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Abstract

A reaction rate maximum occurs around 250°C in the bleaching of chemically discolored sodium beta aluminas. It is determined that the bleaching rate depends on the diffusion rate of oxygen interstitials in the conduction planes of sodium beta alumina. The reaction rate maximum indicates that an irreversible transition occurs from a high mobility to a low mobility oxygen interstitial around 300°C. It is proposed that this transition is one in which a free oxygen interstitial is transformed into a Roth-type interstitial.

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I Introduction

In a recent paper De Jonghe and Buechele [1] reported that sodium-beta aluminas are partly reduced by molten sodium. The reaction introduces oxygen vacancies, compensated by electrons, leading to a gradual discoloration of the electrolyte. At reaction temperatures above 400°C chemical coloration appears to involve an increasing sodium dissolution into the solid, as was reported by Weber and Hunt [2]. The chemical coloration can be completely bleached by heating in an oxidizing atmosphere. Below 400°C, bleaching of chemically colored Na-beta alumina single crystals proceeds in a well defined, layer-like fashion and follows very nearly parabolic bleached layer growth kinetics. The bleaching kinetics of these single crystals, chemically colored by sodium metal at 350°C, exhibit an unexpected maximum around 250°C. In this paper we report on this bleaching rate anomaly, and propose a mechanism that involves interstitial oxygen ion transport.

II Experimental

Sodium-beta alumina single crystals* with dimensions of about 2x2x5mm were immersed in molten sodium at 350°C for 165 or for 266 hours. This experiment was carried out in a glove box, under purified argon with less than 5 ppm oxygen. The molten sodium showed formation of an oxide layer, indicating that the oxygen fugacity in the metal melt should be at the $\text{Na}_2\text{O}/\text{Na}$ equilibrium of about 10^{-55} atm [3]. After this exposure to molten sodium the chemical coloration extended throughout the samples.

The chemically colored samples were bleached in air at 250, 300, 350, and 400°C. Due to the very limited availability of large single crystals only a limited set of experiment could be performed. After the bleaching treatment, the Na ions in the crystals were exchanged with molten AgNO_3 , at 300°C, for about 20 minutes. The silver exchange strongly enhanced the remaining coloration [4] thus facilitating the optical measurement of the bleached layer thickness. Some samples were given a dual bleaching treatment: 24 hours at 350°C followed by 72 hours or 125 hours at 250 or 300°C.

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III Results and Discussions

An example of a partly bleached single crystal is shown in Fig. 1. The crystal coloration has been enhanced by silver staining. The *c* axis is normal to the paper. The bleached layer is very discrete. Such discrete layers are typically formed as a result of the elimination of color centers when the recombination rate of the neutralizing defect with the color center is fast compared to its transport rate. The bleaching kinetics are parabolic as shown earlier [1].

The anomaly in the bleaching kinetics is evident from a comparison of the reaction rate constant *k*, calculated with Eq. 7, from isochronal bleached layer thicknesses as a function of temperatures, Fig. 2. The bleaching rate is maximum around 250°C and minimum around 350°C. The bleaching kinetics appear to be dependent on the chemical coloration treatment: crystals immersed in sodium for a longer time bleach slower. This is shown in Fig. 3, where bleaching rates after a 165hr coloration treatment (solid lines) are compared to those after a 265hr treatment. This result is expected if the equilibrium coloration defect concentration is not achieved rapidly, possibly due to a slow surface step.

