JOURNAL OF MATERIALS SCIENCE 13 (1978) 1515–1520

Acoustic emission studies of the breakdown of beta-alumina under conditions of sodium ion transport

C. A. WORRELL, B. A. W. REDFERN
British Railways Board, Research and Development Division, Railway Technical Centre, Derby, UK

The breakdown of the ceramic electrolyte beta-alumina during the transport of sodium ions has been investigated using an acoustic emission probe. A characteristic feature associated with the onset of electronic conduction through the electrolyte is the presence of sodium metal filaments penetrating the ceramic. The results of this preliminary investigation indicate that the ceramic undergoes a mechanical deterioration which depends on current density, and that the final stage of breakdown is subcritical crack growth.

1. Introduction

The choice of beta-alumina as the electrolyte material in the sodium/sulphur cell arises from a number of important properties. It has exceptionally high Na^+ ion conductivity but negligible electronic conductivity, and since it is apparently inert to both molten sodium, sulphur and sodium polysulphides, it can be fabricated either in the shape of a disc or tube to form a mechanically strong membrane separating the molten sodium and sulphur electrodes. However, experience has shown that degradation of the beta-alumina under conditions of sodium ion transport, either in a sodium/sulphur cell or with reversible sodium electrodes, leads eventually to the onset of electronic conductivity which frequently results in a fragmentation of the ceramic. A common feature associated with this departure from purely ionic conduction is the presence of dark grey filaments usually extending right acrosss the ceramic membrane. These filaments which consist of sodium metal are termed "sodium dendrites", and when dendrite penetration is complete an electronic path is established between the respective electrodes. Although this type of failure has been well established by independent studies on this material, the mechanism by which the penetration proceeds is not fully resolved. Armstrong *et al.* [1] suggest a mechanical failure of the ceramic and postulate that surface imperfections or flaws act as centres of stress concentration and that these imperfections propagate into cracks when filled with sodium. This idea follows from the observation that changes in electrical characteristics and lifetime of the ceramic are markedly dependent on surface roughness. The applied force required to propagate the crack during electrolysis is derived from a pressure build-up at the crack tip due to the restricted flow of molten sodium out of the crack into the reservoir. Thus, the mechanism proposed is that of repeat subcritical crack growth.

A more detailed account of beta-alumina failure during Na^+ ion transport is that presented by Richman and Tennenhouse [2]. The explanation they propose is also a crack propagating mechanism originating from pre-existing surface flaws. However, they assume that initially the flaw extends into a crack as a result of a stress corrosion effect between beta-alumina and molten sodium. Once the crack has reached a critical size, mechanical stresses are induced at the tip according to the method of Armstrong *et al.* [1]. As a result of, and in combination with the stress corrosion effects, the crack continues to propagate across the ceramic membrane.

In this present investigation, a beta-alumina tube that had suffered gross dendritic penetration

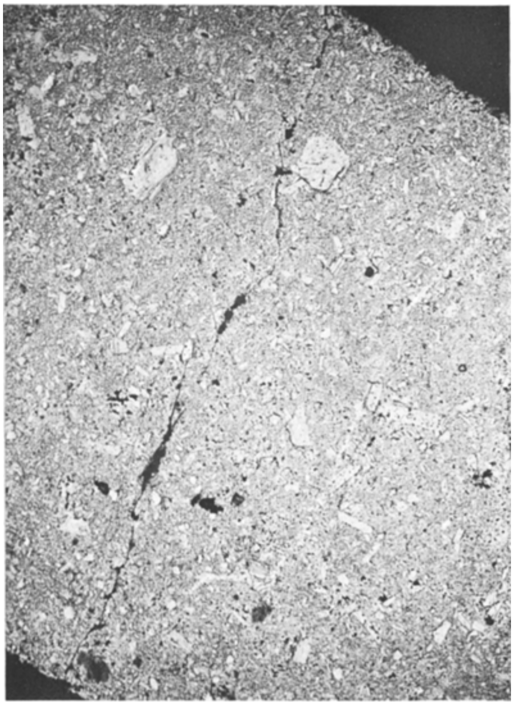

Figure 1 Polished and thermally etched specimen of beta-alumina exhibiting sodium dendrites (× 50).

following sodium ion transport between reversible sodium electrodes was examined with an optical microscope. The tube was sectioned into rings and the faces containing dendrites were polished to 1 μm and then thermally etched at 1500° C for about 20 min. Fig. 1 illustrates a fissure or crack-like feature in an area where a localized filamentary darkening had been observed prior to thermal etching.

