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Zirconia electrolyte cells

Part 1 *Sintering studies*

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The effects of time, temperature and doping additions on the sintered density of CaO and Y_2O_3 stabilized ZrO_2 have been studied, and comparisons of the strength and microstructure of the various materials made. Two mol % Al_2O_3 or 5 mol % TiO_2 additions were the most effective sintering aids, causing densification by a liquid phase mechanism.

1. Introduction

Solid solutions of cubic zirconia stabilized with CaO (CSZ) or Y_2O_3 (YSZ) are important solid electrolyte materials in both high-temperature galvanic cells and fuel cells. One particular application which poses stringent conditions on the materials is the use in the steel industry as an oxygen probe in liquid steel. Because of the mechanical and thermal restrictions, the lifetime of these probes is relatively short. Studies have been conducted to determine the feasibility of making inexpensive electrolytes using simplified fabrication techniques. The systems chosen have been solid electrolytes of CSZ and YSZ of inexpensive commercial grade using Pt electrodes.

The possibility of making cells using the tape process [1] offers a significant economic advantage due to the simplicity of the manufacturing process. Electrode materials can be applied directly to the green (unfired) tape which then requires only a single sintering step for densification of the electrolyte and the production of an intimately bonded porous, conducting electrode, instead of the many conventional processing steps involving an electrolyte sintering step followed by numerous metallization applications and sinters. Due to the flexible nature of the green tape, shaped cells may easily be prepared, thus allowing design flexibility in new applications.

The only limitation to the tape process in this application is that the sintering temperature of the electrolyte be lower than the melting temperature of the electrode, which, in the case of Pt, requires that sintering occur below about 1500° C since Pt powder becomes extremely volatile at higher temperatures. For stabilized ZrO_2, this temperature is considerably lower than the usual manufacturing temperatures which range from 1750 to 1900° C for powders of commercial quality. There are very reactive powders available which sinter readily at temperatures below 1500° C, but they are significantly more expensive.

Initial sintering experiments were carried out with three cubic stablized materials of commercial quality and the results showed that the powders were not amenable to production of high density, impervious bodies at these low temperatures. Consequently, a study was made to find an additive that would enhance the low temperature sintering of the powders. Many studies have been reported in the literature concerning the effects of additives on the sintering of ZrO_2 [2–6], and although some impurities had an enhancing effect on densification, notably $CaTiO_3$ [4], Al_2O_3 [5], and Fe_2O_3 [6], only the latter has been studied in detail. Consequently, a number of dopant additions were studied over a range of additive level and sintering conditions in order to find the most suitable sintering aids for production of solid electrolytes by the tape process. The results of these investigations are reported in this paper, and the electrical properties of both tape-produced and pressed and sintered products containing the most effective additives are reported in a following publication [7].

2. Experimental procedures

Two 5 wt% CSZ powders, a technical grade

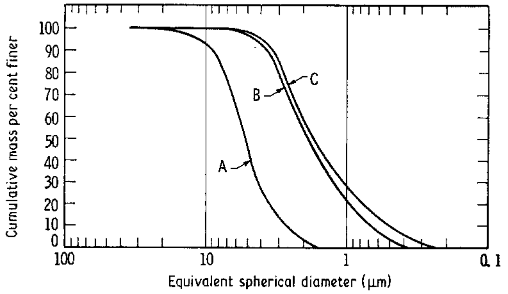

Figure 1 Particle size distributions for YSZ; A, as-received, B, milled 200 h; C, milled 400 h.

nominally 97% pure and a nuclear grade nominally 99.7% pure, and a 12 wt% YSZ powder nominally 99.7% pure were studied.[*] The major impurities in all three powders were SiO_2 and MgO with lesser amounts of Fe_2O_3, Al_2O_3 and TiO_2.

The as-received powders were relatively coarse and were milled in de-ionized water using ZrO_2 balls in a rubber-lined jar to reduce the particle size and increase the surface area and sinterability. A typical particle size distribution is given in Fig. 1, which shows the reduction in size with milling time. BET surface area measurements also reflected the reduction in particle size, with the CSZ materials increasing from about 0.3 to $1.5\,m^2\,g^{-1}$, and the YSZ increasing from 1.8 to $2.3\,m^2\,g^{-1}$ after 200 h.

