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Auger spectroscopy of grain boundaries in calcium-doped sodium beta-alumina

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Air- and vacuum-fractured samples of calcium-doped beta-alumina have been examined using Auger electron spectroscopy. The calcium concentrations at grain boundaries were found to be enhanced over the bulk value by about a factor of 10. Excess sodium was observed on the fracture surface of air fractured electrolytes, and was absent for samples fractured in ultra-high vacuum. Temperature-dependent features in the secondary electron spectrum and the effects of surface charging and radiation damage by the incident electron beam were also observed.

1. Introduction

Sodium beta-alumina type ceramics exhibit an unusually high ionic conductivity and a very low electronic conductivity, making them suitable as solid electrolyte membranes in the Na/S high energy density battery, and as a chemical transducer [1–3]. For battery applications, the ionic conductivity, the purity, and the strength are important factors determining the lifetime of the ceramic [4]. At Cornell we are particulary interested in the effect of impurities and substructure on the properties of this solid electrolyte. Detrimental increases in ionic resistivity due to increase in grain-boundary resistivity can be observed when Ca is present, even in concentrations well below 1 wt% CaO [5]. We will report this work in more detail later. In this paper we report on the observation of the accumulation of calcium at grain boundaries in sodium beta-alumina by means of Auger spectroscopy.

2. Experimental

Samples were prepared by die pressing and sintering of Ca-doped sodium beta-alumina powder*. The sintering was carried out under argon. The heating and cooling rates were rapid: ~100° C min^{-1}; to minimize the sodium loss, the samples were packed in sodium beta-alumina powder. Sintering temperatures and times were ~1720 to 1750° C and 30 to 90 min, and the final density was around 3.15 g cm^{-3} (~95 to 98% theoretical).

The doping was achieved by introducing the Ca as measured amounts of $Ca(NO_3)_2$ into the beta-alumina powder prior to sintering. This method of introducing the Ca impurity can be compared to pick-up of impurities by the powder during preparation steps prior to final firing. At elevated temperatures the $Ca(NO_3)_2$ will then decompose to CaO before it has reacted significantly with the beta-alumina matrix, since the heating rates are fast. At the sintering temperature (~1720° C) reaction between the intergranular CaO and the matrix will take place, either by forming a grain-boundary phase (e.g. a calcium aluminate), or by accommodation in the beta-alumina crystals.

Ca/Al ratios of up to 1.1×10^{-2} (~1 wt% CaO) were studied. It was observed that at the higher calcia doping levels the fracture mode shifted from mainly transgranular to intergranular with a simultaneous significant decrease in the fracture strength (four-point bending). This in itself is already an indication that Ca strongly affects the grain boundaries when introduced as described here. The fracture surface of such an intergranularly fractured specimen with $Ca/Al = 1.1 \times 10^{-2}$ is shown in Fig. 1. This phenomenon allows the direct examination of grain boundaries by means of Auger spectroscopy when the calcia content is

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*Alcoa XB-2 "superground".

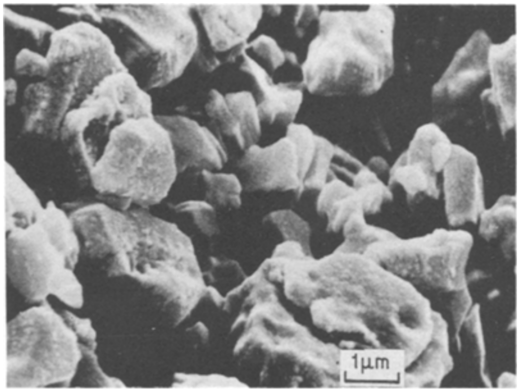

Figure 1 Fracture surface of Ca-doped sodium beta-alumina sample with $Ca/Al = 1.1 \times 10^{-2}$. The fracture mode is intergranular exposing the grain boundaries.

high and specimens are prepared as indicated (rapid firing technique). We note that at lower concentrations Auger spectroscopy is not suitable for grain-boundary examination since the fracture surface does not preferentially expose grain boundaries.