As discussed earlier [1] the bleaching is a reoxidation process. Thus, during bleaching, oxygen ions diffuse into the crystal while electrons are transported out. Electroneutrality requirements will couple the fluxes. Additionally, highly mobile Na^+ ions will screen completely the electrical fields that would otherwise arise. To find which species dominates the bleaching kinetics, the transport equations

need to be considered and reasonable estimates of the coloration defect density need to be made. The transport equations describing the coupled fluxes of electrons and oxygen ions are, in the absence of an electric potential gradient:

$$J_e = -1/2 J_i = - (\sigma_e / F^2) \nabla \mu_e \quad (1)$$

and

$$J_i = -(D_i C_i / RT) \nabla \mu_i \quad (2)$$

where J_e = electron flux, J_i = oxygen ion flux, σ_e = electronic conductivity, F = Faraday constant, D_i = oxygen ion diffusion constant, R = gas constant, T = absolute temperature, μ_e and μ_i = chemical potentials of electrons and oxygen ions, C_i = mobile oxygen ion concentration.

Remembering that

$$\frac{1}{2} \mu_{O_2} = \mu_i - 2 \mu_e, \quad (3)$$

Eg. (1), (2) and (3) lead to:

$$J_i = - [\sigma_e D_i C_i / (D_i C_i F^2 + 2 RT \sigma_e)] \nabla \mu_{O_2} \quad (4)$$

This flux will be controlled by the oxygen ion transport rather than by electrons, if:

$$D_i C_i F^2 \ll \sigma_e RT \quad (5)$$

Here, C_i is the concentration of all mobile oxygen which, in the bleaching below 400°C , is confined to the conduction planes [1]. This puts C_i at about 3.3×10^{-4} moles O_2/cm^3 for the present crystals that have an overall composition of $1.25 \text{ Na}_2\text{O} \cdot 11 \text{ Al}_2\text{O}_3$. The value of σ_e is about $10^{-15} (\Omega\text{cm})^{-1}$ at 300°C (5,6). Thus, for Eq. (5) to be valid, one should satisfy

$$D_i \ll \sigma_e RT / C_i F^2 \approx 1.6 \times 10^{-10} \text{ cm}^2/\text{sec} \quad (6)$$

An estimate of the upper bound on D_i can be obtained from the scaling constant, k . From the parabolic bleaching rates one may write:

$$dx/dt = k/x \quad (7)$$

where x is the bleached layer thickness. Also,

$$J_i = C_D dx/dt \quad (8)$$

where C_D is the total concentration of coloration defects. Since a weight change could not be detected after coloration or bleaching, the maximum value of C_D is about 10^{-3} weight fraction, or about 1×10^{-5} moles O_2/cm^3 . Thus, with $k \approx 2 \times 10^{-10} \text{ cm}^2/\text{sec}$ at 250°C :

$$J_i \times \leq 2 \times 10^{-15} \text{ moles/cm sec.} \quad (9)$$

Integration of Eq. (4) over the bleached layer thickness, ℓ , assuming that Eq. (5) is valid, and further assuming that σ_e , D_i and C_i are about constant within the bleached layer leads to:

$$D_i = - \frac{J_i \ell RT}{C_i} (\Delta\mu_{O_2})^{-1} \quad (10)$$

where $\Delta\mu_{O_2}$ is the oxygen chemical potential difference between the surface and the coloration interface at $x = \ell$. This $\Delta\mu_{O_2}$ should correspond to the oxygen fugacity difference between air and the Na/Na₂O melt. Thus

$$\Delta\mu = RT \ln \frac{p_{O_2}^{x=\ell}}{p_{O_2}^{x=0}} \approx RT \ln 10^{-55} \quad (11)$$

Putting the values of the respective parameters into Eq. (10), it is found that

$$D_i \leq 5 \times 10^{-14} \text{ cm}^2 \text{ sec}^{-1}. \quad (12)$$

Thus, the upper estimate to D_i is 3 to 4 orders of magnitude lower than required by Eq. (6) for oxygen ion diffusion controlled bleaching kinetics. The anomalous bleaching kinetics must therefore be understood in terms of changes in the transport mechanism of the oxygen ions in the conduction planes.

