

Physical and electrical properties of yttria stabilised zirconia prepared from nanosized powders

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Nanosized powders of $ZrO_2-10 \text{ mol-}\%Y_2O_3$ were prepared by a wet chemical process, with the main purpose of verifying changes in the physical properties of powders, and to study their influence on the electrical resistivity of the sintered ceramic. Optimisation of some parameters involved in the synthesis process resulted in a powder with high specific surface area ($>150 \text{ m}^2 \text{ g}^{-1}$) and with monomodal pore size distribution. The rate of shrinkage was a maximum at 1040°C and high density was obtained on optimising the firing schedule. Impedance spectroscopy results show that the intragrain resistivity was approximately equal to that of a single crystal of the same chemical composition. BCT/520

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INTRODUCTION

Fully yttria stabilised zirconia is an ionic conductor that is used as a solid electrolyte for electrochemical devices such as oxygen sensors, fuel cells, and oxygen pumps.¹ Zirconia based ceramics are, in most cases, prepared by the coprecipitation of the desired cations from aqueous solutions. This chemical route offers a simple way to obtain reactive powders with suitable properties for processing of ceramic components.

In recent years a great deal of emphasis has been placed on improving the quality of ceramic powders, since their physical and chemical characteristics determine the microstructural development of the final ceramic. A great improvement in the chemical processing of zirconia based solid solutions is obtained by washing the gel particles with a low surface tension liquid. This procedure facilitates the removal of residual water and avoids the formation of hard agglomerates.² However, for the complete elimination of residual water from the precipitate, a large number of washing cycles is necessary.³ Alternatively, other procedures such as azeotropic distillation^{4,5} or freeze drying^{5,6} may be used for this purpose. Several other parameters involved in the precipitation process are known to affect powder properties,⁷⁻¹⁰ however the agglomeration of fine particles determines the degree of densification during sintering and hence most of the ceramic properties. As a general rule, agglomerates must be eliminated once they are formed. For this purpose, as prepared or calcined powders are wet or

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dry milled. The main disadvantage of this milling step is that it usually causes contamination of the powder. During synthesis certain processing steps may be used to control agglomerate properties, especially agglomerate strength.¹¹ Moreover, most solution methods of synthesis give rise to agglomerated powders. For these reasons, methods that allow for the control of powder agglomerates are still under study.

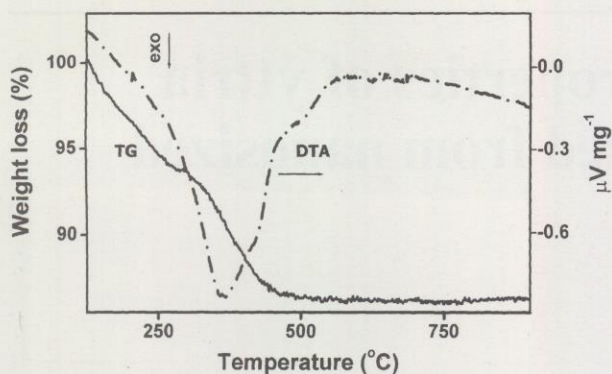
It has recently been shown that $ZrO_2-8 \text{ mol-}\%Y_2O_3$ powders produced by coprecipitation followed by azeotropic distillation have suitable properties for the preparation of ceramic membranes by a dip coating process.¹² In the present work, nanosized powders of $ZrO_2-10 \text{ mol-}\%Y_2O_3$ were prepared by the coprecipitation technique. The aim was to characterise the effect of the synthesis optimisation process on some physical properties, with respect to the application of the fabricated material as a bulk solid electrolyte. The electrical conductivity of a sintered specimen was compared with that of a single crystal with the same chemical composition.

EXPERIMENTAL PROCEDURES

Starting materials were $ZrOCl_2 \cdot 8H_2O$ ($>98\%$ purity) and Y_2O_3 (99.9%). All other reagents were of analytical grade. Deionised water was used to prepare a zirconyl chloride solution. Yttrium nitrate solution was prepared by dissolution of the starting material in nitric acid.

An aqueous coprecipitation technique was used for the synthesis of the solid solution. Precursor solutions were mixed under stirring and the concentration of the resulting solution was adjusted to 0.1M. Coprecipitation was performed using ammonium hydroxide as the precipitating agent. During coprecipitation the pH was continuously monitored and maintained at a value above 9.5 to ensure simultaneous precipitation of cations. After the completion of precipitation, the gel was digested for 2 h. Washing (four times) of the precipitate was carried out with diluted (10 vol.-%) ammonia solution, followed by absolute ethanol (twice) and isopropanol (once). Dehydration was carried out by azeotropic distillation with *n*-butyl alcohol. After drying, the precipitate was calcined at 500°C for 1 h. The nominal yttria concentration was 10 mol-%. Cylindrical specimens were prepared by uniaxial and isostatic pressing. Sintering of compacts was carried out at 1400°C for 2 h in air.