Additive sintering studies involved a number of metal oxides, including CaO, NiO, MgO, SiO, Al_2O_3, La_2O_3, Dy_2O_3, Fe_2O_3, Nb_2O_3, TiO_2, SiO_2 and Ta_2O_5. LiF was also investigated. The additives were added in increments up to 5 mol %.

The milled powder were mixed in an agate pestle and mortar with the impurity dopant and 2 wt% polymethyl methacrylate binder dissolved in methylene chloride to produce a homogeneous die-feed material. After drying, the powders were pressed into 1/2 in. diameter pellets at a pressure of 20 000 p.s.i.

The tape process involves the manufacture of a flexible green tape of ceramic powder intimately dispersed in a plasticized organic resin. During the subsequent sintering operation, the organics are removed at some low temperature (~400° C), and the powder sinters into a monolithic body at the normal sintering temperature. In the present manufacture of ZrO_2 electrolytes by this process, similar procedures to those established in the manufacture of Al_2O_3 substrates were followed [1]. Using the results from the pellet sintering study, two tapes were made using the technical grade CSZ, one using 5% TiO_2 and the other 2% Al_2O_3 as sintering aids. The tapes were made using 1.5% deflocculating agent[†], 5% polyvinyl butyral binder[‡] and approximately 4% polyalkalene glycol plasticizers[§]. These components were milled in trichloroethylene-methanol solvent (the azeotropic composition) for 15 h, filtered through a 200 mesh screen, deaired, and cast onto a 0.050 in. carrier sheet[¶] at a viscosity of about 2000 cP via a doctor blade. After solvent evaporation, the flexible zirconia tapes, approximately 0.050 in. thick, were removed from the sheet and cut into 1 in. x 1 in. pieces for the sintering studies.

Sintering was performed in air using an alumina muffle tube furnace with Pt windings up to approximately 1700° C and an oxygen–acetylene furnace for temperatures up to 2200° C. The effect of temperature on the sintered density and microstructure was studied using isothermal anneals of 3 h, and the effect of time on the sintered density was studied at 1480° C.

3. Results

3.1. Sintering

Some of the additives made significant differences to the sintered density, as seen in Figs. 2 and 3. Nuclear grade CSZ (Fig. 2) sintered to 85% TD (theoretical density) at 1480° C, and the addition of 0.25% SiO_2 gave the greatest increase (>10%)[‖]. Additions of 2% Al_2O_3 and 5% TiO_2 also showed significant increases, of the order of 10% TD. Some additives, notably La_2O_3, decreased the sintered density; this may, however, be due to absorbed water on the La_2O_3.

The sintered density of YSZ was 81% TD at 1480° C. Several additives, notably TiO_2, MgO and Al_2O_3 increased the density by 6%, Fig. 3, while Fe_2O_3 and an equimolar mixture of Al_2O_3 + TiO_2 increased the density by about 10%. The other additives either did not increase the density significantly, or reduced the density as in the case of La_2O_3 and Ta_2O_5.

[*] Powders obtained from the Zirconium Corporation of America, Solon, Ohio, USA.

[†] Castung 103G-H, Baker Castor Oil Co., Bayonne, NJ, USA.

[‡] Type B98, Monsanto Co., St. Louis, MO, USA.

[§] UCON 2000, Union Carbide Corp. and 61P, Allied Chemical Corporation.

[¶] Teflon or Mylar.

[‖] All density increases on an absolute basis.

