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TRANSIENT EUTECTICS IN SINTERING OF SODIUM BETA ALUMINA

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I. INTRODUCTION

Sodium beta alumina solid electrolytes for use in the sodium/sulphur battery¹ have been prepared by a wide variety of methods. Two different powders can be used: component oxides or other precursors to give a reactive sintering²⁻⁴, or prereacted powders⁵ with or without additives⁶. Fast heat-up rates and zone sintering² seem now universally accepted as the preferred sintering schedule. Additional improvements in ionic conductivity and mechanical strength can be obtained by post-annealing treatments⁴. Generally, for prereacted β alumina powders, such as the Alcoa powder XB-2 "superground", heat-up rates are between $50-100^{\circ}\text{C min}^{-1}$, and time-at-temperature ($\sim 1750-1800^{\circ}\text{C}$) is between 5 to 10 minutes. The high sintering temperatures are not an absolute necessity, as was recently demonstrated by Cannon and Chowdry⁶ who obtained 97% dense β -alumina from the submicron agglomerate fraction of preconverted XB-2 powder sintered at 1530°C . Sintering times then get prohibitively long for commercial application, however. The high rates of densification during zone sintering led to the postulate that a transient liquid phase might be active during the densification of sodium beta alumina⁷. Additionally, preconverted beta alumina (Alcoa XB-2 "superground") mixed with a small amount of metastable NaAlO_2 - β alumina eutectic showed improved sinterability^{8,9} lending further support to the hypothesis that transient liquid phases are present at one point during the zone sintering process. In this paper we explore further if indeed a transient eutectic liquid phase is responsible for the improved sinterability of preconverted sodium beta alumina powders when mixed with a small amount of metastable eutectic additive.

II. EXPERIMENTAL

The principle of the transient eutectic additive sintering is illustrated in Fig. 1. Eutectic material is added to the ceramic such that its composition after sintering remains within the useful phase field. The range of the single phase field for β -alumina¹⁰ permits the addition of 5-10 wt.% of eutectic material.

Two types of experiments were performed. In the first ones, the arrested zone sinterings, long bars of sodium beta alumina with and without eutectic additive were fed into a hot furnace at different rates. The sintering was then arrested by quickly withdrawing the samples from the furnace. This procedure gives a sample along which length one can follow the microstructural evolution and local shrinkage as a function of position in the sintering schedule. In the second type of experiments, samples were fed through the hot zone of the furnace kept at 1640°C. The densities and 300°C D.C. ionic resistivities of the samples were compared as a function of post-annealing at 1375°C. The samples were in all cases packed in β -alumina powders of the same soda contents.

2.1 Arrested Zone Sinterings

The microstructural evolution and local shrinkage were examined for long, bar shaped samples partially fed into the hot zone of the furnace kept at 1700°C. Two different types of samples, prepared from preconverted Alcoa XB-2 "superground" sodium beta alumina, with 5 wt.% eutectic additive and without additive, were used. The feed rate was 0.63 cm.min⁻¹. At this feed rate thermal impedances were negligible and a direct comparison of local shrinkage, $\Delta L/L_0$, and microstructure was possible. The sintering history of each element of the specimen can then be found from the temperature (T)-time (t)

Figure 1. Principle of the eutectic additive method.

Figure 2. (a) T - x diagram; (b) dT/dt - T diagram. From these data the sintering history of each sample element in the arrested zone sintering can be found. x is the distance from the sample front.

diagram recorded at the sample front. The T - t history and the heating rates, dT/dt - T , are shown in Fig. 2a and 2b. Maximum heating rates of about $150^{\circ}\text{C min}^{-1}$ occur between 1000 and 1200°C . Near 1600°C the heating rates are about $30^{\circ}\text{C min}^{-1}$. The measured local shrinkage as a function of place in the actual sintering schedule is shown in Fig. 3 for the eutectic additive sample A, and for the additive free sample B. The green densities of the samples were 60% of the theoretical density (3.26 g.cm^{-3}). A significant, rapid increase in density is noted for the additive sample, A, between 1550°C and 1600°C . Such an effect is absent for the additive free sample, B. We attribute this anomalously high sintering activity in the vicinity of the NaAlO_2 - β alumina eutectic temperature (1580°C) to the presence of the transient liquid eutectic. The microstructures in the region of interest are compared in Fig. 4. The micrographs labeled Aa-Ac are fractographs of the eutectic additive sample A, where a-c correspond to the positions indicated in Fig. 3, while those labeled Ba-Bc are from the additive free sample. The difference in micromorphology between A and B is rather pronounced. Especially the sudden increase in grain size from Ac to Ab is striking. Note, however, that the rapid densification and grain growth does not seem to entail the development of pronounced grain facets. We do not see this as incompatible with the activity of minor amounts of a transient liquid phase. If the grains are not surrounded completely by a liquid in which they are partly soluble, there is no particular reason for developing such facets. In sodium beta alumina, faceting results from high temperature grain growth in which size increase in the direction normal to the basal planes

Figure 3. Local shrinkage $\Delta L/L_0$ as a function of position. A: eutectic additive sample; B: additive free sample. The green densities are 60% of the theoretical density.

proceeds by propagation of single or multiple spinel block ledges. Evidence for such a mechanism may be seen in transmission electro-micrographs of samples prepared at 1750°C, Fig. 5. Samples sintered at lower temperatures invariably show more wavy boundaries and grain aspect ratios closer to 1. The grain morphology thus is mainly dependent on kinetic factors rather than grain boundary energy anisotropy. Classical behavior in which the nucleation rate/growth rate ratio increases with decreasing temperatures may thus simply account for the observed grain morphologies as a function of temperature.

