important feature of the present paper is that it has demonstrated that a simple technique such as indentation can be effective in determining both the plastic flow properties of a material (from the hardness value) and the fracture surface energy. This is particularly useful with explosive materials where samples cannot conveniently be obtained for more conventional fracture mechanics tests.

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The dependence of the fracture stress of beta-alumina on microstructural defects

The use of sodium beta-alumina as a solid electrolyte and separator in the sodium–sulphur battery is now well established [1–5]. The majority of cell designs use polycrystalline beta-alumina in the form of a thin-walled tube although flat plate designs have been considered [6, 7]. In either case, the electrolyte contributes substantially to the overall cell impedance and in order to minimize this, the electrolyte should be a thin membrane with a low intrinsic ionic resistivity. At the same time, the membrane must have adequate mechanical strength to allow construction and operation of the cell without premature ceramic failure.

The fracture strength, σ_f, of ceramic materials is largely governed by the stress necessary to propagate small microstructural flaws according to the familiar Griffith relationship,

$$\sigma_f = (2E\gamma_i/\pi c)^{1/2} \quad (1)$$

where γ_i is the fracture initiation energy, c is half the length of an elliptical flaw and E is Young's modulus. Experimental data on the tensile strength of ceramics in short-term tests can be conveniently analysed statistically using Weibull's weakest link concept [8]. The probability of survival, P, is given by,

$$P = \exp[-D(\sigma_f - \sigma_u/\sigma_0)^m], \quad (2)$$

where D is the stressed volume, σ_u the zero probability stress, σ_0 a normalizing constant and m the Weibull modulus. Consequently,

$$\ln \ln 1/P = m \ln(\sigma_f - \sigma_u) - m \ln \sigma_0 + \ln D, \quad (3)$$

and so a plot of $\ln \ln 1/P$ against $\ln \sigma_f$ with σ_0 set equal to zero yields a straight line with a slope equal to the Weibull modulus. In this note we report strength measurements of beta-alumina with two extremes of sample size and describe a preliminary study of the types of microstructural defect responsible for weakening the material.

The beta-alumina used in this work was prepared as closed-ended tubes by direct mixing of the constituent oxide powders together with small amounts of Li_2O and MgO to promote the formation of the more conductive β''-phase. Green shapes with uniform density and close dimensional tolerances were prepared by isostatic pressing and these were rapidly sintered at temperatures between

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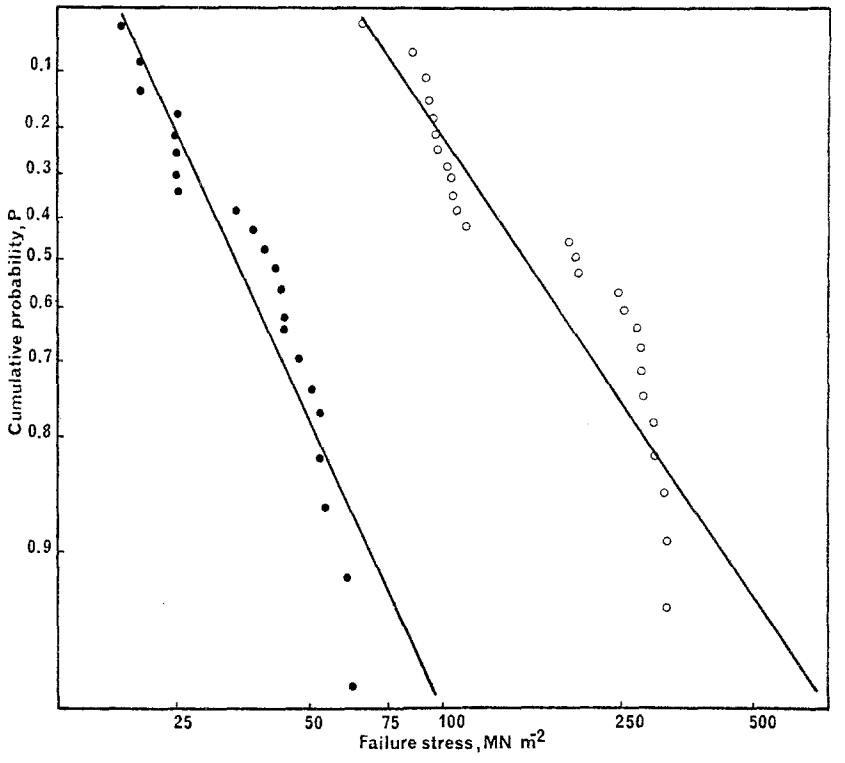

Figure 1 Cumulative probability of failure, P, of beta-alumina tubes (•) and small rings (○). The tubes were tested by internal pressurization and the small rings by diametral compression.