Simultaneous thermogravimetry and differential thermal analysis (STA 409, Netzsch) were carried out on dried precipitates in air with a heating rate of 10 K min^{-1} . The reference material was α -alumina. Specific surface area and pore size distribution of the calcined powder were determined by nitrogen adsorption (ASAP 2010, Micromeritics) using, respectively, the Brunauer, Emmett, and Teller (BET) and Barret, Joyner, and Halenda (BJH) methods. The linear shrinkage of powder compacts was followed from room temperature up to 1650°C (DIL E/7 402, Netzsch) with a heating rate of 10 K min^{-1} . Apparent density measurements



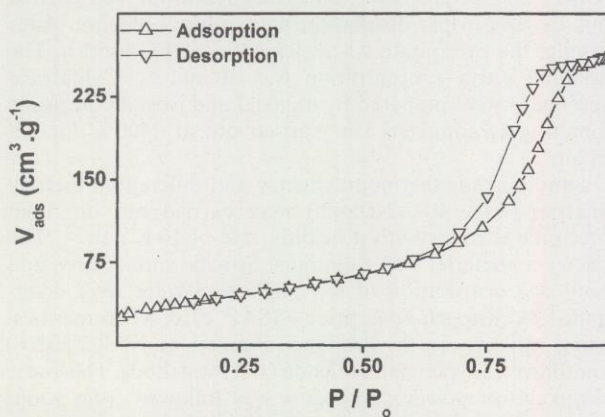
1 TG-DTA curves of dried precipitate

were carried out by the water immersion technique. Fractured surfaces of sintered pellets were observed by scanning electron microscopy (XL30, Philips). Electrical resistivity measurements were carried out by impedance spectroscopy using an HP 4192A impedance analyser in the 5 Hz–13 MHz frequency range, and in the 250 to 550°C temperature range. Platinum paste (A308 Demetron) was applied by painting onto pellet surfaces and firing at 800°C for 1 h for use as electrode material. For comparison purposes, impedance measurements were also carried out on a fully yttria stabilised zirconia single crystal (Crysmatec, Gière, France) with the same chemical composition as that of polycrystalline specimens.

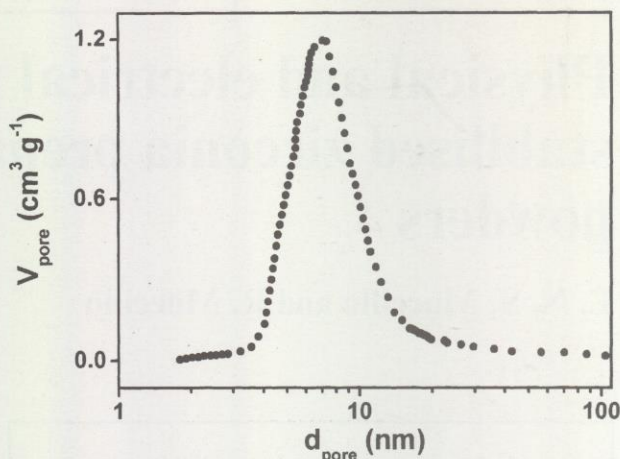
RESULTS AND DISCUSSION

Figure 1 shows results on the decomposition of the precipitated material obtained by thermal analysis. Most weight loss occurred between 150 and 450°C, and beyond this temperature it was negligible. Total weight loss was 15% and is attributed to the thermal decomposition of precipitated hydroxides and to residual organic matter from the alcohol washings. The differential thermal analysis curve shows that loss of organic matter and crystallisation were the main thermal events in this temperature range. From these results the temperature for the decomposition of the precipitate was selected as the crystallisation peak temperature (500°C).

Typical adsorption and desorption isotherms of the calcined powder are shown in Fig. 2. This behaviour is characteristic of type IV in the BDDT classification,¹³ assigned to a well developed mesopore system. The specific surface determined by the BET method was 152 m² g⁻¹. This comparatively high value is attributable to the optimised parameters of the synthesis technique. Recently¹² the same technique was used to prepare ZrO₂-8 mol-%Y₂O₃ powders with specific surface of 90.7 m² g⁻¹. In that study



