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# Hot isostatic pressing of beta-alumina

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The effect of hot isostatic pressing on the properties of sintered beta-alumina has been investigated. The mechanical strength is increased as compared with as-sintered material. The ionic resistivity is decreased by hot isostatic pressing but this has been shown to be related to the heat treatment rather than the application of pressure. The changes in mechanical and electrical properties are related to changes in ceramic microstructure.

## 1. Introduction

Beta-alumina is continuing to attract considerable attention because its high sodium ion conductivity in the solid state and negligibly small electronic conductivity offers the possibility of a variety of applications in electrochemical devices, especially the sodium–sulphur cell [1–5]. In addition to the electrical requirements, the material must also have an adequately high mechanical strength to withstand the stresses encountered during manufacture, assembly and operation of cells. This is generally achieved by the use of fine-grained polycrystalline materials but full densification is never achieved by conventional sintering techniques. Hot isostatic pressing offers the possibility of full densification and so the present work was undertaken to measure the strength of beta-alumina with virtually theoretical density.

Hot isostatic presses use an inert gas, generally argon, as the pressure transmitting fluid contained in a suitable pressure vessel and heated by an electric resistance furnace. The technique has been developed for densification of metal and ceramic powders by encapsulation in a suitable canister of metal or glass that will deform under pressure at elevated temperatures [6]. Alternatively a material with closed porosity, either in the form of a metal casting or a sintered powder compact may be hot isostatically pressed to remove residual porosity [7–9]. This has found commercial application in the manufacture of sintered carbides (WC–Co) and has been examined for a variety of ceramic materials including $\alpha$-alumina, magnesium oxide, barium titanate and perovskites such as (Pb, La) (Zr, Ti)$O_3$. For most of the ceramic materials investigated, conditions under which virtually all porosity was eliminated without significant grain growth have been identified and improvements in mechanical and electrical properties obtained.

In the present study, polycrystalline beta-alumina has been hot isostatically pressed at various temperatures and pressures after sintering. The effects of this treatment on the mechanical and electrical properties of beta-alumina have been measured and related to changes in the ceramic microstructure.

## 2. Experimental procedure

Beta-alumina samples were prepared as thin-walled, closed-end tubes from high purity starting materials in the form of finely ground $\alpha$-$Al_2O_3$ and $NaAlO_2$ with small doping additions of MgO and $Li_2CO_3$. The overall composition was $Na_2O{\cdot}6.5Al_2O_3$ with less than 2% by weight of dopant and the sintered material had approximately equal proportions of $\beta$- and $\beta''$-alumina. The starting materials were vibro-energy milled together using cylindrical $\alpha$-$Al_2O_3$ grinding media to produce a fully-dispersed, homogeneous mixture which was consolidated into a "green" shape by cold isostatic pressing at 275 MN $m^{-2}$. Green shapes were then rapidly fired in a pass-through zone-sintering furnace with a maximum temperature of 1975 K and a short hot zone at a speed of 50 mm $min^{-1}$. The atmosphere in the hot zone was oxidizing and saturated with sodium oxide vapour. The short, buffered firing cycle minimized

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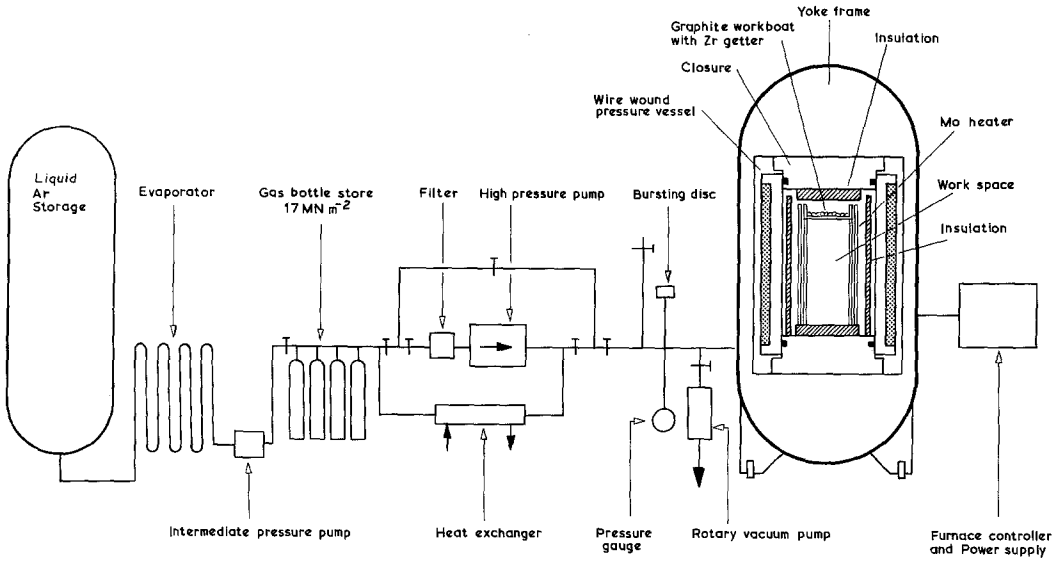


