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Electrical degradation of ß-alumina

T. B. TANG, M. M. CHAUDHRI
Physics and Chemistry of Solids, Cavendish Laboratory, Madingley Road, Cambridge, UK.

An experimental study has been made of the electrical degradation of monocrystalline and sintered samples of Na^+ β-alumina with blocking electrodes. When the applied voltage exceeds the critical value of about 800 V for single crystals or 270 V for polycrystals, sparks are observed at the anode after about one minute. Examination of the surface before the sparking indicates there is formation of sodium globules near the cathode. It is suggested that this decomposition is due to the combination of mobile Na^+ with trapped electrons which have been injected by the high field at the polarized cathode. A "memory effect" is found in the time dependence of the critical voltage.

1. Introduction

This paper is concerned with changes in sodium β-alumina caused by the application of high direct current (d.c.) voltages. Polycrystalline β-alumina is used as the ceramic electrolyte in reversible sodium–sulphur cells being developed for electric vehicles and for load-levelling uses. When a battery configuration consisting of many cells in series is charged, one of the cells may undergo catastrophic failure [1]. This usually occurs near the end of the charging cycle, when one cell can become fully charged before others. It will then have much higher resistance than the others and its electrolyte will have to support almost the entire charging voltage. An investigation of the behaviour of the ceramic when a high voltage is applied is therefore relevant. Our experiments have been done at room temperature with blocking electrodes to obtain the condition of low steady-state current; another reason for working at room temperature is that above 370 K any metallic sodium formed becomes liquid and its spatial origin will no longer be easily identifiable. Monocrystalline samples have also been used, so that the effects of grain boundaries are eliminated.

It has been known for some time that β-alumina fails by cracking and by the penetration of metallic sodium from the cathode, when the charging current density exceeds a threshold value. These physical processes are related to the discharge of sodium ions at the cathode and have been modelled by several workers [2–5]. The present study suggests that the superionic conductor decomposes to form sodium metal and oxygen when the applied voltage is above a critical limit. This degradation is also associated with current instabilities but is chemical and an entirely different mechanism will be proposed for it.

2. Experimental procedures

Large specimens of sintered β-alumina were acquired from Chloride Silent Power Ltd, and cut into rectangular blocks of dimensions $1 \times 6 \times 2$ to 20 mm. The blocks were mounted in wax, ground flat and polished. They were then washed in Inhibisol, hydrochloric acid and distilled water, and dried by heating to 700 K for 16 h. Monocrystalline samples measuring roughly $0.2 \times 2 \times 3$ mm were obtained by cleaving a Monofrax* brick. Symmetrical electrodes were made on the ends of the pieces, using either indium or copper in pressure contact for polycrystals and either silver or carbon dag in the case of single crystals.

The sample to be studied was placed either under an optical or in a scanning electron microscope (SEM). The SEM employed was a Cambridge Stereoscan S4-10 operated at 30 kV with a specimen current of 3 nA. All experiments on polycrystals were performed in air but, for optical microscopy of single crystals, some were immersed

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*From the Harbison Carborundum Company.

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in either glycerine or silicone oils so that any gaseous evolution would be observed. With the use of a Flute 412B power supply (0 to 2.1 kV, 0 to 30 mA) a d.c. voltage was applied and gradually increased. The current was monitored on an Avometer as well as on an oscilloscope; any changes occuring in the sample were examined *in situ* with the microscope. For single crystals a resistance of 1 MΩ was always connected in series.

In another series of experiments, the voltage drop along the length of polycrystalline specimens was measured with a fine copper probe, a Keithley 616 electrometer, and a travelling microscope.

3. Results

3.1. Polycrystal

In polycrystals, the current decayed exponentially and became almost constant at 2 μA in about 30 sec for all voltages below a threshold value, 280 V ± 10% for copper electrodes and 260 V ± 10% for indium electrodes. Both the steady-state current and the critical voltage were apparently independent of the interelectrode distance.

