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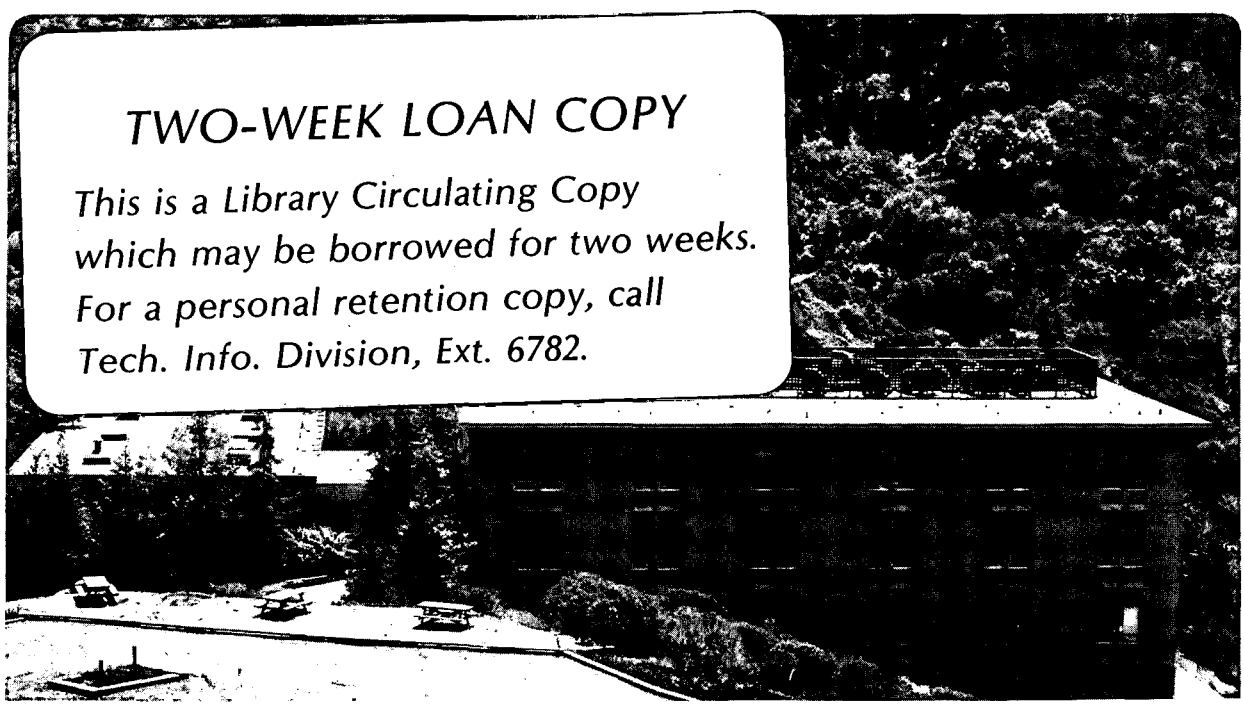

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LOCAL ELECTRODE CURRENT DENSITY AND FLAW DECORATION OF SODIUM-BETA" ALUMINA

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ABSTRACT

Simple decoration methods are described that can qualitatively reveal local electrode current densities and permit decoration of fine, sodium filled cracks in sodium beta" alumina solid electrolytes.

Introduction

When ionic currents are passed through sodium-beta alumina, metal filled cracks may propagate from the cathodic to the anodic interface. Several authors have modeled the progression of this type of electrolyte failure. Armstrong and Turner et al.[1] first described the essential aspects of the degradation: pressures generated by sodium electrodeposited into the crack caused crack extension. This model was further developed by Richman and Tennenhouse,[2] and by Virkar et al.[3] Additional observations by De Jonghe et al.[4] demonstrated that the degradation propagated both trans- and intergranularly, and that the crack network could be highly branched.

Generally, a critical macroscopic electrode current density is found at which degradation initiates. Once initiated, the sodium filled crack network propagates readily through the electrolyte, as was pointed out by Brennan.[5] Therefore, the initiation stage is the most important one. The lateral dimensions of the flaws from which the degradation initiates are thought to be very small - on the order of the grain size or smaller. Local electrode current densities are thus expected to be of significance in the very early stages of degradation propagation. Both local electrode current densities and small sodium filled flaws are not readily observable. In this paper, we describe simple decoration methods that can qualitatively reveal local electrode current densities and permit decoration of small sodium filled cracks. Two techniques were found to be useful: an electrolytic decoration and a chemical decoration.