Fracture surfaces of samples of Ab and Bb (Fig. 4) are compared at a higher magnification in Fig. 6. Curiously, the additive free sample, Bb, contains needle-like features. Such needles are not found in the additive samples. It is possible that such needles might be produced as a result of gaseous Na transport down the temperature gradient during rapid zone sintering. If very steep temperature gradients exist, it is not inconceivable that gas phase transport of Na in porous samples might lead to transient phases

Figure 4. Aa-Ac: fractographs of sample corresponding to positions a-c marked in Figure 3. Note the rapid microstructural evolution from Ac to Ab. Ba-Bc: fractographs of additive free sample.

with Na contents higher than the NaAlO_2 . Such phases might be partly responsible for densification below 1500°C at high feed rates in zone sintering. These effects would tend to obscure the action of transient NaAlO_2 - β alumina eutectics at high feed rates in zone sintering, as was observed for samples fed into the furnace at 2.5 cm min^{-1} . Thermal impedances were very significant at these feed rates and microstructure/T-t history could not be reliably correlated.

When sample densities exceed 90% theoretical, a state of closed porosity is reached, as can be noted from the lack of penetration of liquid into samples during Archimedes density measurements. The arrested zone sinterings thus suggest that the additive samples might be sintered at temperatures as low as 1600 to 1650°C . They also show that the advantages of eutectic additive sintering are negligible for sinterings above 1700°C .

Figure 5. Single and multiple spinel block ledges observed in electrolyte prepared at 1700°C . The ledges are parallel to the basal plane (00.1). The fringe spacings in all micrographs is $11.3\text{\AA}$ (transmission electron microscopy).

Figure 6. Comparison of the microstructure of Ab and Bb (Figure 9). Note the needle-like features in Bb marked with an arrow.

Figure 7. Densities and 300°C D.C. ionic resistivities of samples sintered at 1640°C. A: eutectic additive sample; B: additive free sample.

2.2 Complete Zone Sintering at 1640°C

As suggested by the arrested zone sintering, complete zone sinterings were carried out with the furnace at 1640°C and with a feed rate of 0.63 cm min^{-1} , for samples with 5 wt.% eutectic additive and for additive free samples. The densities and 300°C D.C. Na^+ ionic resistivities were determined as a function of post annealing at 1375°C. The results are shown in Fig. 7. Curve A is for the additive sample, while B is for the additive free sample. Clearly, when the starting density of the solid electrolyte is too low, post annealing at 1375°C, while slightly improving the density, does not have marked effects on the ionic resistivity. The additive sample, however, has an initial density of about 98% theoretical and does improve the resistivity to an acceptable 300°C value for pure β alumina. In this case the density was unaffected by the post-annealing treatment. At the same time, little over-all grain growth was observed. The main microstructural changes were found in pockets of micron or submicron grains where significant local grain growth seemed to have occurred. It is thus possible to improve the sinterability of commercial, prereacted sodium beta alumina powders between 1500–1600°C by the addition of a minor amount of metastable NaAlO_2 - β alumina eutectic.

III. SUMMARY

The presence of an active transient eutectic during zone sintering of sodium beta alumina to which 5 wt.% of the NaAlO_2 - β alumina eutectic had been added, has been demonstrated when heating rates are high.

Rapid zone sintering of commercial, preconverted β -alumina to which extra soda was added in the form of the metastable NaAlO_2 - β alumina eutectic gives high density electrolyte. A post-annealing treatment is, however, necessary to bring the 300°C ionic resistivity to an acceptable level.

ACKNOWLEDGEMENTS

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DISCUSSION

Jim Reed (Alfred University): Do you control the partial pressure of alkalis in the sintering atmosphere? Is this of significance in sintering β and β'' alumina?

Author: Soda loss during sintering can be an important factor in the properties of the electrolyte. Usually it is minimized by sintering in dry oxygen,⁵ by encapsulating in platinum,⁷ or by packing in coarse powders of the same composition. We use this last method and find no loss of soda during sintering. If such precautions are not taken, a high resistivity surface layer is developed that contains α -alumina.

W. J. Huppmann (Max Planck Institute for Metals Research): Can you give any information on how long the liquid phase is present during sintering and how fast homogenization occurs?

Author: The shrinkage data in Figure 3 suggests that the liquid phase is active for approximately $\frac{1}{2}$ to 1 minute at these heating rates.

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