At voltages above the threshold, superimposed on the decaying current were intermittent spikes up to 2 mA in height and roughly a second in duration. Each current spike was associated with (a) a spark in front of the anode, (b) black filamentary growth from the cathode, and (c) formation and growth of cracks, not all of which extended to one of the electrodes. The spark was inside the translucent specimen but was sufficiently luminous to be observable with the naked eye. If an indium anode was used it melted after a minute or so. Deposits of metallic appearance were subsequently found on the specimen surface, both in front of the anode and at the cracks. In air these deposits eventually turned white. Occassionally at some sites they were observed in a liquid state. At still higher voltages (~ 600 V), the current no longer showed a decay but displayed large fluctuations, which sometimes became negative, as the sparking became more intense and the filamentary growth and the accumulation of deposits became more rapid.

3.2. Single crystal

Single crystals, whether with silver or carbon electrodes, behaved rather similarly, but because of the transparency of the samples as well as the limitation of current by the large series resistor, it was possible to identify an earlier stage of degradation. Moreover, the critical voltage was higher and varied considerably from sample to sample.

When the voltage exceeded a critical value (800 V ± 20% in a direction normal to the *c*-axis, independent of the inter-electrode distance and the ambient liquid) bubbles up to 100 μm in diameter were observed to form at freshly-developed cracks. Some bubbles drifted away from their original sites and collected preferentially at surface steps. This bubbling is depicted in Fig 1c, 2a and b. Soon afterwards opaque deposits could also be seen on the surface. These deposits were near to the cathode but when examined at high magnifications, were revealed to be in the form of isolated globules which were generally not in contact with the cathode; they were invariably found at freshly formed cracks (Fig 1d and 2a). On exposure to air, the deposits would turn into a white and diffuse material.

During this early stage, the steady current remained small though superimposed on it were sharp pulses of millisecond duration and amplitudes on the order of 10 μA. Furthermore the discrete deposits were always found on the cathode side, even when the current density was less than that on the anode side (as was the case of the sample in Fig. 1).

If the critical voltage was maintained for approximately 1 min (shorter if a higher potential was first applied) intermittent discharges became visible at the anode, accompanied by large current spikes (bipolar fluctuations if about 2 kV was applied) whose durations were around 1 sec and maximum amplitude was roughly 1 mA. This was the case, whether the crystal was in air, glycerine, oil or vacuum inside the SEM. In air it was possible to photograph the sparks clearly (Fig. 1e); as in the polycrystalline case, each arc produced deposits and therefore the next arc was further away from the anode, always occurring at the tip of the spreading deposits.

Experiments in high vacuum (~ 1 mPa) with the SEM confirmed the observation that, above the critical voltage, deposits were formed on the surface in the cathode region. The globules were seem to remain quite spherical in shape until they grew to 50 μm or more in diameter. Groups of these deposits formed line segments near the cathode, but along each chain they were neither uniform in size nor uniformly spaced (see Fig. 3). When further degradation was allowed, individual particles could become bigger (see for example in