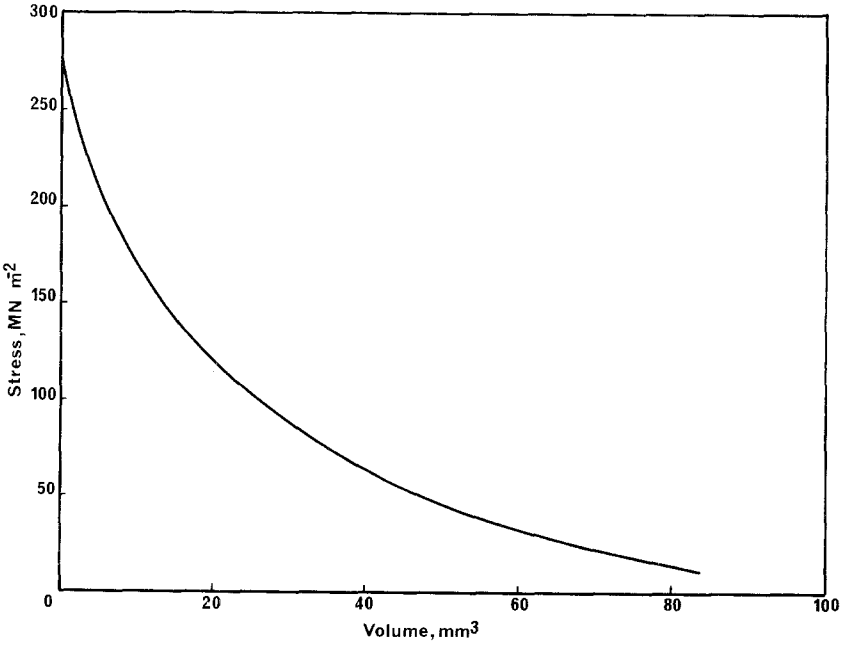

Figure 2 Stressed volume in beta-alumina rings under diametral compression calculated by finite element stress analysis. Rings 10 mm long, 26 mm o.d. 1.5 mm wall thickness, 35 N load.

1800 and 2100 K in a pass-through furnace. The tensile strength (hoop strength) of whole tubes which had an external diameter of 26 mm, a wall thickness of 1.5 mm and a length of 200 mm was measured by internal pressurization using hydraulic oil. The tensile strength of small rings 10 mm long slit from the tubes was measured by compressing the rings in an Instron testing machine with a cross-head speed of 0.5 mm min^{-1}. Thin lead shims were placed between the sample and the loading platens to avoid loading at asperities. Surface damage from cutting the rings with a diamond slitting wheel was shown not to cause significant weakening by measuring the strength of a group of control samples whose cut faces had been finished uniformly with 6 μm diamond paste. The fracture stress was calculated using the approximations of thin walled elasticity theory and due allowance made for any eccentricity in the rings [9].

The measured fracture strengths of the two groups are shown in Fig. 1. The stressed volume of the tubes is $\sim 2.3 \times 10^5$ mm^3 whereas the stressed volume of the small rings falls very rapidly to the fracture stress as shown in Fig. 2. For example, in a ring loaded to produce a peak stress of 280 MN m^{-2}, the volume in excess of half of the peak stress is only 15 mm^3. The displacement of the two sets of data in Fig. 1 is clearly the result of the difference in stressed volume in a material with a random distribution of microstructural defects. A number of rings with discrete defects were tested with the defect at the point of maximum stress and the effect of defect size on strength is shown in Fig. 3. There is a straight line relationship showing cracks in beta-alumina behave as Griffith cracks and a value of γ_i of ~ 24 J m^{-2} was calculated in the Griffith Equation 1 using a value of 2.1×10^{11} N m^{-2} for Young's modulus. This allows an approximate value for the critical stress intensity factor, $K_{IC} = (2E\gamma_i)^{1/2}$, of 3.2 MN $m^{-3/2}$ to be calculated, in reasonable agreement with other reported values [10].