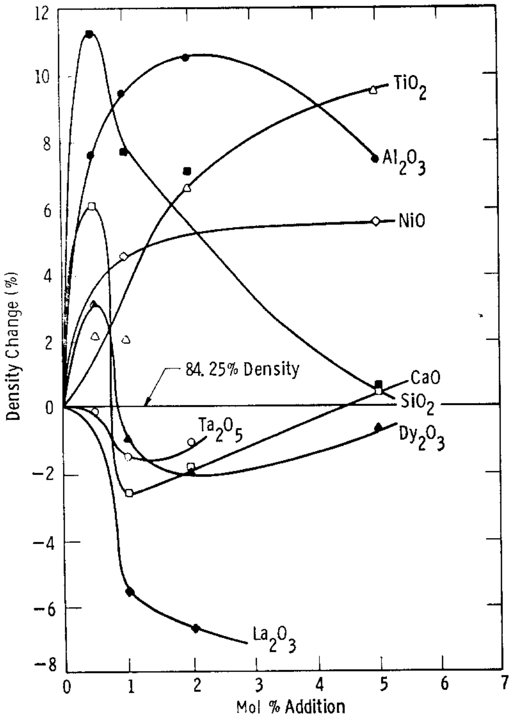

Figure 2 Effect of doping additions on the sintered density of nuclear grade CSZ at 1480° C.

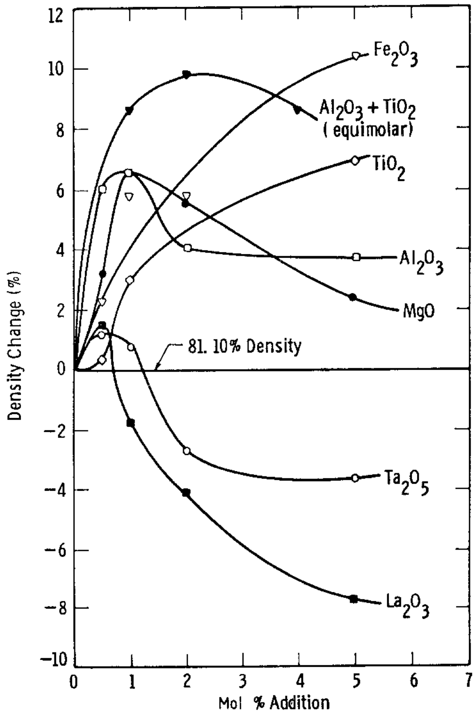

Figure 3 Effect of some doping additions on the sintered density of YSZ at 1480° C.

The influence of temperature on the density of the three grades of ZrO_2 is shown in Figs. 4 and 5 up to 1700° C. The effects of the sintering aids were most pronounced at the lower temperatures but the improvement in sinterability persisted up to the highest temperatures investigated. At 1360° C, the lowest temperature studied, the technical grade CSZ sintered to the highest density (83.5% TD) while both the nuclear grade and YSZ did not densify significantly above the as-pressed densities. Al_2O_3 and TiO_2 additions increased all the densities. At 1470° C, some of the doped nuclear grade and technical grade CSZ samples showed similar densities, giving fairly high values (>91% TD). The YSZ also increased significantly in density with values approaching 93.5% TD. At higher sintering temperatures, most of the sintered densities approached limiting values. The technical grade tape doped with 5% TiO_2 and the nuclear grade material doped with Al_2O_3 reached a limiting density of about 98% at 1690° C, while the other CSZ materials exceeded 91% TD. The YSZ material doped with TiO_2 and Al_2O_3 also reached approximately 97% TD at 1690° C, while undoped the

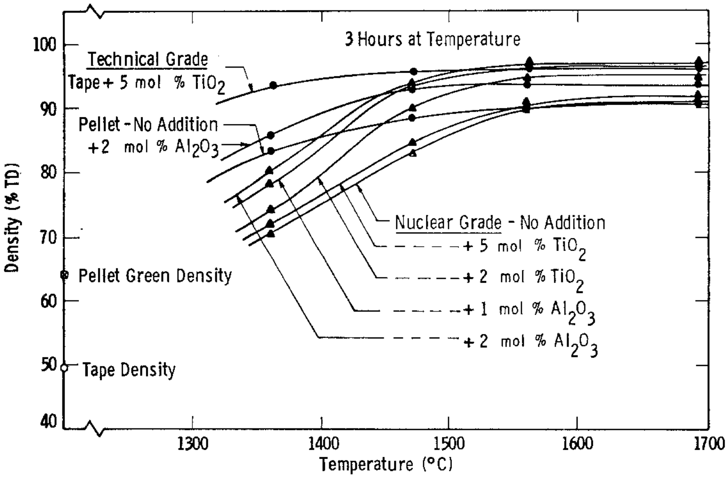

Figure 4 Effect of temperature on the sintered density of CSZ.