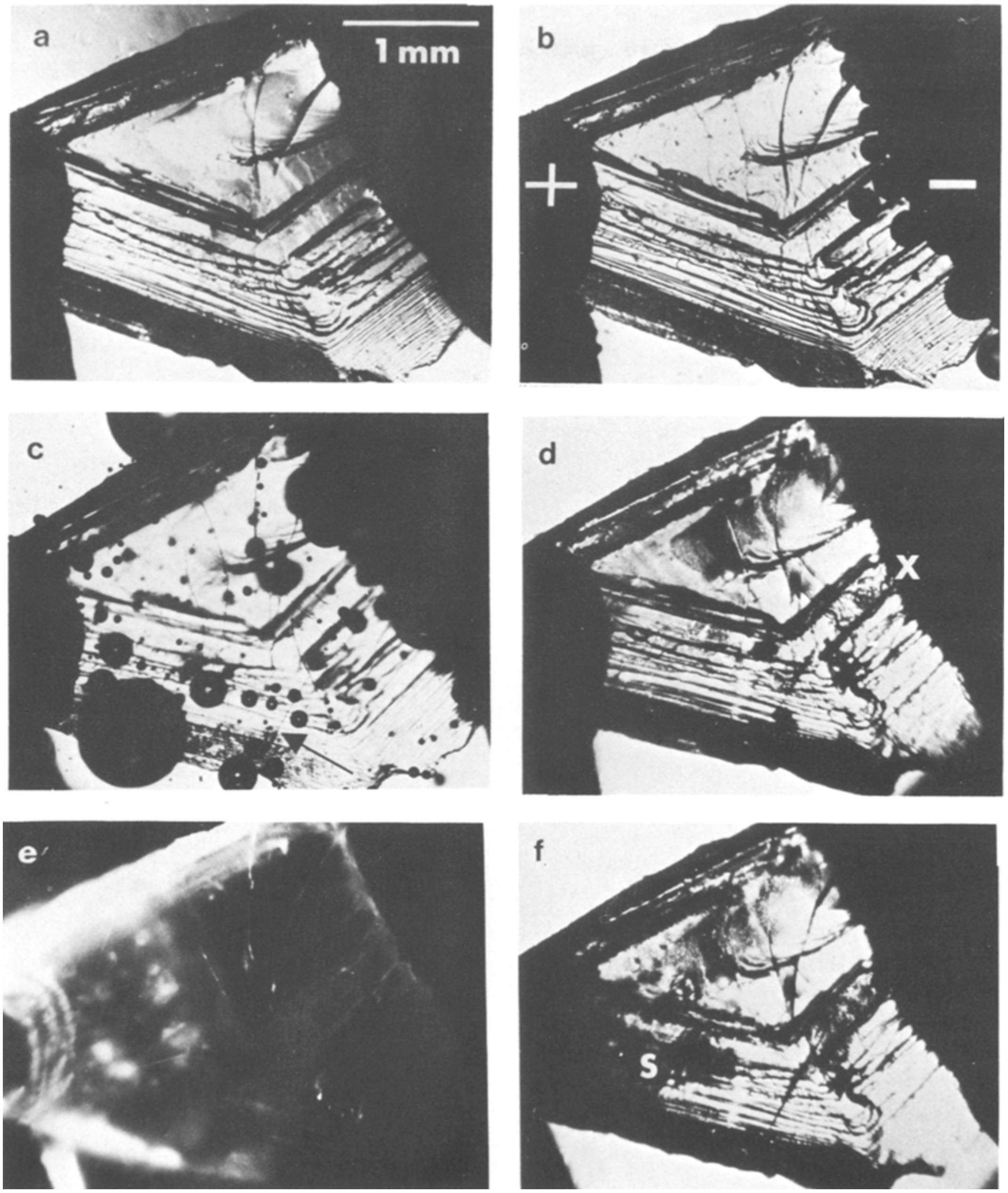

Figure 1 Degradation of a single crystal: (a) immersed in glycerine but before application of any voltage, (b) after 10 V 10 V applied for 10 sec, (c) after 1 kV applied for 10 sec, arrow identifies a new crack, (d) after 1 kV applied for 10 sec five times, and then glycerine washed off, X indicates white deposits, (e) 2kV being applied, accumulative exposures (contrast in the print has been greatly reduced to show the structure of bright areas), (f) afterwards, white deposits indicated at S. Observations by reflected light showed that the deposits reside on the crystal surface. Carbon electrodes were used. In (b) and (c), bubbles bigger than 0.1 mm in diameter, that evolved at the cathode and streamed towards the anode, were produced by the electrolysis of water absorbed in to the glycerine from the air.

Fig. 3, the change from c to e) and new particles could form further along the chain (a to g, b to h and d to f in Fig. 3), or an entirely new chain may appear (Fig. 3i). Energy dispersive X-ray analysis of the particles indicated the presence of sodium. When these particles were exposed to air they turned into white, shapeless layers spread on the surface.