The results of the dual bleaching treatments are also shown in Figs. 2 and 3. After bleaching for 24 hrs at 350°C in air followed by

bleaching for 72 hr at 250°C, the total bleached layer thickness is 50 μm . The total equivalent time at 250°C, t_{250} , is obtained from:

$$t_{250} = 72 \text{ hr} + t_{250} k_{350}/k_{250} \quad (13)$$

where $t_{350} = 24 \text{ hr}$, and k_{350} and k_{250} are the scaling constants at 350 and 250°C in Eq. (7). It is seen that the bleached layer thickness is significantly less than expected from a reversibility postulate. Similar results of dual bleaching experiments are included in Figs. 3 and 4. It must thus be concluded that the changes in the bleached layers above 300°C are irreversible.

The above results can all be interpreted simply if it is assumed that the transported species is an oxygen interstitial. In the coloration process a number of these interstitials get removed, permitting the recombination of the $V_{\text{Al}}^{\text{'''}} - \text{Al}_i^{\text{'}}$ defect pairs associated with the Roth oxygen interstitial configuration [7]. When oxygen interstitials are re-introduced in the bleaching process, they should have a high mobility if they are not bound by the $\text{Al}_i^{\text{'}} - V_{\text{Al}}^{\text{'''}}$ Frenkel pair. The bleaching rate anomaly data would then indicate that in sodium-beta alumina the conversion of free oxygen interstitials to bound oxygen interstitial occurs between 300 and 350°C.

It is interesting to note that in Na- β aluminum conduction plane oxygen interstitials are not present, and one should therefore expect slower bleaching kinetics. This is indeed observed [8].

IV Conclusions

- a. A bleaching rate maximum occurs at around 250°C during the reoxidation of chemically colored sodium-beta alumina.
- b. The bleaching rates decrease for increased coloration times.
- c. The bleaching rate anomaly can be understood if oxygen interstitial are the rate controlling species. The re-introduced oxygen interstitials would irreversibly covert to trapped interstitials between 300 and 350°C.

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Discussions in the W. L. Roth are gratefully acknowledged.

References

1. L. C. De Jonghe and A. Buechele, J. Mat. Sci. 17 (1982) 885.
2. N. Weber and T. K. Hunt "Stability of Beta/Beta" Ceramics". To be published, 1983.
3. See e.g. L. S. Darken and R. W. Gurry, "Physical Chemistry of Metals", McGraw-Hill, New York, 1953.
4. L. C. De Jonghe and L. Feldman, Mater. Res. Bull. 15 (1980) 777.
5. N. Weber, Energy Conversion 14 (1979) 1.
6. R. McClelland and L. C. De Jonghe, unpublished data (1982).
7. W. L. Roth, F. Reidinger, and S. LaPlaca, in "Superionic Conductors", G. D. Mahan and W. L. Roth, Ed., Plenum Press, New York, 1976, pp. 223.
8. L. C. De Jonghe, A. Buechele, and K. H. Yoon, Advances in Ceramics, 1982 (in press).

Figure Captions

Fig. 1. Example of a partly bleached sample after silver staining.

The crystal was immersed for 165 hr in sodium at 350°C, and then bleached in air for 98.5 hr. The bleached layer is discrete. The micrograph was taken looking down on the conduction plane.

Fig. 2. The scaling constant, k , calculated with Eq. (7) from bleached layer thickness measurements after a 24 hr annealing in air.

A bleaching rate anomaly is observed between 250 and 350°C.

Fig. 3. Bleaching data for samples immersed for 226 hrs in liquid Na at 350°C. The solid data points are the results of dual bleaching treatments.

Fig. 4. Bleaching data for samples immersed for 162 hr in liquid sodium at 350°C. The solid data point is the result of a dual bleaching treatment. The dashed lines are the bleaching data of the samples, shown in Fig. 3, that were immersed longer in liquid sodium. Longer immersion time lead to slower kinetics.

1.0 mm

Fig. 1

XBB 831-191

XBL 8211 - 7361

Fig. 2

Fig. 3

XBL 8211 - 7360

Fig. 4

XBL 8211 - 7359

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