Defects were characterized by direct examination in the scanning electron microscope coupled with energy-dispersive analysis of X-rays (EDAX). The majority took the form of small pores with various associated impurities although some small cracks were also present. The most numerous type of defect were areas of high porosity, typically

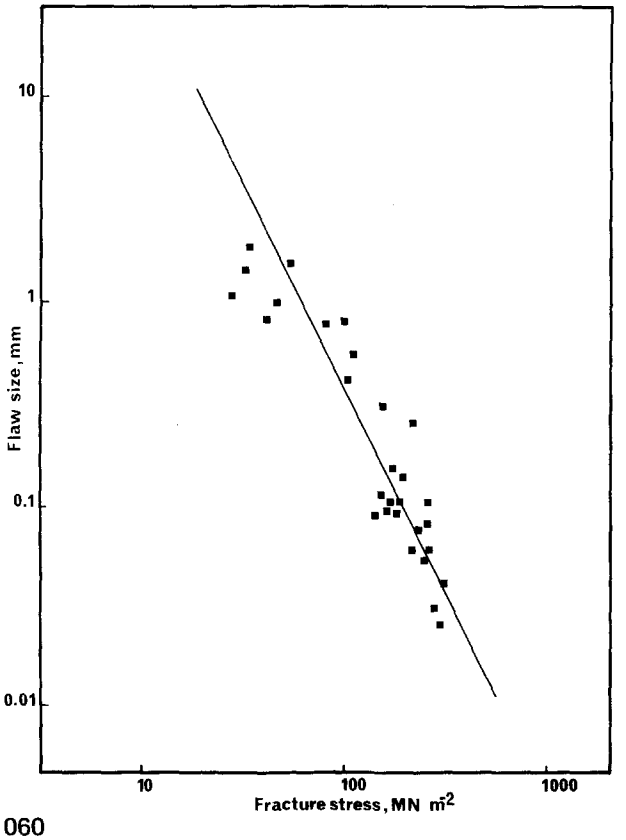

Figure 3 Fracture strength of beta-alumina samples as a function of defect size.

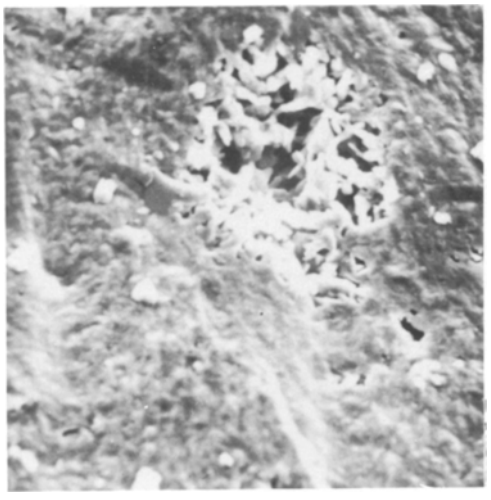

Figure 4 Defect containing small beta-alumina crystals on fracture surface. SEM, × 280.

250 μm in size, containing well-developed crystallites of beta-alumina. There were either discrete pores as in Fig. 4 or localized groups of smaller pores. They showed slightly higher Na contents and are evidently the result of local inhomogenities in the powder. Another group of defects were either rounded or somewhat elongated and contained bubbled, glassy material that appeared to be a solidified liquid phase (Fig. 5). Some of these were white with no detectable impurities but others were blue in colour and showed EDAX peaks characteristic of Ni and Fe. Brown or black defects were also observed and contained fairly large, well-developed crystallites rich in Co, Ni and Fe. Defects in beta-alumina result from local inhomogenities in the precursor powder and from the incorporation of impurities in the powder. It is doubly important to eliminate defects from beta-alumina, not only because they weaken the ceramic but also because they may contribute to the failure of the solid electrolyte during cell operation by causing inhomogeneous ionic transport.

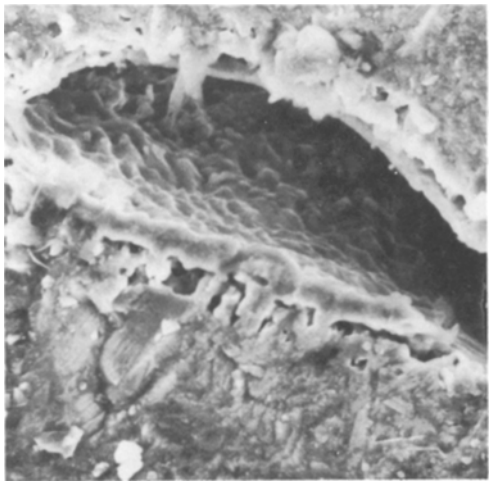

Figure 5 Blue coloured defect with Ni and Fe impurities and solidified, glassy material on the inner surface of the defect. SEM, × 640.

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