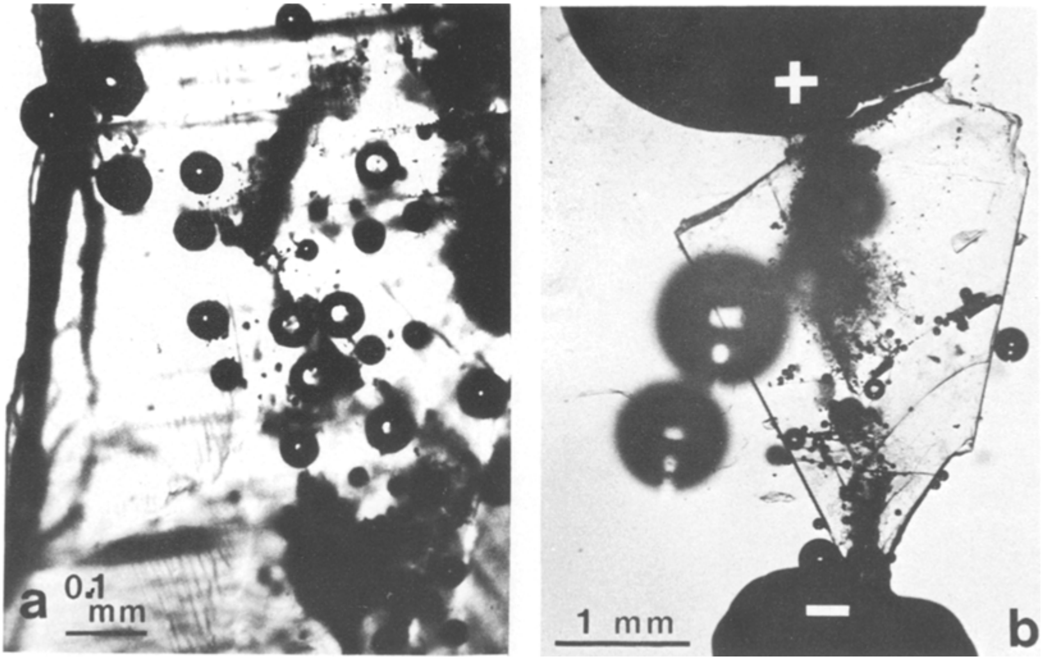

Figure 2 Crystals degraded under oil: (a) an area near the cathode; (b) another crystal in an advanced stage of degradation. Surface features were absent before voltage applications and ensuing sparkings. Silver dag electrodes were used in (a), carbon electrodes were used in (b).

3.3. Critical voltage and potential distribution

It has been mentioned that the high voltage was maintained for some time before sparking took place. The time dependence of the critical voltage for a single crystal was therefore investigated. After each arc the voltage was immediately reduced to zero and, after a certain interval which was lengthened each time, increased until sparking re-occurred. The new threshold was plotted against the total time elapsed in Fig. 4. The graphs reveal a "memory effect" whereby the magnitude was significantly lower and gradually recovered only after long intervals. As the sparkings were repeated many times, however, the critical voltage often went higher than its value at the beginning of the experiment.

The last series of experiments were concerned with measuring potentials along polycrystalline specimens, and the results are summarized in Fig. 5. After the application of a voltage ($\leqslant \frac{1}{3}$ critical voltage) the potentials decayed exponentially: the values plotted were those obtained after 10 min or longer, when the current through the specimen showed no detectable decrease over the time scale of the potential measurements. Since the electrode potential of Cu|β-Al_2O_3 at room temperature is unknown, the steady state potentials measured have significance only relative to one another, but they do show that within the bulk of the sample the field was low, $0.07\,\text{V mm}^{-1}$ and increasing only slowly with the applied voltage. Combined with the average steady-state current density of $2\,\mu$A per $6\,\text{mm}^2$ this implies a conductivity of $5 \times 10^{-3}\,\Omega^{-1}\,\text{m}^{-1}$. The majority of the voltage drop occurred, therefore, necessarily near the electrode interfaces.

