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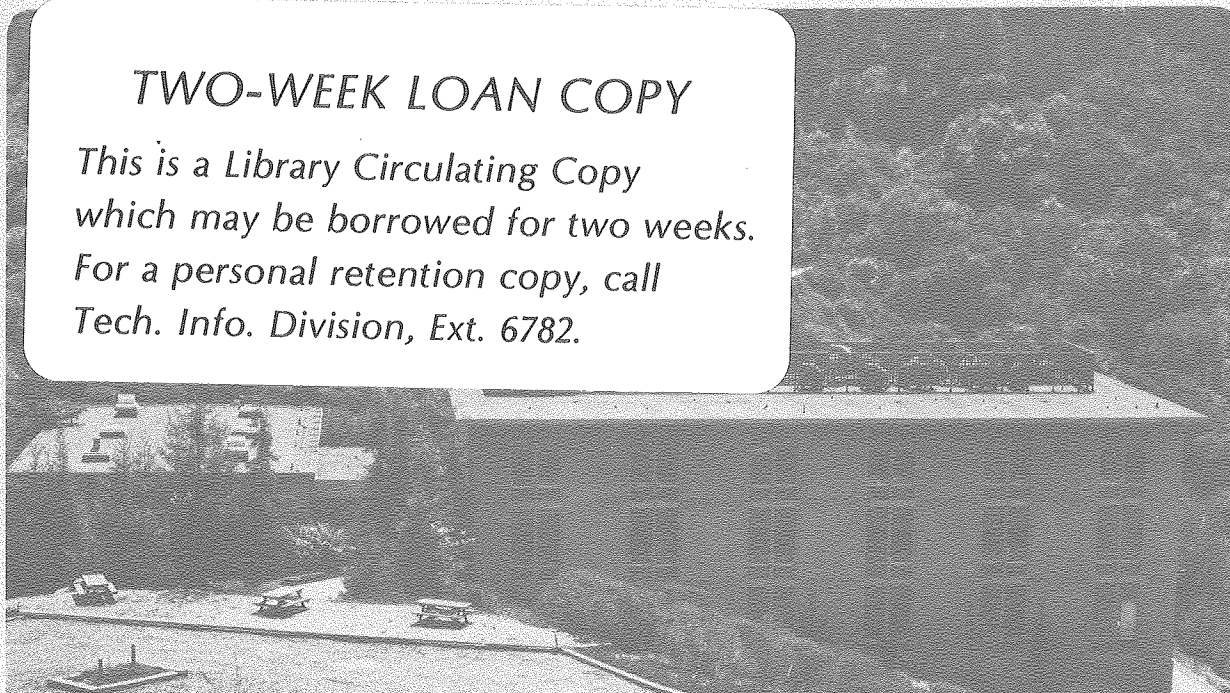
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SOME GEOMETRICAL ASPECTS OF BREAKDOWN OF SODIUM BETA ALUMINA

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ABSTRACT

The breakdown of single and polycrystalline sodium beta alumina was studied at 300°C and at room temperature. The breakdown in polycrystals involves a propagation of a highly-branched sodium-filled crack network. In single crystals the fracture surface could be studied directly. It was found that the crack network is filled with sodium from the crack faces rather than the crack tip.

Introduction

It has been reasonably well established that under certain conditions of current, temperature and electrolyte composition a breakdown can occur in sodium beta aluminas involving the penetration of metallic sodium into the bulk of the electrolyte.(1,2) This metal penetration and the crack-like features thought to be associated with it, has been modeled by several workers.(3,4)

In this paper we report on some breakdown experiments of sodium beta aluminas under a variety of conditions, involving Na metal penetration from the negative electrode.

Experiments

A variety of experiments were conducted, both at 300°C and at room temperature with blocking and with non-blocking electrodes.

In a first experiment an electrolyte was subjected to a high Na^+ current with Na^+ electrodes (NaNO_3 - NaNO_2 eutectic) at 300°C. The electrolyte was constricted in the center so as to give a high bulk current density, but a low electrode current density. The geometry of the sample is shown in Figure 1.

Other experiments involved the room temperature breakdown of single and polycrystals with blocking and non-blocking electrodes, as shown schematically in Figure 2.