Since it is necessary to establish the mode of failure of beta-alumina for future development of an improved ceramic, the concept of a crack propagating mechanism due to the transport of sodium was investigated. A convenient technique for detecting subcritical crack growth or mechanical deformation in strong materials of limited ductility is acoustic or stress wave emission [3]. Acoustic emissions are stress waves caused by release of the stored elastic strain energy following deformation, degradation or flaw growth. If the mode of beta-alumina failure is a crack propagation mechanism then it should be possible to detect acoustic emission at the time of failure, during sodium ion transport. A method by which this was examined is given below.

2. Experimental

The apparatus used for monitoring acoustic emission from beta-alumina during sodium ion transport is a modification of the apparatus used by Demott and Redfern [4], and is shown in Fig. 2. The cell was assembled in an inert nitrogen atmosphere and the beta-alumina tube was filled electrolytically with sodium. A relay was used to cycle the sodium level between the upper and lower tungsten electrodes by reversal of the direction of current flow through the ceramic tube. The time required for the sodium level to traverse the volume between these probes is directly related by Faraday's law to the number of coulombs passed. An increase in the time required to transport this fixed volume of sodium can be attributed to the onset of electronic conduction and hence, the reduction in Faradaic efficiency is an indication of beta-alumina failure arising from a penetration by an electronically conducting filament. The alpha-alumina rod cemented to the beta-alumina tube above the sodium level was used to guide any stress waves from the ceramic to the acoustic emission detection instrument [5]. The cell was immersed in a sand filled furnace which was heated to a temperature of 350 ± 10° C.

In the first experiment reported, an alpha-alumina ring was sealed around the exterior surface of a beta-alumina tube with a potassium borosilicate glass, and the complete assembly was immersed in the sodium of the sodium/beta-alumina/sodium pump test. Previous experiments have shown that such an assembly will accelerate dendrite formation probably as a result of stresses derived from thermal mismatch at the glass/beta-alumina interface. This alpha-alumina ring attachment was not used in the second experiment.

The number of acoustic events recorded in certain periods during both experiments was far too numerous to quantify with the data retrieval system used. Only a qualitative description of the levels of acoustic activity is given, and this is derived from a visual interpretation of the chart recordings. Ring down counts per ten seconds were recorded in the frequency range 20 kHz to 2 MHz. The tubes tested were 15 mm overall diameter and were fired according to a standard production procedure.