2 Adsorption/desorption isotherms of calcined powder

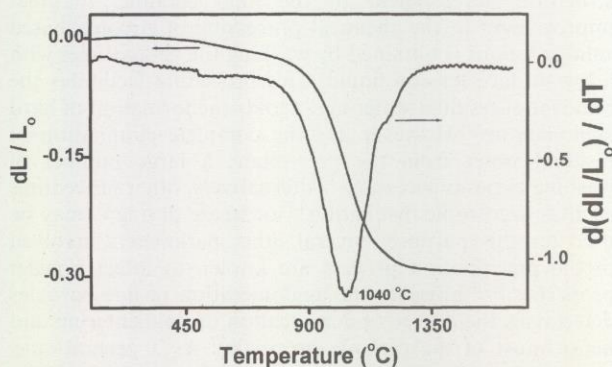


3 Pore size distribution of calcined powder obtained by BJH method

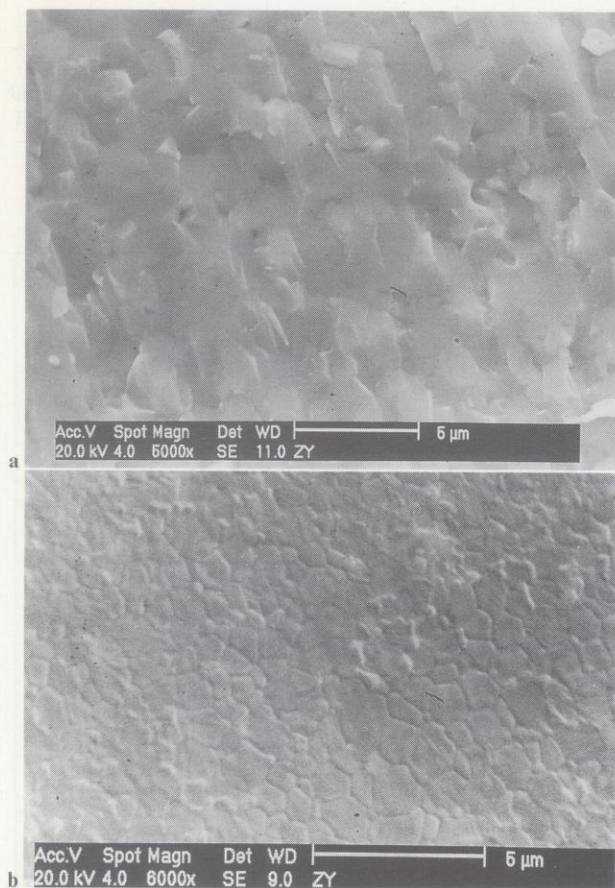
some aspects of the synthesis process, for example the washing cycle, concentration of the cation solution, solvent, and the way in which precipitation was performed, differed from the present work. In addition, the dried precipitate was calcined at a temperature 100°C higher than in the present case. It is already known that varying such parameters in the synthesis process can produce powders with quite different characteristics. In this context, coprecipitation is a synthesis technique sensitive to a large number of parameters that should be rigorously controlled in order to maintain the reproducibility of the process.

From the specific surface area determined by the BET method and for a theoretical density of 5.96 g cm⁻³, the calculated equivalent spherical diameter is 6.6 nm. Assuming a cylindrical pore shape, the pore size distribution in the calcined powder determined by the BJH method is shown in Fig. 3. This distribution shows a monomodal distribution of pore sizes with an average size of 9 nm. In general, zirconia solid solutions show a bimodal pore size distribution, the two pore size populations being attributed to intra- and interagglomerate pores. The latter are believed to be responsible for retarding ceramic densification.¹⁴ The distribution shown in Fig. 3 exhibits only the peak due to intra-agglomerate pores and, consequently, a high densification at a comparatively low temperature can be expected.

Figure 4 shows the linear shrinkage of a powder compact. The total shrinkage is approximately 30%. The compact started to sinter at around 600°C, and up to 900°C the shrinkage was less than 5%. This should correspond to the rearrangement of particles characteristic of the first stage in solid state sintering. In the temperature interval between 900 and 1200°C rapid shrinkage (about 20%) occurred. At temperatures higher than 1200°C the rate of