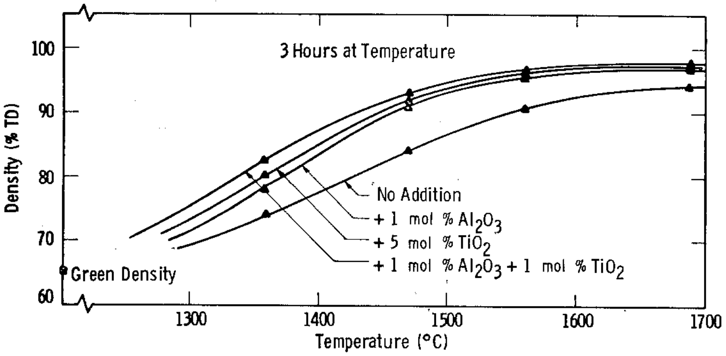

Figure 5 Effect of temperature on the sintered density of YSZ.

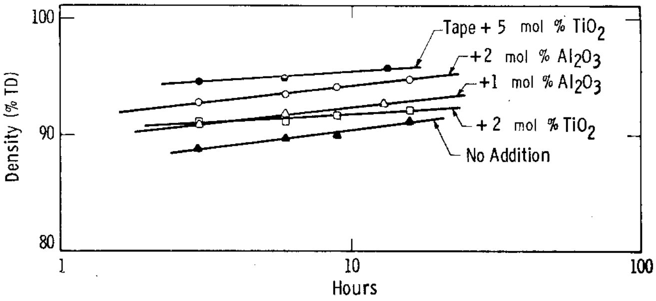

Figure 6 Effect of time on the sintered density of technical grade CSZ at 1480° C.

highest density obtained was 93.5%. Some undoped nuclear grade CSZ pellets were sintered at 1950° C for 2 h giving densities of 94.7%, and pure YSZ pellets sintered at 1950° C and 2210° C showed densities of 93.3 and 95.0% respectively.

The effect of sintering time was studied at 1480° C, and the results are shown in Figs. 6 and 7. The data were obtained by successive resinters of the same pellets. Fig. 6 shows the effect of time on the density of pure and doped technical grade CSZ. It was found that the sintered density increased linearly with respect to log (time) over the range investigated without reaching a limiting density for both the pure and doped materials. The highest density (95.5% TD) was achieved with 2% Al_2O_3. Most of the curves were approximately parallel indicating that the additives did not influence the densification kinetics over this time period, but enhanced the sinterability during the earlier stages of the sintering process.

The same trend was shown by YSZ, Fig. 7, except that two of the curves were not linear with log (time) but showed a progressive increase in slope with extended time. The densities of both pure and doped material increased with time, but none reached a limiting value. The highest density was obtained with 1% Al_2O_3 + 1% TiO_2 additions with a value of 94.7% TD which was sufficient to give an impervious material.

The pure nuclear grade CSZ increased in density with log (time) in a linear manner, whereas all the doped samples tended to reach a maximum density. After 16 h, the highest densities were obtained with 5% TiO_2 and 1% Al_2O_3 additions, with values of 97 and 96.25% TD.

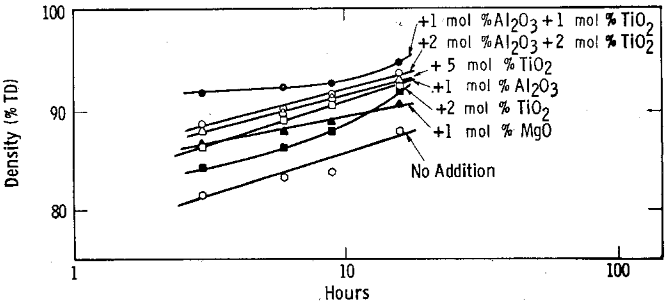

Figure 7 Effect of time on the sintered density of YSZ at 1480° C.

3.2. Microstructural investigations

Microstructural evaluation of pellet and tape-produced materials gave some insight into the problem of sintering dense, pore-free material.

