyte with microstructure B.

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

Table I. Microstructural Data

	MATERIAL		
	A	B	C
Average grain size	1.1 μm	5.4 μm	5.2 μm
Large grain volume fraction	0.	0.59 (>10 μm)	0.83 (>10 μm)
Average large grain size	2.4 μm	15 μm	20 μm
Average largest grain dimension	---	38 μm	54 μm
Small grain volume fraction	1.	0.41	0.17
Average small grain size	---	2.8 μm	1.1 μm

Table II. Coloration Kinetics at 350°C

Material	D^{eff} (cm^2/sec)	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}	---

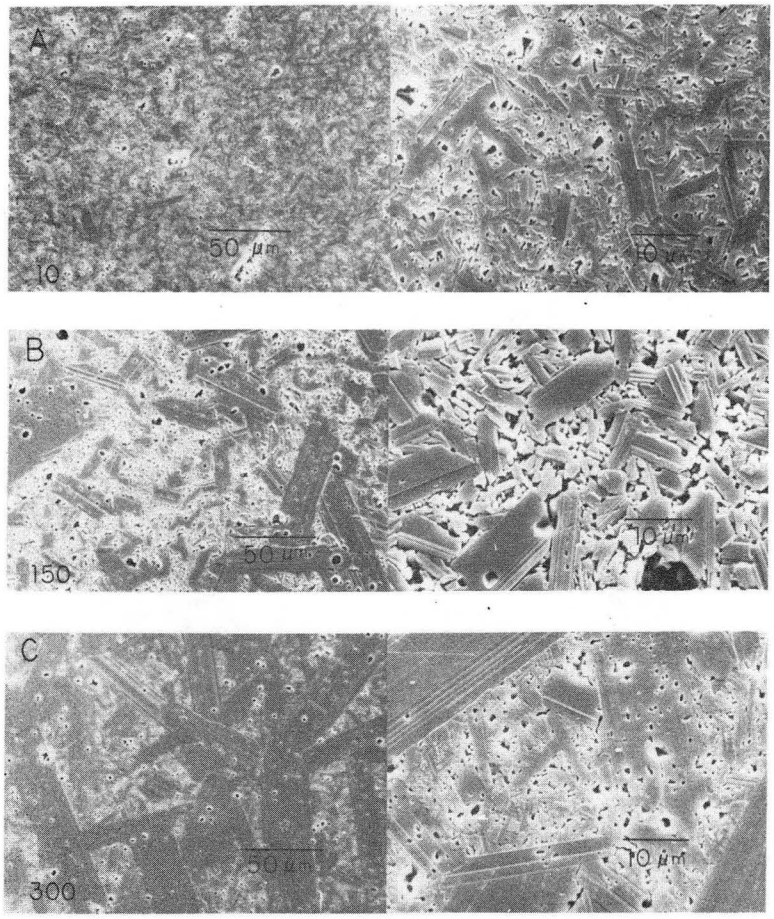

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Figure 1

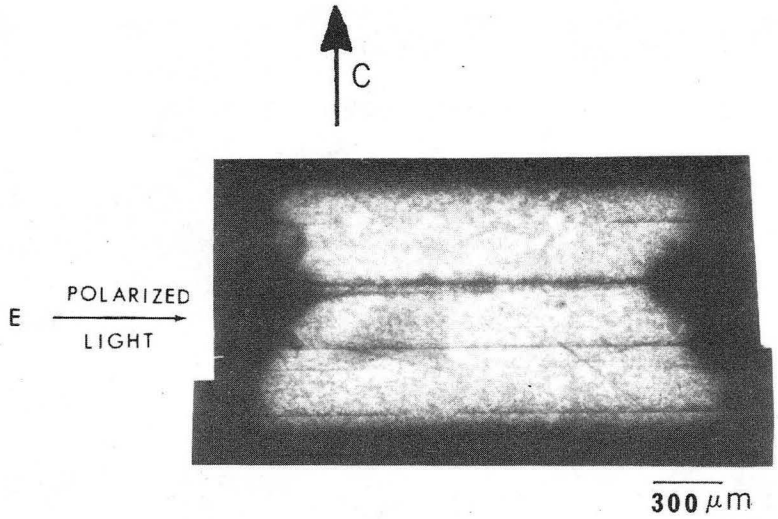

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Figure 2

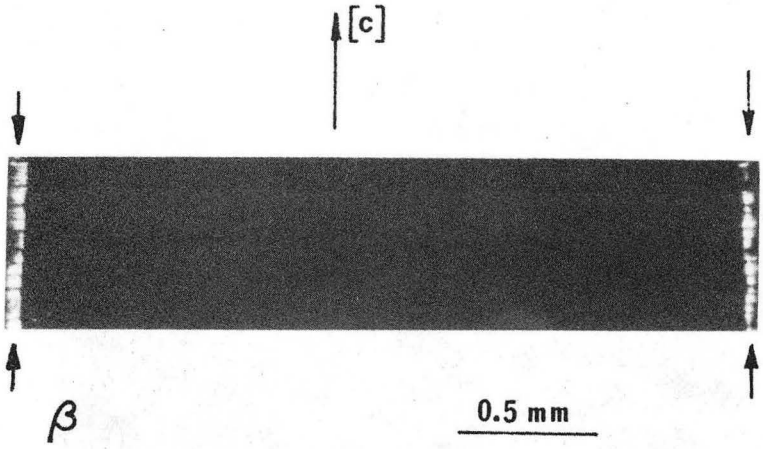

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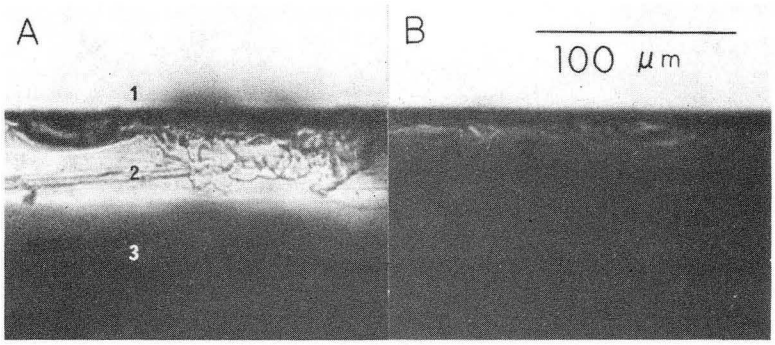
Figure 3



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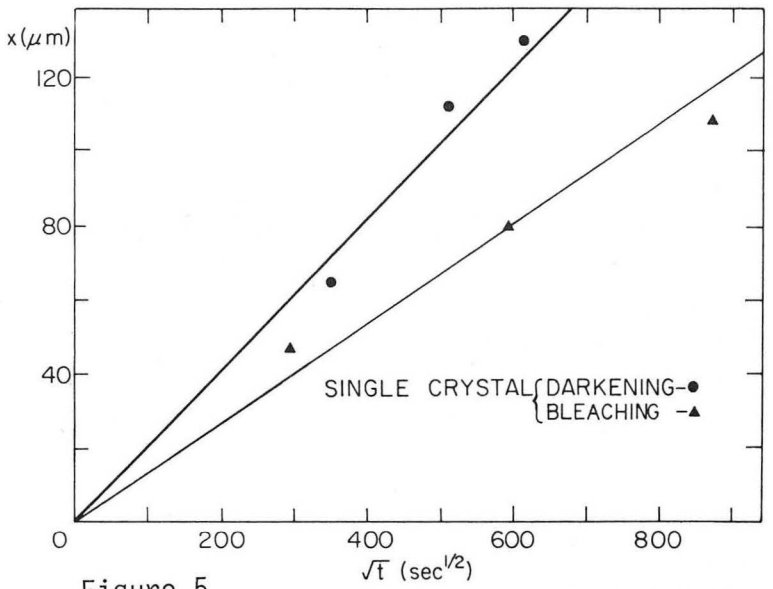

Figure 5

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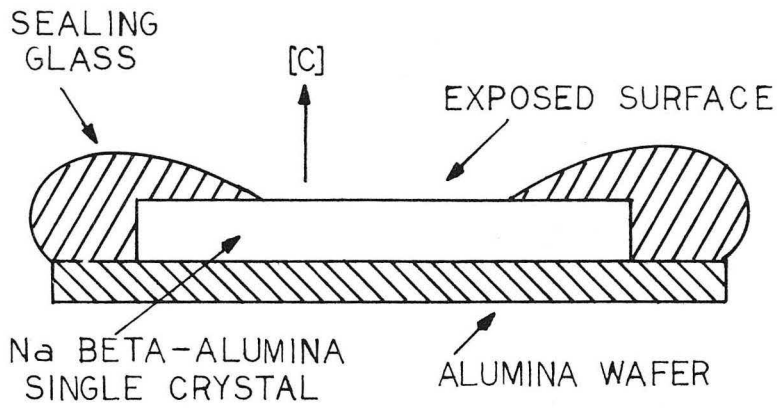