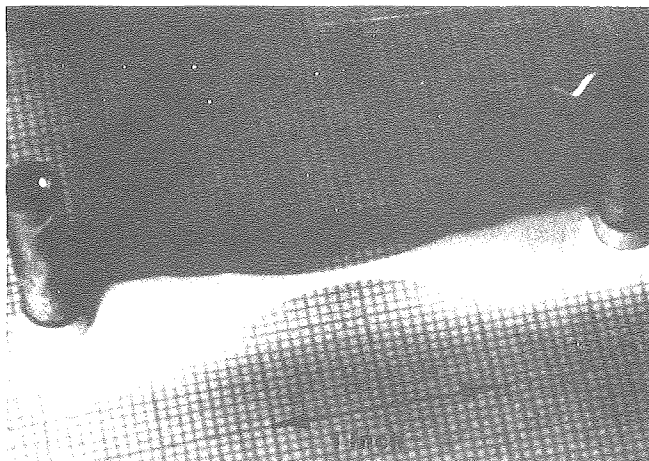


FIG. 1

Constricted electrolyte with Kovar sodium reservoirs for 300°C, D.C. breakdown experiments.

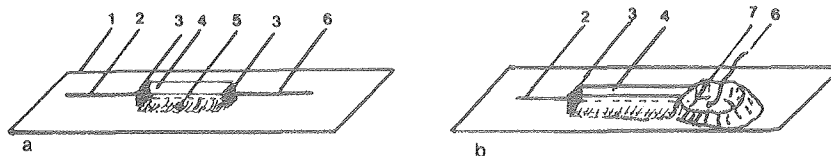


FIG. 2

Electrode arrangements for room temperature D.C. breakdown. a) 2 blocking electrodes (Au); b) negative electrode blocking, positive electrode non-blocking. 1: glass slide; 2: negative electrode lead; 3: Au blocking electrode; 4: electrolyte; 5: mounting glue; 6: positive electrode lead; 7: positive electrode reservoir for alcohol-Na I solution.

Results

1. 300°C constricted electrolyte, Na⁺ electrodes

Increasing currents were passed through samples as shown in Figure 1, until a blackening was seen to emerge rapidly from the negative electrode. Sectioning of the sample revealed that the blackening had started at a point where the Kovar reservoir was welded directly to the electrolyte, providing a Na⁺ blocking site with electron injection. The geometry of the breakdown shown in Figure 3 strongly suggests that the Na metal penetration is not readily described in terms of a single metal filled crack propagating through

the sample. Transmission electron microscopy was carried out of the blackened region as well as of the constricted sample center. In the blackened region features were found as shown in Figure 4.



FIG. 3

Geometry of the 300°C, D.C. breakdown after partial propagation. The degradation apparently initiated at the place where the Kovar reservoir welded to the electrolyte (arrow at lower right corner).

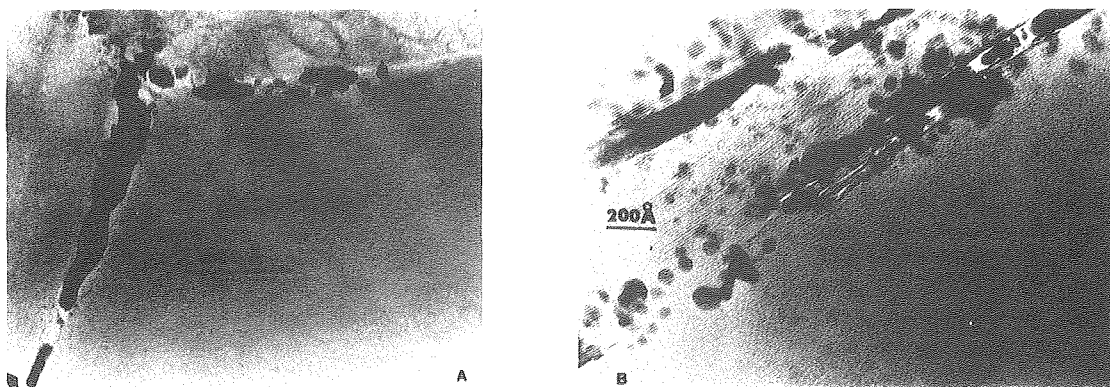


FIG. 4

Transmission electron microscope observations in regions blackened by degradation. The material indicated with arrows is sodium carbonate, resulting from the reaction of sodium metal with atmosphere. a) Intergranular breakdown; b) Transgranular breakdown along (00.1) planes. The fringes in this picture are the $11.3\text{\AA}$ 00.2 lattice fringes.