Polished and etched sections of pressed nuclear grade CSZ and YSZ sintered at 1950° C for 2 h showed that considerable porosity was present, both within the grains and at the grain boundaries. The YSZ microstructure had an average grain size of 35 μm with 10 to 15 μm pores at the grain boundaries, particularly at the triple points. The bulk of the porosity lay within the grains and was somewhat smaller, about 5 μm, although some larger pores were present. The CSZ microstructure was similar and had a similar average grain size but the porosity was slightly smaller, being 5 to 8 μm at the grain boundaries, An area denuded in pores close to the grain boundaries was observed in most of the grains.

Microstructures of the tape-produced technical grade material sintered at 1480° C for 3 h is shown in Fig. 8. For the TiO_2 doped material, the average grain size was approximately 19 μm, with most of the porosity located at grain boundaries and in the centre of the grains. The etched microstructure exhibited channels between the grains due to the selective etching of segregated impurities. The sizes of the pores were about 2 to 8 μm at the grain boundaries, and about 2 μm within the grains. Al_2O_3 appeared to inhibit grain growth to a certain extent, since the Al_2O_3-bearing tape exhibited an average grain size of 12 μm. Again chanelling between grains was seen due to etching, with larger pores (4 to 6 μm) at the grain boundaries. White spots were observed within the grains in both the tape-produced sections and also in the technical grade pellets; these spots were not evident in the nuclear grade CSZ or YSZ materials.

The state of the TiO_2 and Al_2O_3 dopants in the zirconia was studied by electron microprobe analysis. X-ray intensity traces were made for these and other main impurities, notably Fe, Mg and Si. The Fe impurity was found to be at a very low level throughout the sample, with no difference between the grain and grain boundary levels. The Mg impurity was also at a low level, but was more concentrated at the grain boundaries; this was more pronounced in the Al_2O_3-doped tape. The Si impurity was present at a very low level within the grains, with high concentrations at the grain boundaries. Zr was depleted at the grain boundaries.

The main difference between the two sintering aids was that whereas the TiO_2 was present both within the grains and at slightly higher concentrations in the grain boundaries, Al_2O_3 was predominantly present as a grain boundary phase. The electron probe analysis also identified the white spots visible metallographically as either free SiO_2 or some silicate phase, since these areas were very high in Si and depleted in Zr and Mg. No change in Fe content was observed, and when doped with TiO_2, these areas were depleted in Ti, while the Al content was high in the Al_2O_3 doped tapes.

3.3. Strength measurements

Strength data for the tape-produced material was obtained from a three-point bending test over a 1.2 in. span. The material was cut into bars prior to sintering at 1480° C for 3 h. The strengths of the Al_2O_3 and TiO_2-doped tapes were 32 500 p.s.i. and 31 300 p.s.i., respectively, which were slightly higher than that for the pressed material (27 100 p.s.i.). The flexural moduli for the two compositions were also measured, giving values of approximately 24×10^6 p.s.i.

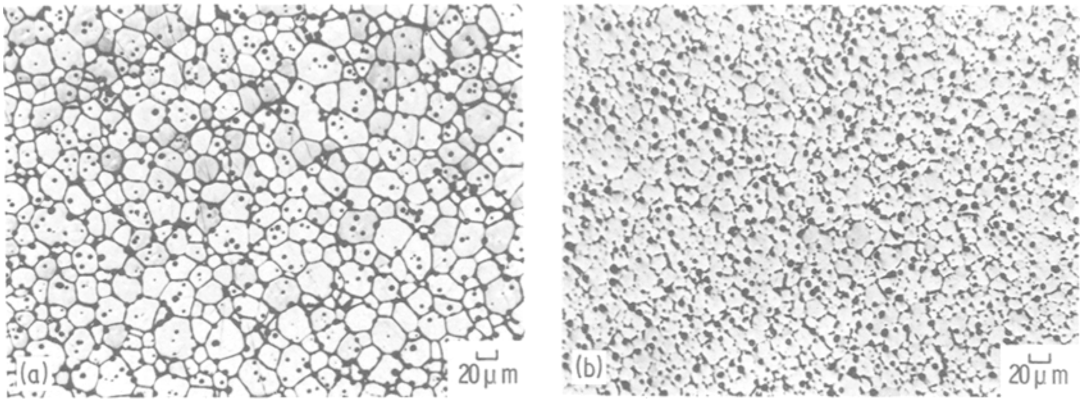

Figure 8 Etched microstructure of CSZ with (a) 5 mol % TiO_2 and (b) 2 mol % Al_2O_3.

