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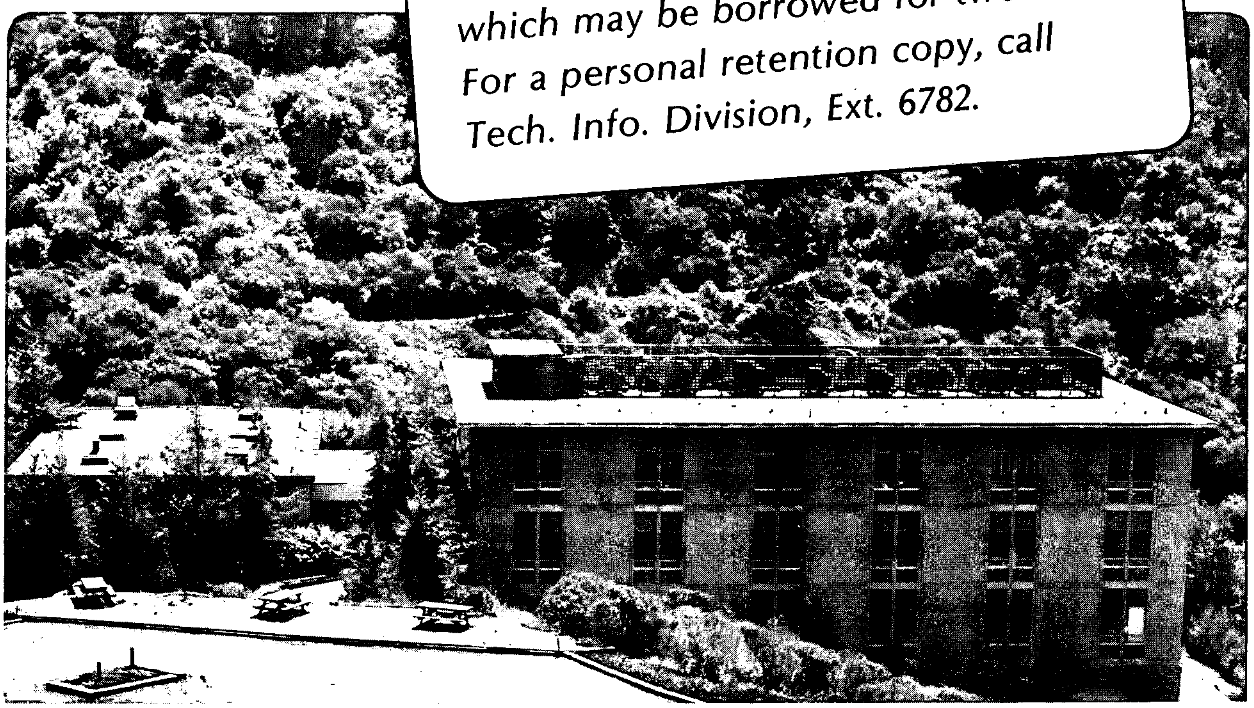

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Abstract

The fracture toughness anisotropy has been determined for sodium-beta alumina single crystals, using a hardness indent method. For cracks with a habit plane normal to the 00.1 planes the fracture toughness is about 2 $MPa.m^{1/2}$, while for cracks running parallel to the 00.1 planes the fracture toughness is about 0.16 $MPA.m^{1/2}$. This extreme anisotropy may partly explain the difference between calculated and observed critical current densities for Mode I failure initiation of polycrystalline solid electrolytes.

I. Introdution

When sodium-beta and beta" alumina are used as solid electrolytes in a Na/S battery, fracture may be initiated from the electrolyte surface at which metal is formed at a sufficiently high ionic charging current density. This current density is called the critical current density. Buechele et al. (1), using acoustic emission detection methods, reported recently that first crack initiation events occured at an average current density of about 300 mA/cm^2. This value is significantly below the current densities at which rapid, macroscopic crack propagation, Mode I failure (2,3), is usually observed for similar electrolytes. (4) Theoretical considerations of the critical current densities for Mode I failure initiation predict that the critical current density, j_{crit}, is related to the fracture thoughness, K_c, by:

$$j_{crit} = A\, K_c^4 . L^{-n} \tag{1}$$

where n is a parameter that ranges between 1 and 3 depending on the way in which the elastic relaxation is taken into account and on the details of the crack geometry selected for the model (5,6). For reasonable flaw lengths, using the fracture toughness measured on polycrystalline electrolytes by macroscopic fracture mechanics methods (7), the calculated j_{crit} is found to be several orders of magnitude above the observed one. However, for materials that are as anisotropic as the beta aluminas macroscopic fracture toughness should not be used when flaws are on the order of the grain size. In the early stage of growth small cracks should advance through regions of low critical stress intensity, with the fracture toughness rising to the value appropriate for macroscopic fracture mechanics as the crack gets larger.

For sodium-beta and beta" aluminas features are known that have very low strength. The layered crystals cleave easily along the 00.1 conduction planes and may show spontaneous fractures when left in ambient moist air. Grain boundaries with 00.1 habit planes are also known to be mechanically weak (8). Since 00.1 cleavage is most likely to be involved in the initial crack configuration and growth, it is necessary to determine the K_c anisotropy. The microhardness indenter fracture toughness method (9,10,11) had to be used since only small crystals were available.

II. Experimental Procedures

A single crystal of sodium-beta alumina* and polycrystalline sodium-beta" alumina** were heated for 24 hours, at 900°C, in beta alumina packing powder, prior to mechanical polishing. This polishing is necessary to allow an accurate measurement of crack length after indentation. The 00.1 cleavage surface of the single crystals was smooth and needed no further preparation. The prismatic planes of the single crystals could only tolerate a minimum of preparation since, however carefully the sanding and polishing was performed, some 00.1 cleavage cracks would result. The few cracks that were produced did not interfere with the measurements, since indents could be made on unflawed

*Union Carbide, Linde Division, San Diego, California. Composition: 6.4 w Na_2O, balance, Al_2O_3.