4. Discussion

The bubbling observed probably represents the evolution of oxygen from β-alumina and the deposits are sodium metal, which then react with the water vapour in air, turning into white sodium hydroxide. The degradation is therefore chemical, leading to electrical failure similar to that arising from high current density [2–5], but necessarily due to a different mechanism. It is clear that the large amount of sodium found near the anode is due to the sparking (possibly caused by electron avalanche) or the hot spots so produced. The interesting process is, however, sodium formation in front of the cathode before sparking occurs.

It is expected that all the electrodes used in the experiments were blocking electrodes. The potential distribution measurements support the idea

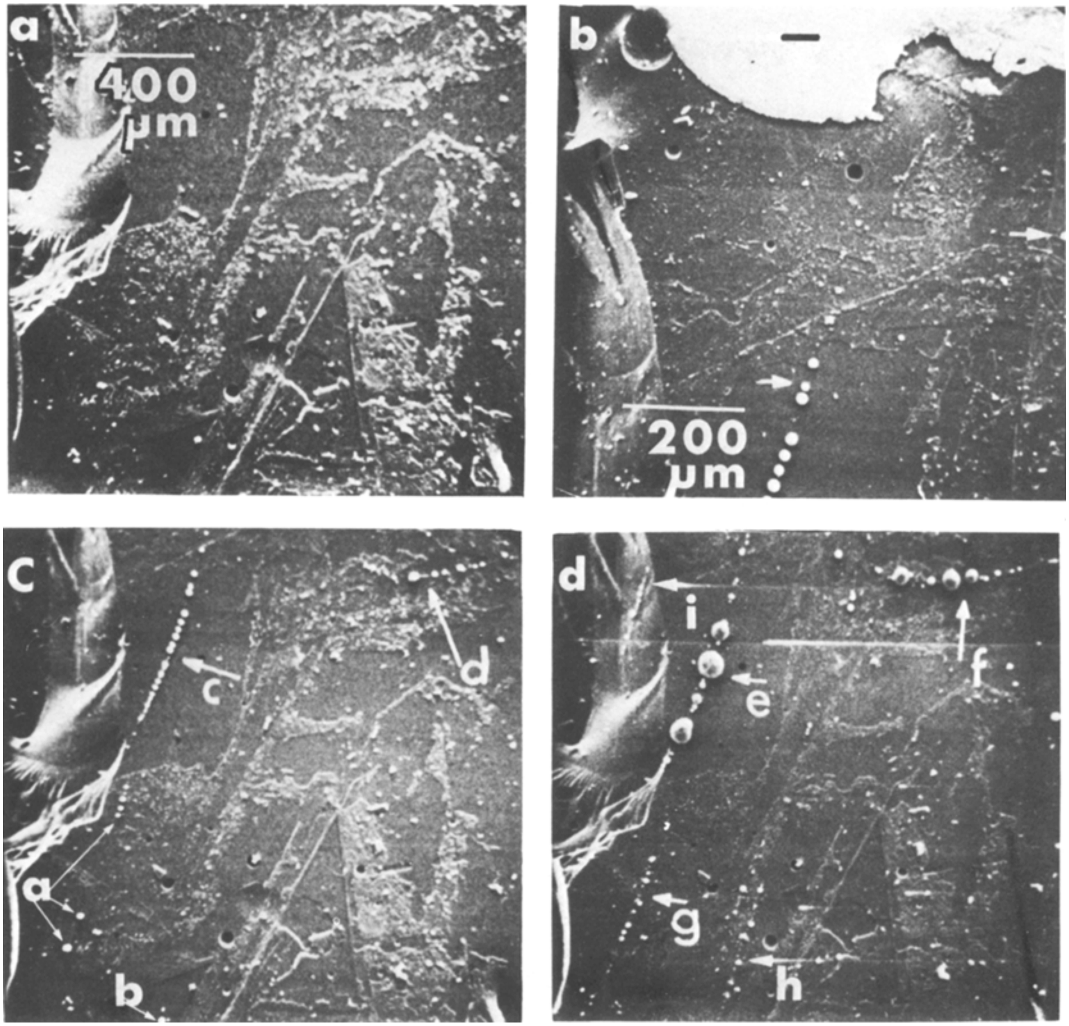

Figure 3 Electron micrographs of a single crystal degraded in vacuum: (a) region just beyond the cathode, before voltage application; (b) cathode area after 0.9 kV applied for 10 sec, arrows indicate groups of spherical sodium particles not present originally; (c) region (a) after degradation; (d) after second application of voltage at 1.4 kV for 10 sec (positions of scale bars in (a) and (b) correspond to same location on crystal). Labels in (c) and (d) are referred to in the text.