3. Results

The acoustic emission traces observed in the

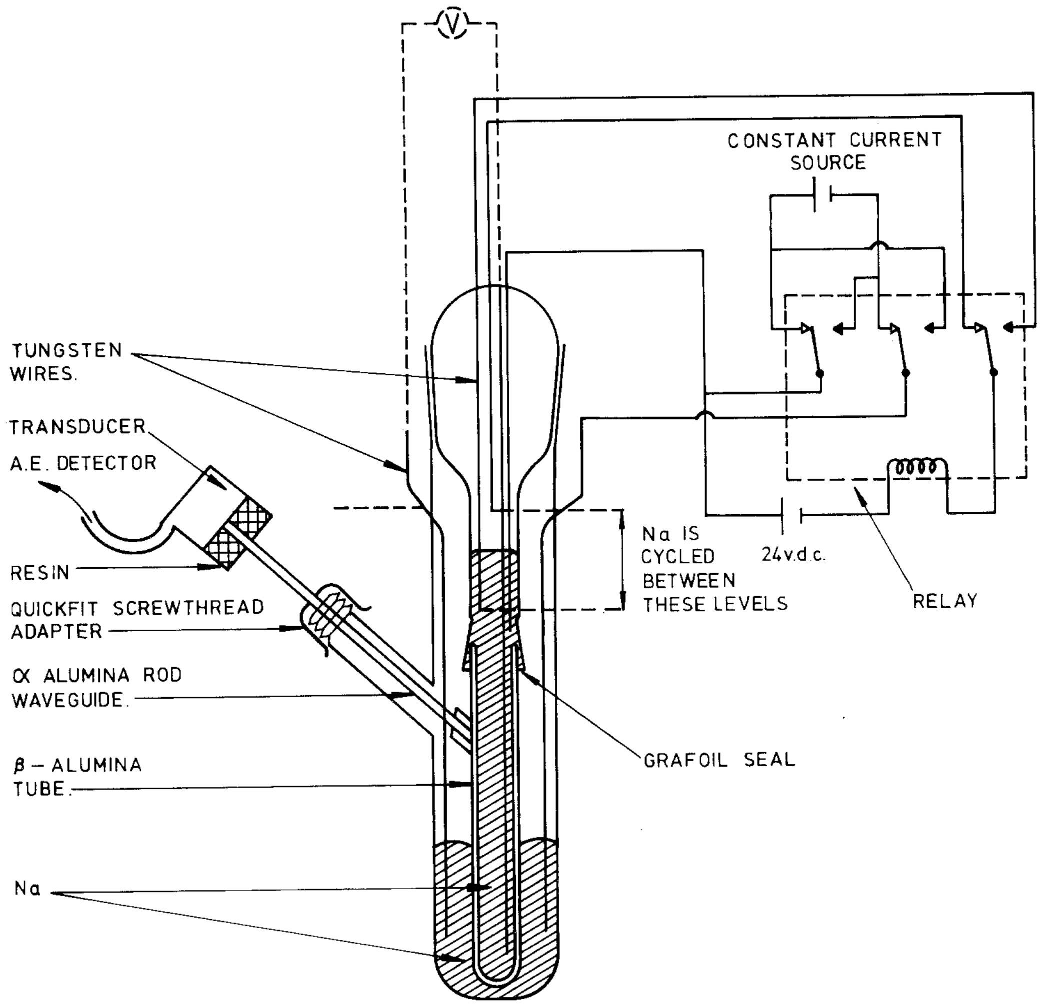

Figure 2 Apparatus for acoustic emission detection during a sodium/beta-alumina/sodium pump test.

first experiment gave some interesting information. Initially, few acoustic events were detected, but as the test continued the emission gradually became more frequent. When the current was switched off and the beta-alumina was no longer transporting sodium ions, the acoustic emission count rate dropped to almost zero. Increasing the current density from $1\,A\,cm^{-2}$ to $2\,A\,cm^{-2}$ resulted in a noticeable increase in the rate of emission (see Fig. 3), and then on reducing the current density back to $1\,A\,cm^{-2}$ the number of counts decreased but to a higher level than previously observed. After approximately $200\,A\,h\,cm^{-2}$ the cycle length increased as did the level of acoustic activity, and so the test was terminated. On sectioning the tube, dendrite penetration was observed around the area of the alpha-alumina/glass/beta-alumina interface, see Fig. 4.

In the experiment reported above, the beta-alumina tested was of the composition 0.1 MgO, 0.7 Li_2O, 8.9 Na_2O (wt%) balance Al_2O_3, and of the quality which is considered to be most susceptible to sodium dendrite penetration. The results showed that acoustic emission was observed after a relatively short time on test. In the second experiment a beta-alumina tube of the composition 0.7 Li_2O, 8.9 Na_2O (wt%) balance Al_2O_3 was tested since this has given considerably longer lives in a sodium/sulphur cell. After a total of $44\,A\,h\,cm^{-2}$ at a current density of $0.5\,A\,cm^{-2}$ no acoustic events were detected. On increasing the current density to $2\,A\,cm^{-2}$ a few isolated acoustic