Electrodeposition

When a metal salt is electrolyzed into beta alumina in the presence of small amounts of water, H_3O^+ will be partly inserted to replace Na^+. The OH^- that is thus produced at the anolyte/beta" alumina interface can, at sufficiently high electrode potentials, reduce the metal ions. For $AgNO_3$ solutions, the following reactions are thought to occur.

$$2H_2O \rightarrow H_3O^+ + OH^-$$

$$Ag^+ + 2OH^- \rightarrow Ag^o\downarrow + H_2O + 1/2\ O_2 + 2e^-$$

The silver metal deposits on the anolyte/solid electrolyte interface.

At sufficiently short times it is expected that the sample interelectrode resistance rather than electrode polarization phenomena determine the local electrode rates. The electrolyte polarization phenomena due to grain boundaries have average relaxation times in the MegaHertz range, while the electrode processes have relaxation times of several seconds. For reaction times of about 1 second, it is then expected that the amount of deposited silver will be roughly proportional to the local electrode current density of a sample with identical structure but with reversible electrodes. It is also expected, since the electrolyte is a passive ohmic system, that current distributions would be similar for reversible anolyte/electrolyte and for catholyte/electrolyte interfaces.

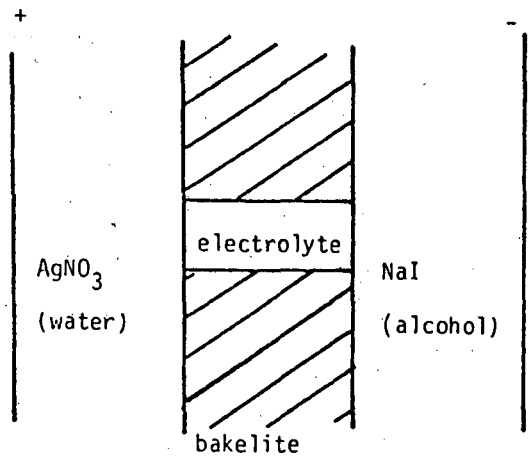

FIG. 1 XBL 801 7600

Experimental setup for electrodeposition of silver.

The experimental set up is sketched in Figure 1. The conditions for obtaining optimum contrast between low and high current density areas were, at room temperature, found to be rather critical. Electrolysis times were about one second and applied electrode potentials were about 18 to 20 volts.

An example of a decorated anodic electrolyte surface is shown in Figure 2. The areas of high silver deposit appear bright in this reflection optical micrograph. A large circular grain appears dark as would be expected, since its conduction planes are approximately parallel to the surface. This leads to local current blocking. Interestingly, grains which are oriented for favorable ionic current injection do not show a uniform current distribution. Apparently different parts of the same grain can carry different current densities. This phenomena is probably caused by microstructural differences, such as soda content or syntactic beta-beta" phases, within one grain. The magnitude of the electrode current density inhomogeneities were difficult to assess quantitatively. Scanning electron microscopy and energy dispersive x-ray analysis of decorated samples showed that the amount of silver in low and high deposition areas differed by a factor of 2 to 3.