*Figure 1* General arrangement of hot isostatic pressing equipment.

the loss of sodium oxide by evaporation and so the final composition was close to that of the green body which was confirmed by X-ray fluorescence analysis of the sintered material. The density of the material after sintering and after hot isostatic pressing was measured by a simple Archimedean technique.

The general arrangement of the hot isostatic pressing equipment is shown in Fig. 1. This consists of a pressure vessel containing an electrically heated furnace with a pumping arrangement to pressurize the vessel with an inert gas, in this case argon. The samples were supported on graphite fixtures. The sequence of operation was as follows; the vessel was closed-off, evacuated to $\sim 1.4\,kN\,m^{-2}$, pressure was equalized between an intermediate pressure store ($17\,MN\,m^{-2}$) and the vessel then pumped to the working level whilst heating. After holding at maximum temperature and pressure for a pre-determined time, the heaters were disconnected and argon returned through a cooler to the intermediate pressure store. Typical pressure/time and temperature/time curves for hot isostatic pressing are shown in Fig. 2.

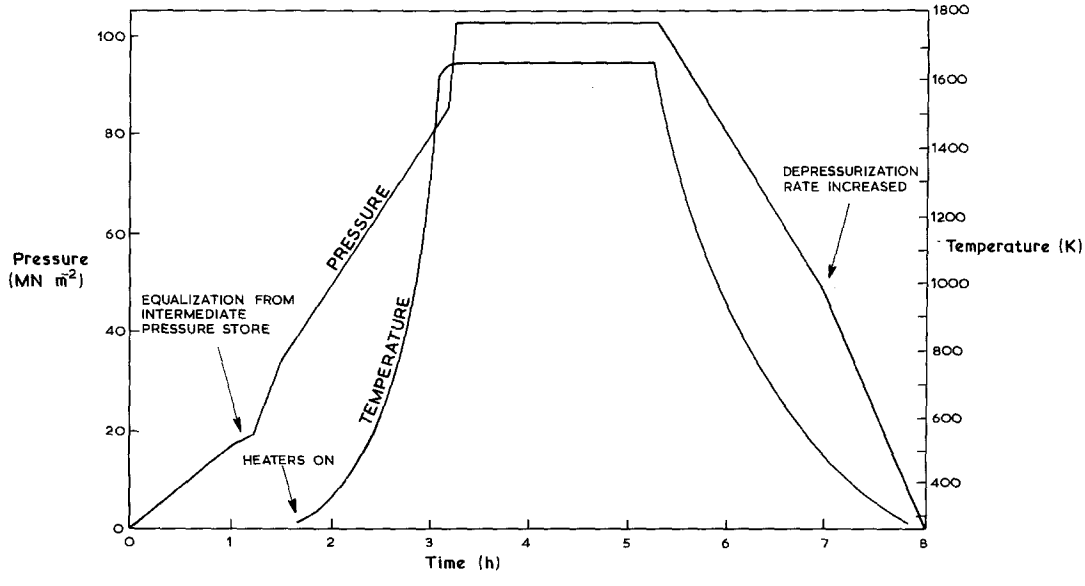


*Figure 2* Typical pressure/time and temperature/time curves for hot isostatic pressing of beta-alumina.

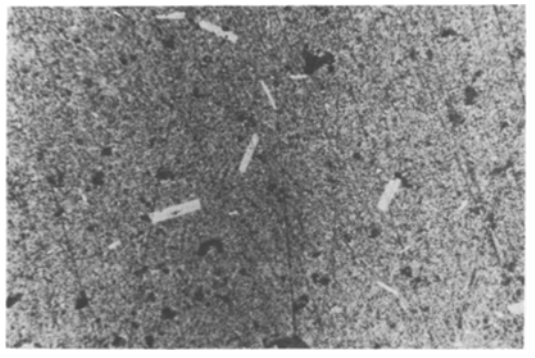

*Figure 3* Microstructure of beta-alumina in the as-sintered condition with a porosity level of ~ 1%. The material has a duplex micromorphology consisting of a fine grained (0.5 to 2.0 $\mu$m) matrix and occasional large laths with a maximum size of 20 × 80 $\mu$m (× 180).