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Figure 6A

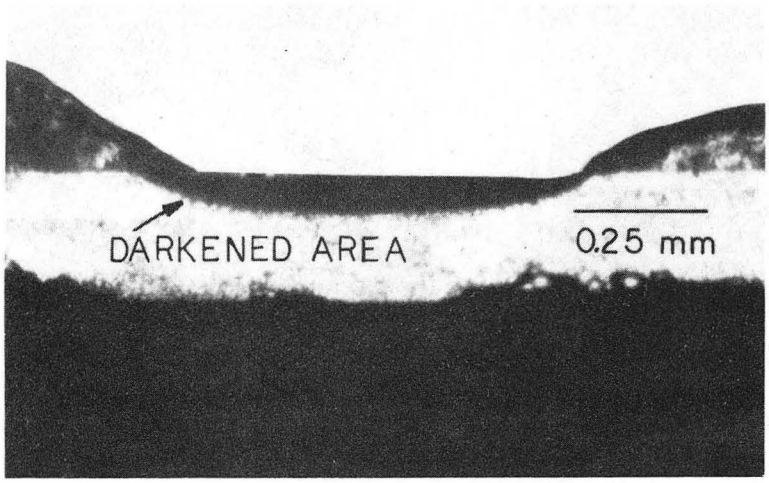
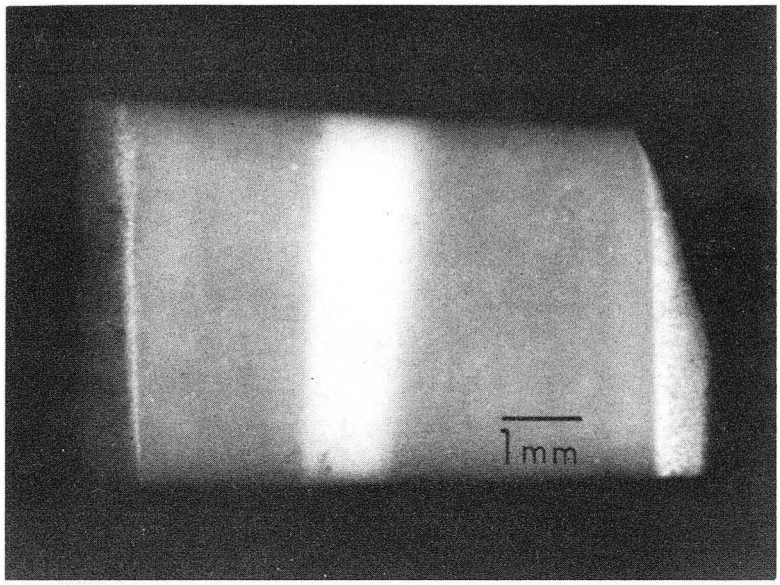


Figure 6B XBB 813-2316



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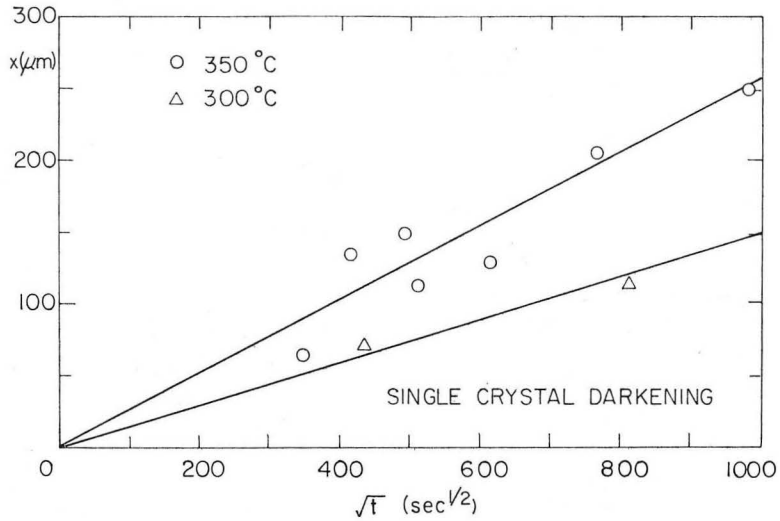