The material appearing dark and rather shapeless in these electron micrographs was identified as sodium carbonate. We attribute it to the reaction of the metallic sodium with the atmosphere upon thin foil preparation. The sodium carbonates can thus be conceived as "relics" of the metallic sodium that formed in the degradation process. Interestingly, both transgranular and intergranular degradation is observed. The transmission electron microscopy thus strongly suggests that the sodium filled crack morphology is a highly branched one in which the crack is deflected, as one would expect, by microstructural features. No other compounds, such as sodium aluminates or alumina were found to be associated with this degradation.

The center of the samples was also studied by means of transmission electron microscopy. No traces of breakdown were found, even for electrolytes that had withstood a local ion current density of about 10 amps for 1 hour. We thus feel that we can conclude that intrinsic degradation, i.e., decomposition away from electrodes when electron injection is absent, does not occur in beta aluminas.

2. Room temperature single crystal, blocking and non-blocking electrodes

Small single crystals, .1 cm x .1 cm x 1 cm were cleaved from a larger crystal. The cleavage plane is the conduction plane. Na metal formation was initiated with electrodes as shown in Figure 2. In configuration a breakdown occurred at about 700 V. In configuration b breakdown occurred at about 40 V. The geometry of the metal formation was very similar in both cases. In case a, an electrode depletive situation, the breakdown did not progress after an initial burst, unless the voltage was raised further. In case b, a supply situation, the breakdown progressed rapidly at constant voltage until the metal was seen to reach the supply electrode (+). At the same time, the metallic sodium slowly seeped out of the crystal reacting with the ambient air and moisture.

The geometry of the metal formation is clearly shown in Figure 5. The formed metal is highly reflective, permitting direct interferometric study of the cleavage plane. Also, evaporation of some gold on one of the cleaved faces of the crystal permitted to find the approximate metal filled crack opening, assuming the crack opening was symmetrical with respect to the cleavage plane. The results of these examinations are shown in Figures 6a and 6b for the breakdown produced with blocking electrodes (Figure 2a).

It is clear that depleting of a single conducting plane cannot provide sufficient sodium to fill the crack. Therefore, the crack must be fed from the steps, or rivermarks that intersect many conduction planes. Since the crack propagation mode and morphology is identical in the configuration where the positive electrode is supplying Na^+ , it is thought that in all cases the crack steps play an important role as sites where Na is fed into the crack. The observations suggest that in modeling beta alumina breakdown progression, one cannot simply assume that the crack is only tip fed. This introduces another difficulty in the modeling of sodium filled crack propagation due to current passage in sodium beta alumina.

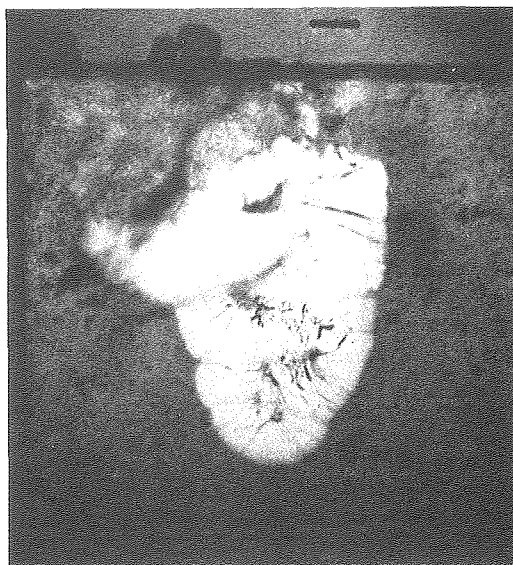


FIG. 5

Sodium metal formed at negative electrode in D.C. breakdown of a sodium beta alumina single crystal. The sodium metal at the top of the picture has reacted with atmospheric oxygen and moisture.