The sintered samples, in the form of bars 0.2 cm x 0.5 cm x 2 cm, were gold plated to improve the electrical contact with the Auger spectrometer sample holder. A sample holder which allows fracturing *in situ* (described elesewhere [6]) was used to fracture the samples. The Auger spectroscope detector was a four-grid retarding field analyser operated to electronically detect the first derivative of the secondary electron spectrum. The incident electron energies were between 1 and 4 keV, and the current density was about $3\,\mu A\,mm^{-2}$. A modulation of 20 V peak-to-peak at 1440 Hz was used.

Fig. 2a shows the first derivative of the secondary electron intensity as a function of energy. The spectrum was obtained within 10 min after fracture in vacuum ($p < 5 \times 10^{-8}$ Pa). The transitions due to Auger processes are identified in Fig. 2. Exposure to the electron beam caused a dark-brown spot about the size of the beam to develop in about 20 min at room temperature; no changes in the Auger spectrum were observed. This discoloration could be completely removed by annealing the sample at 800 K *in situ,* but it reappeared with room-temperature electron bombardment.

The secondary electron emission coefficient was found to be greater than 1 for the primary electron beam energies used here. Thus, more electrons leave the surface than are incident upon it causing a positive potential to develop at the surface. Two effects result from this surface potential. First, the highly mobile sodium ions diffuse away from the surface region [8, 9]. This is a dynamic process which depends on the energy and current density of the primary beam, on the sample temperature, and on diffusion rate of the sodium ions since these factors determine the rate of charge build-up on the surface. We believe that the electron beam-induced discoloration may be due to the formation of sub-surface colloidal metallic sodium. Second, energy levels near the surface are shifted by the charge accumulation on the surface. This results in a uniform shift of the Auger peaks to lower energies; for example, the energy of the oxygen KLL Auger signal shifted to about 500 eV for 1 keV primary electrons, and to about 507 eV for 4 keV electrons. Similar shifts have been reported previously [8, 9].

Auger peaks due to carbon (260 eV), calcium (284 eV), oxygen (502 eV) and aluminium (1385 eV) are present as shown in Fig. 2a, with relative peak-to-peak heights of 4:8:100:9 respectively. (The carbon signal decreased with continued exposure to the electron beam and will not be considered further here.) Using the inverse sensitivity factors based on the theory of Chang [7], published spectra [10] and tables [7], the average atomic ratios in the region sampled by the Auger electrons can be calculated. Because of surface roughness, and because these inverse sensitivity factors were derived for cylindrical mirror detectors rather than the four-grid retarding field analyser, only approximate values of the atomic concentrations can be derived from the measurements reported here. The resulting average atomic ratios are

$$O:Al:Ca = 100:60(\pm 15):9(\pm 2).$$

These ratios are to be compared to the ratios calculated from the bulk composition of the sample assuming uniform Ca distribution: 100:63:0.7. It can be concluded that the calcium concentration in the surface region is enhanced over the bulk value by a factor of about 10. Based on published electron attenuation data [11], the thickness of the surface layer sampled by the Auger electrons is less than 20 Å. Removal of a thin surface layer by sputtering of the surface with 400 eV argon ions can establish whether the excess calcium is concentrated near the fracture surface.