that free space charges are created in the solid electrolyte when a current is passed. The degree of polarization is greater at the anode and at the cathode than at grain boundaries in the bulk (Fig. 5). At the critical voltage, if 2 to 3V is dropped in front of the cathode over an accumulation space charge region of thickness of the order of nanometers; which is quite probable due to high density of mobile ions, the cathodic field will be high enough to cause the cold emission of electrons into the superionic conductor, despite its large dielectric constant.

It is proposed that the current pulses of millisecond duration, which were monitered before anodic sparkings, represent electronic injection. The excess electrons (or polarons), in their drift towards the anode, are localized on the way by traps and combine with mobile cations. The resulting atoms, if on the surface, can migrate and aggregate. The "germ nuclei" so formed are expected to be unstable because of the high surface-strain to volume ratio but, if the supply rate of free electrons, and thus the accretion rate of additional atoms are sufficient, large nuclei appear which will grow; they may have high "work functions" ($\gg kT$, where k is Boltzmann's constant and T is the temperature) so that they are themselves long-period electron traps. In summary, the steps are:

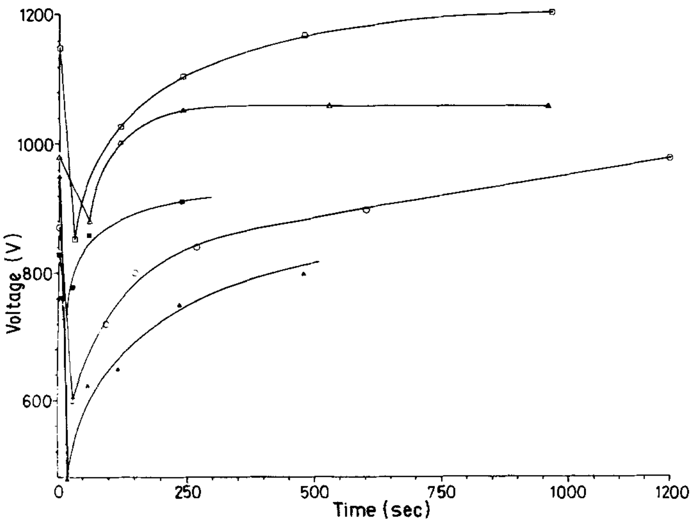

Figure 4 Voltage at which sparking takes place "instantaneously" as a function of the time delay after a previous event. Measurements taken in air, using silver electrodes.

(a) $T + e^- \rightleftharpoons T^-$

(capture of a free electron, by a trap, T, which is assumed to be neutral when empty);

(b) $T^- + Na^+ \rightleftharpoons T + Na$

(neutralization of Na^+ and resetting of the trap);

(c) $Na_n + e^- + Na^+ \rightarrow Na_{n+1}$

(on the surface, the irreversibility holds when n exceeds a critical number).

This mechanism is analogous to that previously proposed for electronically induced chemical decomposition in AgN_3 [6]; it is noted that electronic injection has also been invoked to account for metal formation in CdF_2 crystals [7] and, earlier, copper formation in AgCℓ containing 0.05 mol % Cu^+ [8]. The present work discloses clearly that isolated sodium can form on β-alumina crystals along steps where Na^+ planes come out to the surface. However, the morphologies of the sodium particles and of their chains remain to be explained; also more experiments are neede to examine other possible mechanisms.