Figure 8

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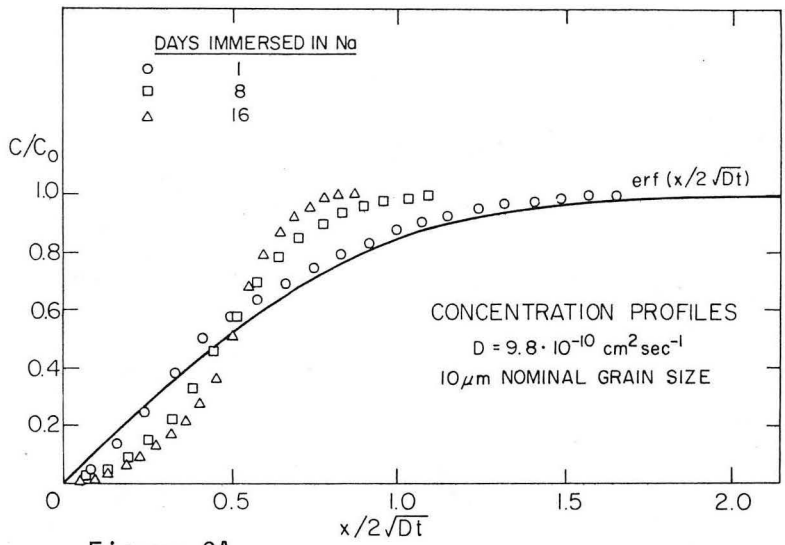

Figure 9A

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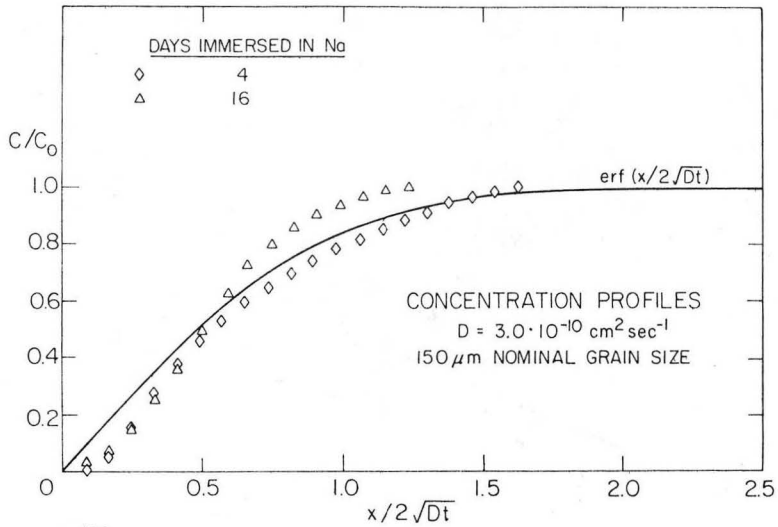

Figure 9B

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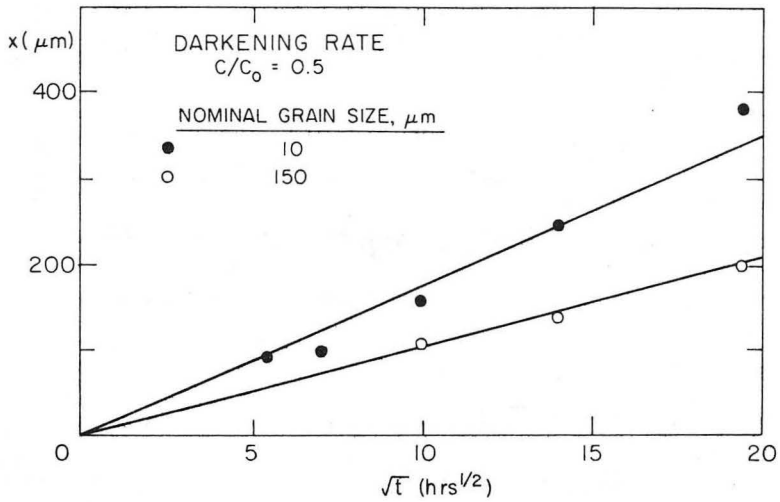

Figure 10

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