4 Linear and derivative shrinkage curves of powder compact

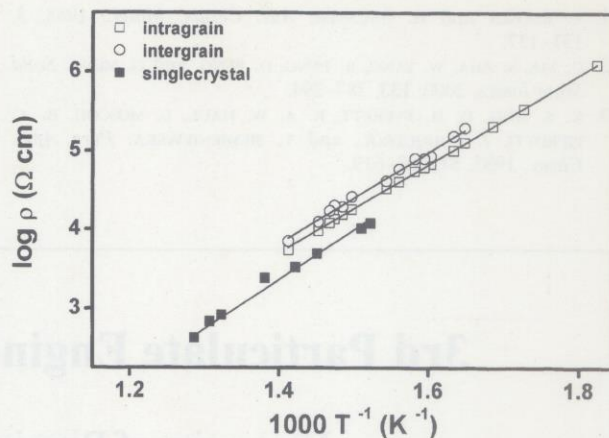


5 Scanning electron micrographs of sintered specimen

densification was quite low owing to the predominance of grain growth. The shrinkage rate reached a maximum at 1040°C, as shown in the derivative curve of the linear shrinkage (Fig. 4). This curve shows only one peak, in agreement with the monomodal pore size distribution. It was shown recently that pressed commercial powders of ZrO_2 -8 mol-% Y_2O_3 had maximum shrinkage at temperatures between 1330 and 1380°C.¹⁵ Considering that most commercial powders are also produced by coprecipitation, differences in powder densification may be attributed to the optimisation of the synthesis parameters. The apparent density value obtained by the immersion technique was 99.6% after sintering at 1400°C for 2 h. These are the sintering conditions normally used, especially for fully yttria stabilised zirconia compacts.

Fractured surfaces of a sintered specimen are shown in the scanning electron micrographs in Fig. 5. A transgranular fracture mode predominated (Fig. 5a). Some regions, however, showed a different appearance (Fig. 5b): in these regions, the grain size was submicrometre and the porosity negligible. It is already known that in zirconia based ceramics cubic grains are larger than tetragonal or monoclinic grains.¹⁶ Moreover, intragranular porosity is usually observed in cubic zirconia ceramics. These microstructural characteristics of fully yttria stabilised zirconia prepared using nanosized powders are believed to be a consequence of the controlled agglomeration of the powder.

Electrical resistivity measurements were carried out by impedance spectroscopy on single crystal and polycrystalline specimens. The impedance diagrams of the single crystal show only one semicircle due to lattice resistivity. The impedance diagrams for the polycrystalline ceramics show two semicircles known to be related to intragrain (high frequency) and intergrain (low frequency) resistivities. Figure 6 shows Arrhenius plots obtained over the temperature interval 250–550°C. For a given temperature, the



6 Arrhenius plots of electrical resistivity of single crystal and polycrystalline specimens

relative magnitudes of intragrain and lattice resistivities agree within the experimental error of 10%. Activation energy values are 1.13, 1.15, and 1.18 eV for intragrain, intergrain, and lattice resistivities respectively.

CONCLUSIONS

Nanosized zirconia–yttria powders were prepared by a coprecipitation technique. By optimising the processing parameters powders with specific surface areas larger than $150 \text{ m}^2 \text{ g}^{-1}$ and average pore size of 9 nm were obtained. Sintered specimens with relative densities >99.5% were obtained at the sintering temperature of 1400°C frequently used for this ceramic material. The intragranular response of the polycrystalline specimens, observed by impedance spectroscopy, had the same magnitude as that of a single crystal with similar chemical composition. The main conclusion is that electrical resistivity does not depend on many of the physical and microstructural properties that are significantly modified by the processing of zirconia powders.

ACKNOWLEDGEMENTS

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3rd Particulate Engineering Technology Fair

University of Birmingham, 26 March 2003

Organised by the Particulate Engineering Committee of the Institute of Materials, Minerals and Mining in conjunction with the new Faraday network for Rapid Manufacturing through Powder Processing, the third Fair will follow the format of the previous successful events in March 1999 and 2001. The objective will be to bring together those involved in powder metallurgy, particulate engineering, and materials handling to review important developments and to provide networking opportunities. An extended poster session will be followed by specialist workshops which will report back to a concluding plenary session.

This will be a modestly priced event with a preferential rate for students.

Preliminary programme

- 0930 **Registration**
- 1000 **Plenary session**
PE Technology Fair Lecture Printing and Painting from a Palette of Particles
Professor Julian Evans, Queen Mary University of London.
Automotive Needs Tom Chatterly, MIRA
Nanopowders speaker to be confirmed
- 1130 **Poster and exhibition session:** coffee and a buffet lunch will be available during the session, which will provide an extended opportunity for delegates to network and discuss topics of mutual interest.
- 1345 **Workshops:** potential topics include ♦ the Faraday network on Powder Processing
♦ powder handling and characterisation ♦ health and safety and environmental issues
♦ sintering ♦ mechanical performance ♦ EC Framework 6 topics. Those attending will be asked to indicate in advance to which session they wish to contribute.
- 1515 **Concluding plenary session** reporting on the workshops.

Those interested in attending the Technology Fair or in submitting a poster should contact Dr Bryan Roebuck (Chairman, IOM³ Particulate Engineering Committee), National Physical Laboratory, Teddington, Middx TW11 0LW, UK, tel. +44 (0) 20 8943 6298, fax. +44 (0) 20 8943 2989, email br@npl.co.uk or Dr Isaac Chang, Metallurgy and Materials, School of Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, tel. +44 (0) 121 414 5167, fax. +44 (0) 121 414 5232, email i.t.chang@bham.ac.uk.