The beta-alumina tubes were cut for strength tests into rings of 26 mm outer diameter and 23 mm inner diameter by 10 mm long using a diamond slitting wheel with a paraffin-based coolant. Care was taken to minimize damage to the cut faces. Strength was measured by testing the rings in diametral compression at a strain rate of $\sim 2.5 \times 10^{-5}$ sec$^{-1}$. Under these conditions, fracture originates from the point of maximum tensile stress, which is located on the inner surface of the tube adjacent to the compression platens. Strengths were calculated from the applied forces and the specimen dimensions using the approximations of thin-walled elasticity theory but making due allowance for any eccentricity in the rings.

The microstructure was examined by optical microscopy after polishing to a 1 $\mu$m diamond finish and etching in boiling $H_3PO_4$ for 30 min. The ionic conductivity was measured using a d.c. four-probe method taking care to avoid errors due to electrode effects.

## 3. Results and discussion

Under the sintering conditions employed in this work, the beta-alumina has an as-sintered density of 99% theoretical and virtually all of the porosity was closed. The microstructure consisted of a fine-grained (0.5 to 2.0 $\mu$m) matrix and occasional large laths with a maximum size 80 × 20 $\mu$m (Fig. 3). A range of hot isostatic pressing conditions of temperature (1603, 1653 and 1723 K) and pressure (69, 103 and 172 MN m$^{-2}$) were studied, each with a fixed time at the maximum temperature and pressure (2 h). The results are summarized in Table I from which it may be seen that full densification was achieved under all conditions except at the two lower temperatures at the lowest pressure. The establishment of full densification was confirmed by examination of the microstructure of the samples which showed a complete absence of porosity except in a narrow region within ~ 30 $\mu$m of the surface where some pores are connected to the surface. There was some evidence of pores trapped in large grains not being closed because of difficulties associated with mass transport in these areas. The grain structure of the samples after hot isostatic pressing was consistent with the effects of temperature alone. At 1603 K, the matrix grain structure differed little from the as-sintered material, with an average grain size of 1.0 to 1.5 $\mu$m and a few large laths whose maximum size was 70 $\mu$m × 15 $\mu$m (Fig. 4). At 1653 K, the average grain size of the matrix remained in the range 1.0 to 2.0 $\mu$m and a few large laths up to 80 $\mu$m × 20 $\mu$m were present. On treatment at 1723 K, there was a small, but discernable, amount of matrix grain growth with an average grain size in the range 2.0 to 4.0 $\mu$m and some small lath-shaped crystals up to 15 $\mu$m long with a few large laths, typically 100 $\mu$m × 10 $\mu$m. Hot isostatic pressing will close porosity by compressing the residual gas trapped in pores until the pressure equilibrates with the pressurizing medium provided gas does not diffuse from the pores and the material can creep at a sufficiently rapid rate to accommodate the dimensional change. Heat-treatment after hot isostatic pressing should produce increases in porosity if this is the case and this was demonstrated in samples hot isostatically pressed at 1603 K and heat-treated for 1 h at 1773 K where the density decreased from 3269 ± 3 kg m$^{-3}$ to 3258 ± 5 kg m$^{-3}$ on samples pressed at 69 MN m$^{-2}$, from 3274 ± 2 kg m$^{-3}$ to 3257 ± 3 kg m$^{-3}$ at 103 MN m$^{-2}$ and from 3276 ± 1 kg m$^{-3}$ to 3268 ± 2 kg m$^{-3}$ at

TABLE I Density measurements* (kg m$^{-3}$)

| Temperature (K) | | 1603 | 1653 | 1723 |
|---|---|---|---|---|
| Pressure (MN m$^{-2}$) | | | | |
| 69 | before | 3235 ± 4 | 3236 ± 4 | 3236 ± 4 |
| | after | 3269 ± 3 | 3270 ± 3 | 3273 ± 2 |
| 103 | before | 3236 ± 4 | 3235 ± 4 | 3237 ± 3 |
| | after | 3274 ± 2 | 3275 ± 3 | 3273 ± 2 |
| 172 | before | 3236 ± 4 | 3235 ± 4 | 3237 ± 4 |
| | after | 3276 ± 1 | 3273 ± 2 | 3273 ± 2 |

*Errors are given as one standard deviation and the values given are the mean of fifteen results.