At the critical voltage anodic sparks initiate after a delay, which can be interpreted as the time for depletion of Na^+ carriers in the anode region to produce a sufficiently high field. Indeed, if an anode is used which supplies Na^+ or any ions to which β-alumina is conductive, then sparking is not observed [1] and at the same time the critical voltage for filamentry growth from the cathode is greatly reduced in both poly- and single-crystals [1, 9]. In the absence of polarization at the node, the current is higher despite the reduced voltage; Heavens [1] has determined that there is a threshold current density for filamentary growth which, at room temperature, is about 250 A m^{-2}. When anodic sparking occurred in the present specimens

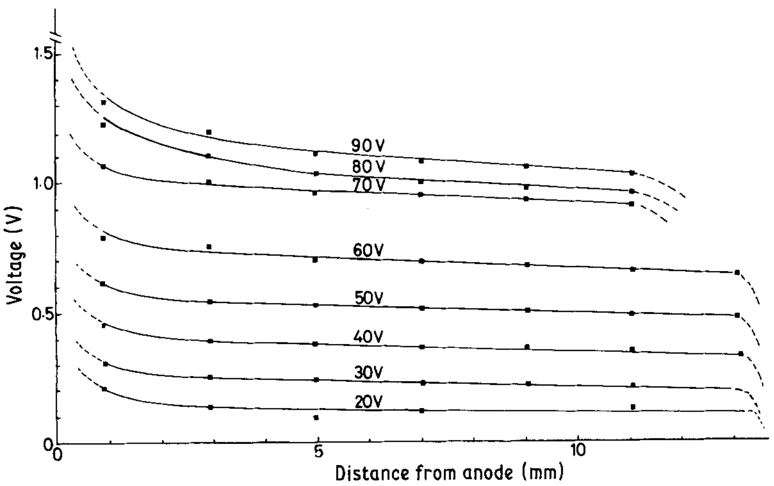

Figure 5 Steady-state voltage distribution along a polycrystal 13.9 mm long, at various applied voltages. Dotted line segments are for illustration only. The error in distance measurements was ± 0.1 mm. Evaporated silver electrodes were used.

the situation should be equivalent to this case. The associated filamentary growth may therefore be attributed to the (ionic) current density of about 330 A m^{-2} during the current spikes of about ~ 1 sec duration, and is due to the classical mechanism [2–5].

The initial decrease of the critical voltage in Fig. 4 may be due to residual space charges produced by the previous arcing. One likely explanation for the rise of critical voltage, often above the original value, at long delay times, is that, originally, there are sharp points in the anode, but the resulting field inhomogenities are gradually removed as the anode deposits build up. If so the true critical value of a voltage applied via planar silver electrodes to cause anodic sparking can be estimated as 1.2 kV.

5. Conclusions

To summarize, it is suggested that β-alumina subjected to a critical voltage with both electrodes as blocking electrodes can degrade in three ways: (a) discrete sodium forms near the cathode where polarization leads to a high field and thus electron injection. As polarization proceeds the field at the anode reaches an even higher value resulting in (b) sodium in front of the anode because of sparkings and (c) sodium filaments from the cathode arising from transient current density.

Two groups have just reported results essentially in agreement with some of the conclusions of this paper. Hooper [10] examined sintered discs at 100 to 375° C, which had been subjected to 125 to 56 V via blocking electrodes. Gross damage was found at the anode face and attributed to breakdown caused by depletion space charge. However, Hooper considered the damage not to be chemical, but merely to result from localized melting of the ceramic, and neither did he observe degradation near the cathode as has been observed in the present work. De Jonghe, Feldman and Beuchele [11] studied, by optical and electron microscopy, polycrystalline β-alumina that had actually been cycled in Na–S cells at 300° C; the detailed conditions of charging were not specified. They confirmed that degradation occurred during the charging cycle, propagated as a damage layer from the Na-side (i.e., cathode), and involved the internal deposition of sodium metal which they explained to be due to the combination of Na$^+$ with conduction electrons. They did not, however, propose that these electrons came from field emission of the Na-electrode. On the S-side (i.e., anode during cell charging) surface degradation was also observed by them, but the exact nature of this phenomenon was not discussed.

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