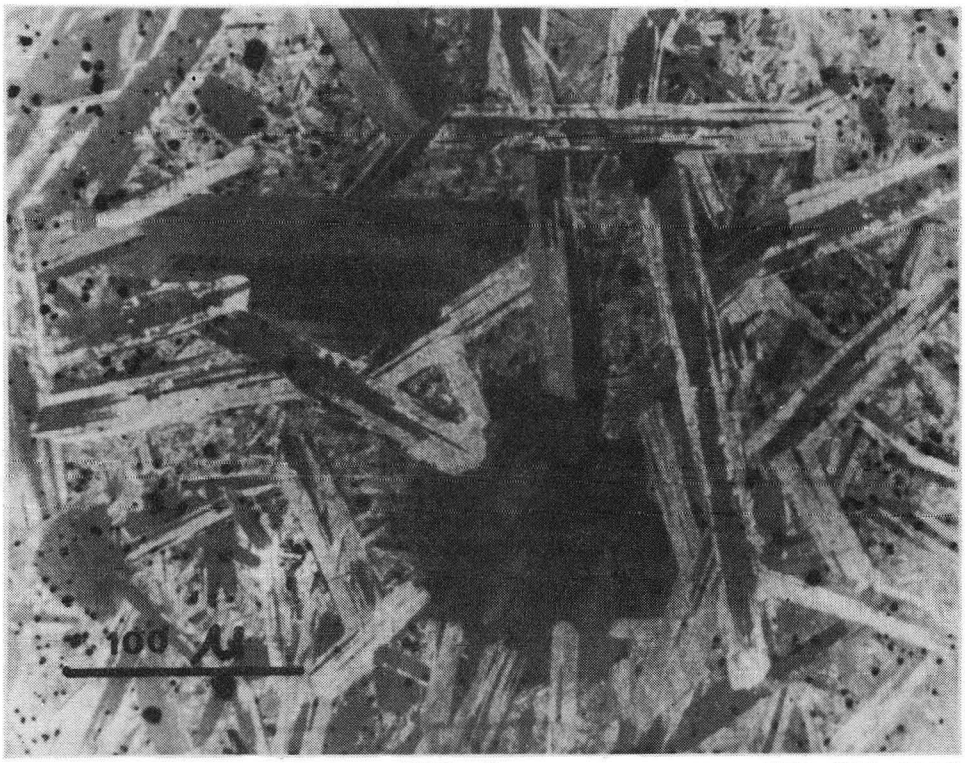

FIG. 2 XBB 794 4263

Anodic interface of sodium-beta" alumina decorated by silver electrodeposition. Dark areas correspond to regions of low local electrode current densities.

The decoration experiments clearly demonstrated the heterogeneous nature of the beta" alumina electrode interface. Figure 2 also reveals that high/low current density boundaries are most frequently found where grain boundaries intersect the electrode/electrolyte interface. The general heterogeneity of the electrode current distribution may be seen as being in qualitative agreement with the non-homogeneity of the bulk current distribution as discussed by De Jonghe[6].

Chemical Decoration

The sodium crack network that has propagated through a degraded sample, appears optically very diffuse. The reason for it is that the polycrystalline electrolytes are translucent rather than transparent, and light scattering prevents a clear examination of the metal-filled cracks. Where the cracks intersect the surface, reaction with the atmosphere depletes the sodium locally, so that the optical surface detection of the cracks is difficult.

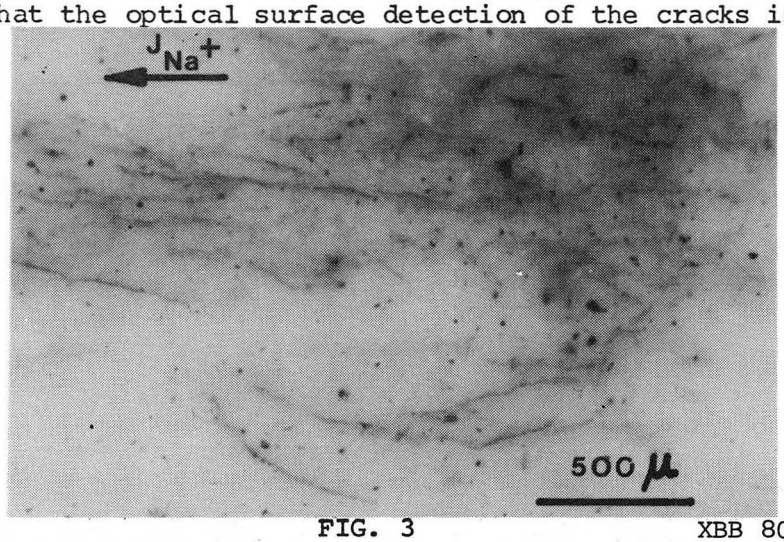

FIG. 3 XBB 801 45

Silver decorated cracks in degraded sodium-beta" alumina sample.

Crack openings are quite small and, as a result, regular dye penetrants seem to be ineffective. In our chemical decoration method, the polished and degraded samples are submerged for about 5 to 20 minutes in an aqueous, one molar solution of silver nitrate, kept at about 80°C. The cracks are then decorated with a dark deposit. Presumably, Ag^+ reacts with the NaOH that has formed in the fine cracks. When viewed with crossed polarizers to reduced surface reflection - the details of the crack network show up clearly. Figure 3 is an example of a decorated crack network in a section parallel to the direction of crack propagation. A multitude of fine cracks intersecting the surface is revealed, indicating again crack branching. Denser cracked clusters can also be observed in the same samples as shown in Figure 4a and 4b. Figure 4a shows a combination of single cracks and crack clusters as they emerge at the anodic interface.