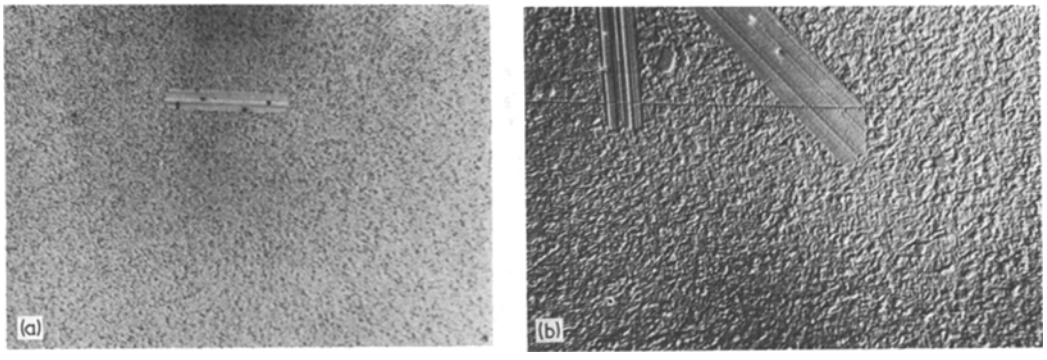


*Figure 4* Microstructure of beta-alumina after hot isostatic pressing at 1603 K and 172 MN m$^{-2}$. The porosity is virtually zero except in some of the large grains. The material has a fine grained (1.0 to 1.5 $\mu$m) matrix and a few large laths (up to 15 × 70 $\mu$m); (a) × 180, (b) × 480.

172 MN m$^{-2}$. Smaller and less consistent decreases in density were observed at the higher temperatures. The rate of density decrease was lower in material with a somewhat larger average grain size.

Shrinkage on hot isostatically pressed tubes was measured on 58 tubes treated at 1698 K and 103 MN m$^{-2}$. The average length and density were 580.0 ± 0.5 mm and 3234 ± 17 kg m$^{-3}$ respectively before and 577.8 ± 0.8 mm and 3273 ± 6 kg m$^{-3}$ after hot isostatic pressing. The change in length (0.38%) is almost exactly one third of the change in density (1.19%) as expected.

Axial conductivity data are shown in Table II. The effect of hot isostatic pressing on conductivity is essentially the same as the effect produced by heat-treatment alone and the changes in conductivity are consistent with the observed changes in microstructure and the relative amounts of the $\beta$- and $\beta''$- phases. Accurate lattice parameter measurements were also made for both phases and no significant changes were detected (< 0.2%).

The distribution of measured tensile strength values $\sigma_f$ for the beta-alumina samples may be fitted to a Weibull distribution of the form

$$P = \exp\{-D(\sigma_f - \sigma_u/\sigma_0)^m\}$$

where $P$ is the survival probability, $D$ the volume under stress, $\sigma_u$ the zero probability stress, $\sigma_0$ a normalizing constant and $m$ the Weibull modulus. Consequently

$$\ln \ln 1/P = m \ln(\sigma_t - \sigma_u) - m \ln \sigma_0 + \ln D$$

and thus a plot of $\ln \ln 1/P$ against $\ln \sigma_f$ with $\sigma_u$ set equal to zero yields a straight line with a slope equal to the Weibull modulus. Tensile strength data for hot isostatically pressed samples are shown in Table III. All showed substantially higher strengths

TABLE II Resistivity measurements*

| Temperature (K) | Units | 1603 | 1653 | 1723 |
|---|---|---|---|---|
| Pressure (MN m$^{-2}$) | | | | |
| 69 | Ωm, 573 K | 0.0955 | 0.0854 | 0.0783 |
| | Ωm, 623 K | 0.0650 | 0.0598 | 0.0564 |
| | Ea, kJ mol$^{-1}$ | 27.84 | 26.46 | 23.24 |
| 103 | Ωm, 573 K | 0.0820 | 0.0838 | 0.0805 |
| | Ωm, 623 K | 0.0566 | 0.0567 | 0.0556 |
| | Ea, kJ mol$^{-1}$ | 27.00 | 28.22 | 26.63 |
| 172 | Ωm, 573 K | 0.0945 | 0.0946 | 0.0801 |
| | Ωm, 623 K | 0.0663 | 0.0656 | 0.0578 |
| | Ea, kJ mol$^{-1}$ | 27.00 | 27.46 | 24.83 |
| Mean values | Ωm, 573 K | 0.0907 | 0.0879 | 0.0796 |
| | Ωm, 623 K | 0.0626 | 0.0607 | 0.0566 |
| | Ea, kJ mol$^{-1}$ | 27.30 | 27.38 | 25.33 |

*In the as-sintered condition, the ionic resistivity was 0.104 Ωm at 573 K and 0.069 Ωm at 623 K with an activation energy of 29.8 kJ mol$^{-1}$.