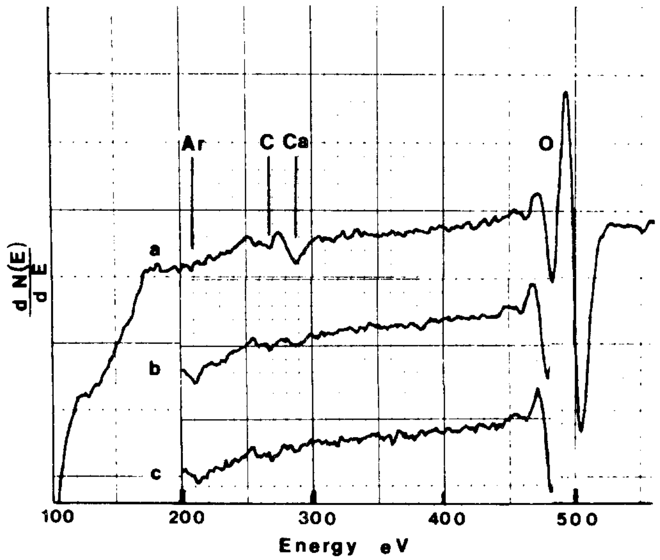

Figure 2 Auger spectra of vacuum fractured beta-alumina (a) immediately after fracture in vacuum; (b) after 3 h bombardment with 400 eV argon ions at 2.5 A cm^{-2}, but before all calcium has been removed; (c) after removal of calcium and with the sample at 800 K. The experimental parameters are described in the text.

Only the total sputtering ion current to the sample and holder could be measured. The sample surface comprised about a 0.02 fraction of the area presented to the ion beam. Assuming that this fraction is equal to the fraction of the ion current incident on the sample surface, we find that about 4×10^{15} ions were required to reduce the calcium signal below detectability while no change was observed in the oxygen and aluminium Auger signals. At 400 eV, the sputtering yield of each of the elements making up the sample is less than one [12], so that at most 200 Å of material were removed. Thus, the calcium was concentrated at the fracture surface. This finding is in agreement with the a.c. conductivity measurements [5], and supports the conclusion that calcium lowers the ionic conductivity by concentrating in the grain boundaries as a low ionic conductivity phase.

On the basis of the inverse sensitivity factor [7], the bulk sodium level was expected to be below the detectability of the present experiment; indeed, sodium was never detected on the vacuum fractured surfaces, even when the fracture was done at liquid N_2 temperature to reduce sodium mobility. However, sodium was observed on the air-fractured surface, and its concentration varied by more than a factor of 5 at different points on the surface, while its Auger signal decreased with exposure to the electron beam as reported by others [8, 9]. The enhanced surface concentration of sodium for air-fractured specimens may thus be due to the interaction of the highly mobile ions with oxygen or water vapour to form a surface oxide or hydroxide.

Additional features in the secondary electron spectra shown in Fig. 2 and b were observed at about 125, 160 and 190 eV on all four surfaces studied which cannot be identified with the Auger transitions of any elements. Their derivative peaks are larger on the low-energy side in contrast to most Auger peaks whose low-energy portions are reduced due to characteristic energy-loss processes. In addition, the intensities of these peaks decreased exponentially with increasing temperature such that they could no longer be distinguished when the sample temperature approached 800 K as shown in Fig. 2c. The Debye–Waller factor describing this decrease was about $\exp(-4 \times 10^{-3}\, T)$ for the feature near 190 eV. Similar temperature-dependent structures have been observed for nickel [13], copper [14], chromium [14] and zinc oxide [15]. For nickel and copper these structures have been correlated with features in the extended X-ray adsorption fine structure which has been shown to depend upon the detailed local atomic environment [16]. Thus, an analysis of these features using the multiple-scattering formalism developed to describe low-energy electron diffraction [17, 18] should provide useful information about the detailed atomic environment near the surface.

3. Conclusions

(1) Calcium is present at grain boundaries of Ca-doped sodium beta-alumina in a grain-boundary region with a thickness of less than 200 Å.

(2) Anomalously high Na surface concentrations are observed on air-fractured samples. This

is due to reaction of the sodium beta-alumina with the ambient atmosphere. No such effects are observed for fractured surfaces produced in ultra-high vacuum.

(3) Evidence of positive surface charging during Auger observations is seen in the surface discoloration of the sample and of shifts in peak positions.

(4) Temperature-dependent structures in the secondary electron spectrum were observed.

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