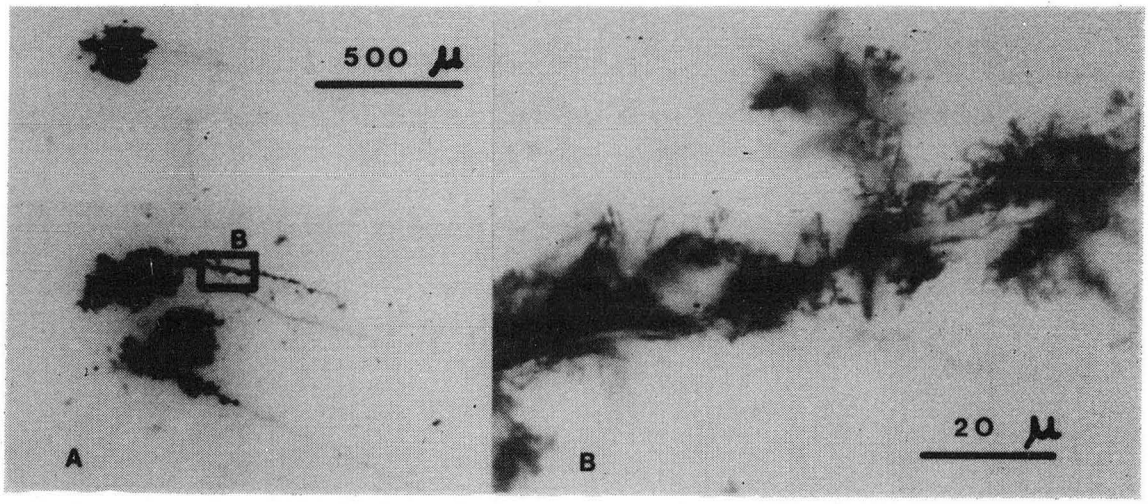

FIG. 4 XBB 801 44

Silver decorated cracks and crack clusters on anodic surface of a degraded electrolyte specimen.

The appearance of crack clusters can vary, as is evident from Figure 5. At this anodic interface, the cracked clusters were mainly along grain boundaries. Interestingly, degradation emerged in this case in a high porosity area. While there are some indications that the cracks prefer paths of high porosity, we have not found a conclusive relationship between pore distribution and degradation path.

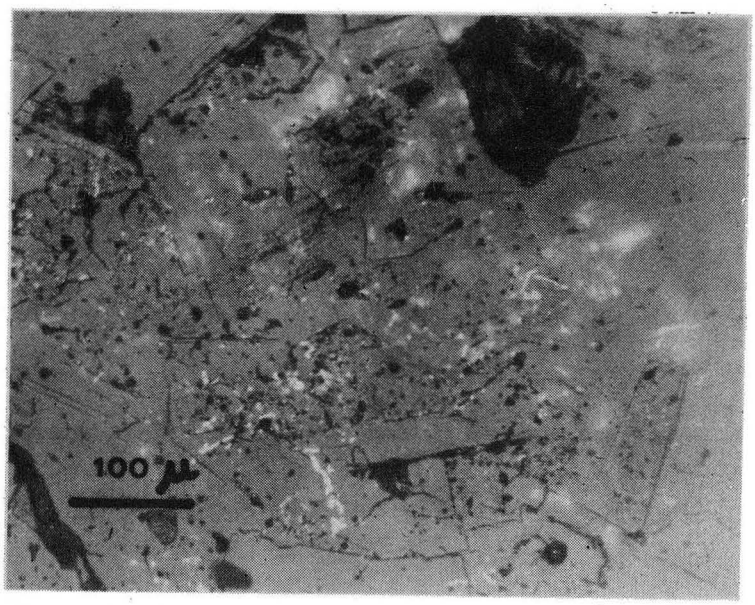

FIG. 5 XBB 801-46

Silver decorated crack cluster. The degradation has emerged in a high porosity area. Extensive cracking along grain boundaries is evident.

Acknowledgments

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