TABLE III Strength measurements ($MN\,m^{-2}$)

| Temperature (K) | Units | 1603 | 1653 | 1723 |
|---|---|---|---|---|
| Pressure ($MN\,m^{-2}$) | | | | |
| | $MN\,m^{-2}$ | 242 ± 43 | 252 ± 24 | 260 ± 37 |
| 69 | $m$* | 5.5 | 10.0 | 6.9 |
| | $n$† | 13 | 12 | 13 |
| | $MN\,m^{-2}$ | 254 ± 32 | 258 ± 36 | 272 ± 37 |
| 103 | $m$ | 7.6 | 6.7 | 7.2 |
| | $n$ | 13 | 12 | 13 |
| | $MN\,m^{-2}$ | 245 ± 31 | 242 ± 53 | 258 ± 30 |
| 172 | $m$ | 8.1 | 4.1 | 8.1 |
| | $n$ | 13 | 13 | 12 |

*$m$, Weibull modulus; †$n$, sample size.

than a control group of 15 rings that had a strength of $147 \pm 21\,MN\,m^{-2}$ (Weibull modulus = 6.8) but no significant difference was evident between any of the hot isostatically pressed groups. This was expected from the density data. Fig. 5 shows the effect of hot isostatic pressing at 1653 K and $103\,MN\,m^{-2}$ on the strength of tubes burst under internal hydraulic pressure. The average density was $3236\,kg\,m^{-3}$ in the as-sintered control samples and $3271\,kg\,m^{-3}$ after hot isostatic pressing. The tubes were 70 mm long with an outer diameter of 13 mm and an inner diameter of 10 mm (volume under stress, $3800\,mm^3$). Under these conditions the average tensile fracture stress was significantly lower than for rings in diametral compression at $\sim 90\,MN\,m^{-2}$ for both groups because of the larger volume under stress but hot isostatic pressing had a significant effect on the Weibull modulus raising it from ~ 3 to ~ 7. This effect may be related to the distribution of large grains in the material as these will act as critical defects in the absence of other defects and this will be related to the volume under stress. Hot isostatic pressing is clearly an effective method of increasing the strength of beta-alumina by reduction of the number of defects in the form of closed porosity.

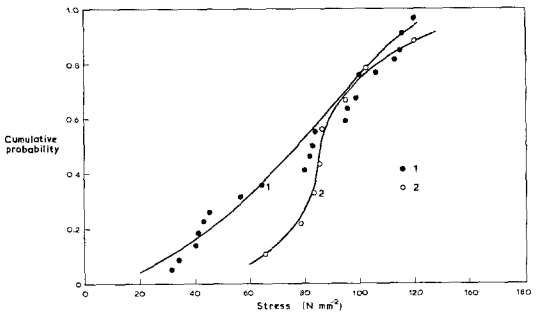


*Figure 5* Cumulative probability of tensile failure of beta-alumina tubes (10 mm i.e., 13 mm od, 70 mm long) burst under internal hydraulic pressure. The as-sintered control samples (1) had a significantly lower Weibull modulus (m ~ 3) than the hot isostatically pressed samples (2) (m ~ 7).

## 4. Conclusions

Hot isostatic pressing of sintered beta-alumina produces material with virtually theoretical density over a wide range of temperatures and pressures. The densification rate is determined by the creep rate of the material. Hot isostatic pressing produced increases in mechanical strength and Weibull modulus because of the reduction in porosity. Changes in ionic conductivity, in the ceramic microstructure and in the relative amounts of the $\beta$- and $\beta''$-phases were consistent with the effects of temperature alone. Hot isostatic pressing would clearly provide an effective method of improving the mechanical properties of beta-alumina for use in electrochemical devices but the capital and operating costs of the equipment needed to carry out the process will tend to preclude its use in all but the most stringent applications unless the process produced very significant improvements in device lifetime or reliability.

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