**Ceramatec, Inc., Salt Lake City, Utah. Composition: 8.7 w Na_2O, 0.75 w Li_2O, balance Al_2O_3. Average grain size: 1.1 micron.

prismatic plane segments, and the crystals could be viewed in transmitted light. After surface preparation, the samples were annealed in packing power of the appropriate Al_2O_3/Na_2O composition, for 3 hr, in air, at 1500°C. This treatment heals many cracks, and roughly corresponds to a sintering cycle. The polycrystals showed considerable thermal etching, but the indent cracks would still be measured with accuracy under oblique illumination in the optical microscope. Indentations were made with a Vickers hardness indenter, with loads between 19.6 and 49.0 N. During the indentation the surfaces were covered with immersion oil to prevent possible crack extension due to ambient moisture. After indentation the immersion oil was removed with acetone, and the crack dimension were measured immediately.

III. Results and Discussions

The expression used to calculate K_c was (9):

$$S = K_c \, (H/E)^{1/2}/(P/c^{3/2}) = 0.016 \pm 0.004 \qquad (2)$$

where S is a materials-independent constant for radial cracks produced by a Vickers diamond indenter, H is the hardness, E is Young's modulus, P is the load on the indenter, and c is the measured length of the radial cracks. The Young's modulus for polycrystalline sodium-beta" alumina is reported to be about 200 GPa (7). For indentation fractures in elastically anisotropic crystals the modulus E used in Equation (2) should be that for the direction perpendicular to the crack habit plane, provided the indenter axes were aligned with the principal axis of the elasticity tensor. Measurements of the elastic anisotropy were not available, but a fairly good estimate can be made from the shape of Knoop indents. The various values of H/E, H, and E found from measurements of Knoop indent shapes are listed in Table I for indents made on prismatic planes of single crystals. It was interesting to note that the hardness, H, measured by the Vicker's indenter method normal to the basal planes, varied as a function of applied load, P, according to:

$$H = 13.5(\text{in GPa}) - 3.37\text{x}10^{-5}\ (\text{in GPa/N}^3)\text{x}\ P(\text{in N})^{\ 3} +/- 0.1\ (\text{in GPa}).$$

The reason for this is not known. The ratio, E1/E2, of the elastic moduli parallel, E1, and perpendicular, E2, to the 00.1 direction was about 1.23. The fracture toughness values were then determined from the measurements of the Vickers indenter cracks and from the values for E1 and E2 listed in Table I. They are given in Table II. An example of an indent on a prismatic plane is shown in Fig. 1. The extreme fracture toughness anisotropy is immediately evident in this micrograph. Note also that the crack running in the 00.1 direction exhibits some crack branching. The values of K_c for the indents made on 00.1 planes and on polycrystals agree well with the values for the polycrystals measured by macroscopic fracture mechanics methods (7). The K_c for cracks in the 00.1 planes are a factor of ten lower than these values. When these 00.1 crack values are inserted into the expression describing initial Mode I crack growth (5,6) values for the critical current densities for failure initiation are obtained that agree reasonably well with those reported by Buechele et al. (1).

It is therefore concluded that Mode I crack initiation in sodium-beta and -beta" aluminas can occur well below the average values observed for rapid, catastrophic electrolyte failure.

Acknowledgements

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Tables

TABLE I

Indent On	H/E	H(GPa)	E(GPa)
Basal plane	0.0632	13.59	215
Prismatic plane	0.0465	8.1	174

TABLE II

Material	Indent on	$K_c(MPa.m^{1/2})$	Standard Deviation
Beta single cr.	prism. plane	0.162	0.067
	basal plane	1.973	0.232
Beta" polycr.	—	1.984	0.226

Figure Caption

Fig. 1. Fractures resulting from a Vickers indent on a prismatic plane of a sodium beta-alumina single crystal. The load on the indenter was 9.8 N.

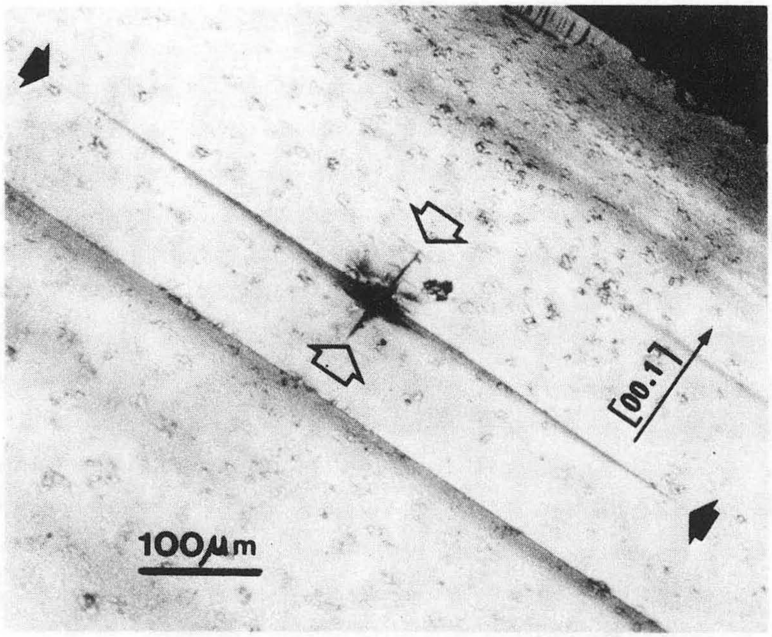

Figure 1

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