4. Discussion

The metallographic study showed that highly porous structures were obtained on sintering the pure ZrO_2 powders, with pores trapped within the grains during grain growth. This situation is not conducive to high densities since pores far from grain boundaries will not diffuse out of the grains. The large pores located at grain boundary triple points also appear to be relatively stable as shown by the negligible change in density and microstructure on sintering at temperatures in excess of 1560° C. This microstructural development is a direct consequence of the starting powder, which even after intensive milling treatments (up to 500 h) did not reduce to a very fine size distribution or increase the surface area significantly. Only by different preparation techniques, such as by decomposition of an organo-metallic material, can an active ZrO_2 powder capable of being sintered to high density at temperatures below 1500° C be produced without recourse to a sintering aid. These powders are more expensive and make the tape process economically less favourable.

Several additives were found to enhance the sinterability of the powders sufficiently to allow the tape technique to be utilized. The most useful additives were TiO_2 and Al_2O_3 (apart from Fe_2O_3 which was found to require somewhat more addition) thus confirming earlier results [4, 5]. It was observed that densification occurred by a liquid phase mechanism as seen by the grain boundary phases and rounded grain morphologies, and was observed to be more pronounced in the case of Al_2O_3 than with the TiO_2, possibly due to the more limited solid solubility of the Al_2O_3.

The observation of liquid formation during sintering at 1480° C is interesting because reported phase diagram studies do not indicate the presence of liquid in either the $ZrO_2-Al_2O_3$ or ZrO_2-TiO_2 systems below 1710° C and 1650° C, respectively [8]. It is probable that reaction of the dopant with impurities results in the liquid phases which enhance sinterability. Such reactions can be very complex due to the number of components present, but are expected to contain primarily the major impurities, Si and Mg, since they are concentrated at the grain boundaries.

A synergistic effect must exist since no binary oxide phase exhibits a sufficiently low melting point to account for the enhanced sintering at the lowest temperatures studied. Liquid phase formation occurs in the $Al_2O_3-SiO_2-MgO$ system at temperatures as low as 1355° C while in the absence of MgO, a temperature of 1546° C is required: The depletion of Mg within the grains supports the contention that a ternary liquid phase is formed. No relevant multi-component phase diagram data exists for TiO_2, but a ternary composition containing SiO_2 and MgO is expected since no appropriate binary oxide phase is liquid below 1500° C. However, since the grain boundaries are depleted in ZrO_2, the formation of a liquid phase containing CaO (or Y_2O_3) is entirely possible: Several liquid compositions having melting points below 1400° C occur with Al_2O_3, and liquid is formed at 1460° C in the $CaO-TiO_2$ system. The combined addition of Al_2O_3 and TiO_2 sintering aids are also predicted to form multi-component liquid phases since binary liquids are not formed below ~ 1700° C and cannot therefore account for the enhanced sinterabilities observed at lower temperatures.

The results show that tape-produced solid electrolytes can be prepared below 1500° C with any of the commercial zirconia powders studied by using either of these two additives or a combination. The sintered density of the tape-produced material was higher at the lower sintering temperatures than those of the pressed pellets. This is a frequently observed phenomenon and is inherent to the process. In the tape, the ceramic powder is extremely well dispersed and very uniform shrinkage occurs on sintering. In contrast, density gradients generally exist within pressed material which result in a less homogeneous sintering behaviour.

5. Conclusions

Addition of 2 mol% Al_2O_3 or 5 mol % TiO_2 to commercial CSZ and YSZ improves the low temperature sinterability of the powders and allows impervious, high density (>93%) electrolytes to be made at temperatures below 1500° C. Sintering occurs by a liquid phase mechanism. Electrolytes made using tape technology show slightly higher densities than conventionally pressed pellets when sintered under the same conditions.

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