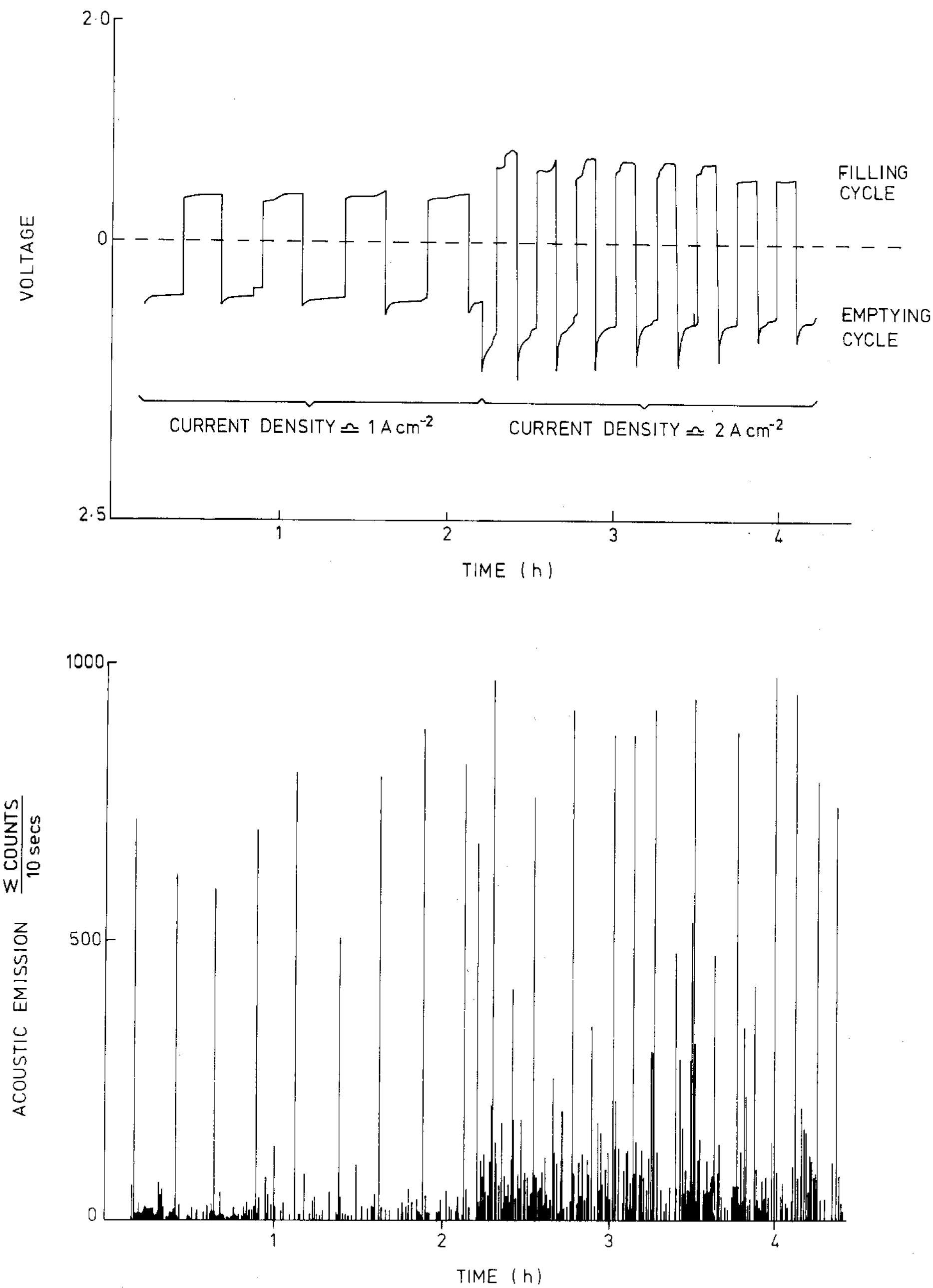

Figure 3 Acoustic emission during sodium/beta-alumina/sodium cycling.

events were detected initially, but as the quantity of charge transported by the beta-alumina increased so did the acoustic emission count rate.

4. Discussion

The results described above suggest that the emission detected was not due to an extraneous noise source. In the second experiment no emission was detected for almost four days, and then only when the current density was increased from 0.5 A cm^{-2} to 2 A cm^{-2}. Furthermore, when acoustic emission was detected it ceased when the current was switched off and the beta-alumina no longer transported sodium ions. These two observations show that emission was as a result of sodium ion transport only, and that under such