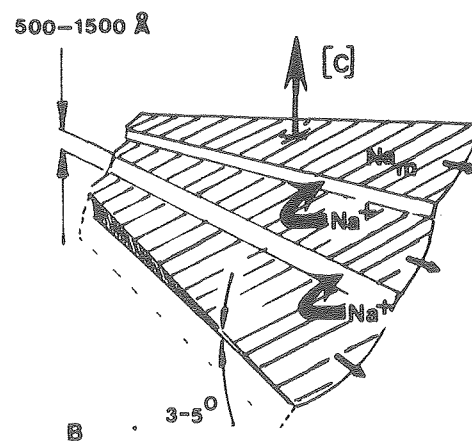


FIG. 6

Geometry of the sodium filled crack. a) Interferometer observation, b) geometry derived from the interferometry.

3. Room temperature polycrystals, blocking, non-blocking electrodes

For polycrystals only electrode configurations were used as described in Figure 2b. For most electrolytes breakdown occurred at 40 to 80 V. An attempt was made to determine the rate of propagation of the blackening. It was found that a constant macroscopic current density, the rate of propagation of the degradation was approximately constant. Definitely no increased rate with increased degradation length was observed under these conditions. An interesting feature of this breakdown experiment is that the electrolytes start showing many surface cracks that accompany the darkening (Na propagation). Na metal seeps out of these cracks and reacts with the ambient. Figures 7a and b compare the polycrystalline surface in the breakdown region near the negative electrode and the unaffected region near the positive electrode. The difference is obvious. This phenomena again points to the highly branched nature of the metal filled crack.

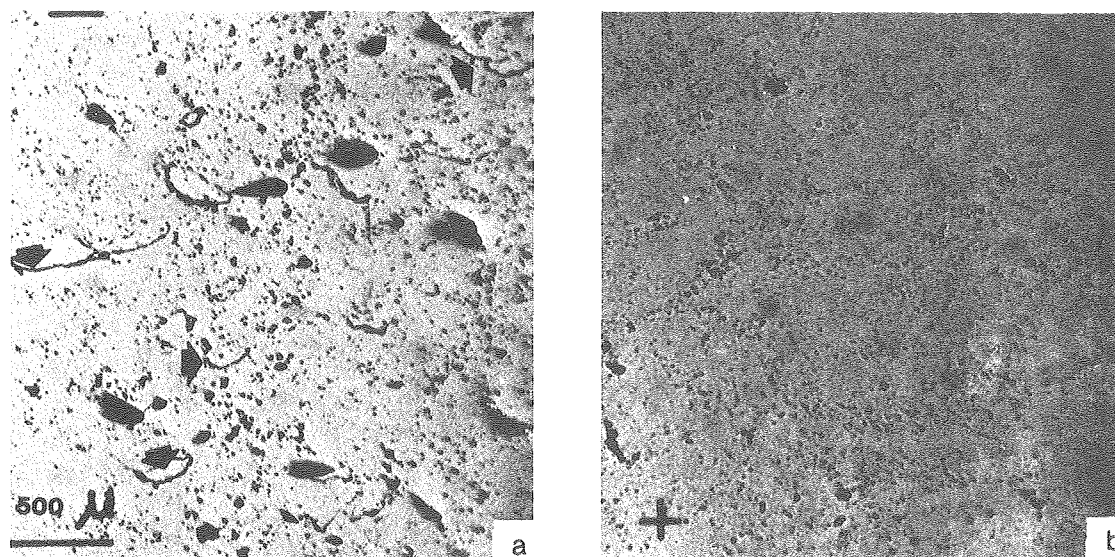


FIG. 7

Surface cracks (arrowed) developing in association with the breakdown propagation. a) Blackened region near negative electrode, b) unaffected region near positive electrode.

Conclusions

The experiments reported here confirm directly the now generally accepted view that sodium metal penetration is associated with beta alumina solid electrolyte breakdown. They also illustrate the complex geometrical aspects of crack morphology. These complexities should be taken into consideration when modeling of degradation is attempted.

The degradation was clearly shown to be originating at the electrodes when electron injection is possible. Direct bulk breakdown does not occur below at least 10 Amp. cm⁻².

The geometrical examination of breakdown in single crystals revealed that the crack is not simply tip fed.

The propagation of the degradation at room temperature (solid Na metal) was observed to proceed at an approximately constant velocity at constant current density.

Further experiments of the type described in this paper are being conducted. In particular, breakdown behavior of different electrolytes, and breakdown above the melting point of sodium are under way and will be reported later.

Acknowledgements

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