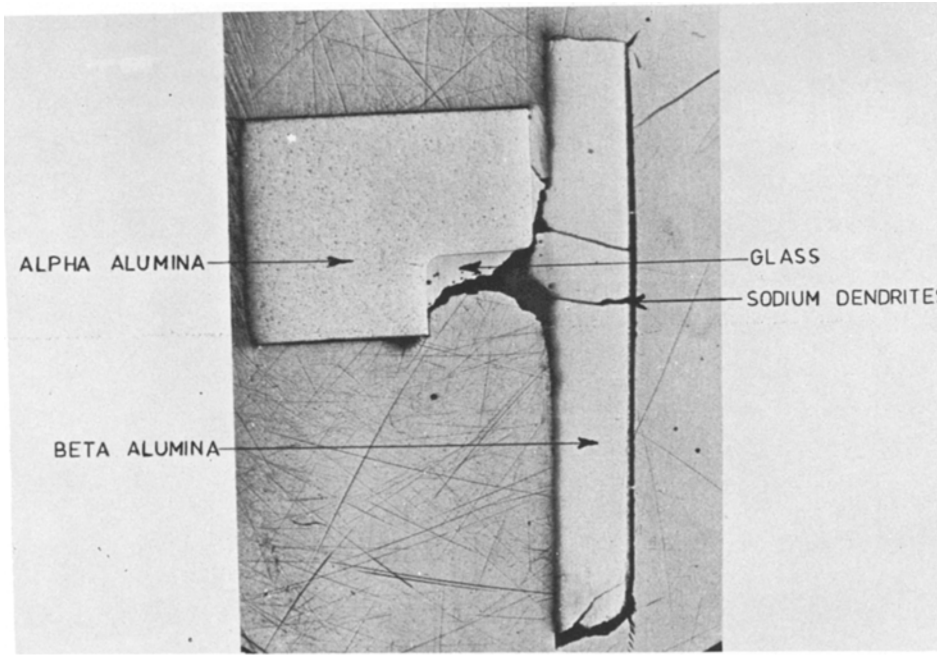

Figure 4 Sodium dendrites at the alpha-alumina/glass/beta-alumina seal (× 6).

conditions the beta-alumina experiences mechanical deformation. It is reasonable to conclude that the mechanical deformation is subcritical crack growth and that this is a result of sodium dendrite penetration.

In Fig. 3 it is clearly demonstrated that an increase in current density results in an increase in the emission count rate, and thus an increase in the rate of mechanical deterioration of the ceramic. This effect is accountable in terms of the Armstrong *et al.* [1] and Richman and Tennenhouse [2] models for beta-alumina breakdown. According to their theories, the high current density will give rise to an increase in the volume of liquid sodium effluxing from any surface flaw or sodium dendrite which may have been initiated. The effect on beta-alumina of an increase in sodium ion flux in combination with an applied stress is shown in Fig. 4, in which an alpha-alumina holder was glassed to the beta-alumina tube. Gross preferential dendrite penetration is apparent in the seal area.

In the first experiment when a reduction in Faradaic efficiency was noted after a passage of charge of approximately 200 $A\,h\,cm^{-2}$, acoustic emission was first detected after approximately 40 $A\,h\,cm^{-2}$. A change in Faradaic efficiency would only be apparent when dendrite penetration is complete, and it is possible that it would require several dendrites to cause a measurable drop in efficiency. These observations suggest that the occurrence of bursts of emission may be a more sensitive indication of impending failure, and at a much earlier stage.

5. Conclusion

The significance of the results discussed are as follows. Acoustic emission from beta-alumina during sodium ion transport using reversible sodium electrodes can be detected. This indicates a mechanical deterioration of the ceramic which could be subcritical crack growth associated with sodium dendrite penetration. The occurrence of acoustic emission prior to a reduction in Faradaic efficiency suggests this technique may provide a more sensitive indication of ceramic failure. Finally, it has been demonstrated, *in situ*, that an increase in current density accelerates this process of mechanical deterioration.

Acknowledgements

Thanks are due to the British Railways Board for permission to publish this paper.

References

1. R. D. ARMSTRONG, T. DICKINSON and J. TURNER, *Electrochimica Acta*, **19** (1974) 187.
2. R. H. RICHMAN and G. J. TENNENHOUSE, *J. Amer. Ceram. Soc.* **58** (1975) 63.

3. R. G. LIPTAI and D. O. HARRIS, *Mater. Res. Stand., M.T.R.S.A.* **11** (1971) 8.
4. D. S. DEMOTT and B. A. W. REDFERN, *J. de Physique* **37** (1976) C7–423.
5. Acoustic Emission Consultants Ltd., 105 Acoustic Emission system.

Received 30 September and accepted 7 November 1977.