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MECHANICAL PROPERTIES OF 8 MOLE% YTTRIA-STABILISED ZIRCONIA FOR SOLID OXIDE FUEL CELLS

A.G. Mawson[1], G.A. Carter[2], R.D. Hart[1], N.M. Kirby[1], A.C. Nachmann[1]

[1]Materials Research Group, Department of Imaging and Applied Physics,
[2]Nanochemistry Research Institute, Department of Applied Chemistry,
Curtin University of Technology, Perth, Western Australia, 6845

ABSTRACT

Both high ionic conductivity and mechanical strength are important when considering the potential application of ceramics in solid oxide fuel cells (SOFC). Yttria stabilised zirconia compounds can be used as both the electrolyte and anode support structure in self supporting SOFC and as a result, there is great interest in the development of these materials. The high ionic conductivity of an 8 mol% Y_2O_3 – ZrO_2 formulation, must be combined with suitable mechanical hardness and toughness, in order to qualify for SOFC application. The availability of suitable materials has been limited with the majority of suppliers having only small scale manufacturing capability. This study has investigated the physical and mechanical properties of a commercially available $ZrO_2(Y_2O_3)_{0.08}$ ceramic,. The product was found to contain only the cubic phase and possess the necessary structural characteristics for use in solid oxide fuel cells.

Keywords: Solid Oxide Fuel Cells (SOFC), Yttria stabilized zirconia, ZY8, Mechanical properties

1. INTRODUCTION

The introduction of Solid Oxide Fuel Cells (SOFC) as an alternative electricity and heat generation system is contingent on the ability of the fuel cell material to consistently withstand the stresses of normal operating conditions. These include the thermal cycling that a fuel cell may undergo as well as the high temperature and high humidity that is associated with their operation. As with all engineering developments, the availability of appropriate material at the right cost and in the right quantity is an important consideration in developing viable manufacturing processes for delivering end user products.

Zirconia based materials are good candidates for SOFC applications due to their ionic conductivity, stability in oxidising and reducing atmospheres and low cost [1]. Zirconia-yttria compositions have the ability to meet the necessary structural requirements with the potential of be mass-produced with the required quality. The processing techniques for materials of these compositions are already used to manufacture oxygen ion conducting parts and are well understood

Fully stabilised $ZrO_2(Y_2O_3)_{0.08}$ is the composition at which maximum oxygen ion conductivity occurs [2]. At typical SOFC operating temperatures (850-1000°C), industrial grade 8 mol% solid solution typically exists in two phases, tetragonal and cubic [3]. SOFC manufacturers therefore use 10 mol% yttria materials to ensure the existence of only a single phase and hence stability under autoclave conditions, at the cost of reduced ionic conductivity [4]. This study outlines results obtained during the investigation of a fully cubic zirconia composition with close to 8 mol% yttria-stabilised zirconia. The final ceramic has been characterised for its mechanical properties including, Vickers hardness, fracture toughness (K_{1c}), modulus of rupture (MOR), density and grain size. The material was examined at a microstructural level using TEM and phase composition determined using x-ray powder diffraction.

2. MATERIALS AND METHODS

8 mol% yttrium zirconia powder marketed as DSC-ZY8 was obtained from Doral Specialty Chemicals. The particle size distribution of the powder was determined using a Coulter LS 320 laser particle-sizing instrument. The specific surface area was analysed using BET conducted using a MicroMeretics Gemini instrument with *Flow Prep*© method. Chemical analysis was conducted by Inductively Coupled Plasma (ICP) optical emission spectrometry and X-Ray Fluorescence spectrometry (XRF). XRF data was obtained using a Siemens SR 3000 using pressed pellets and ICP was conducted on hydrous cake by Ultra Trace Pty. Ltd. Dilatometery was conducted at ANSTO Lucas Heights facility using a scanning laser dilatometer on pressed pellets, in air up to 1500^{o}C.

Sample pellets and bars for mechanical testing were formed by uniaxial compaction at 100 MPa, then cold isostatic pressed for 1 minute at 200 MPa. All samples were sintered at 1500° C for 1 hour, using a heating rate of 300 °C.hr^{-1} over the range 400-1500°C.

Green and sintered densities were measured according to ASTM C20 (1992). Pellets for hardness, toughness and grain sizing, were polished to 1μm diamond finish. The bars used for MOR analysis were diamond machined parallel to the specimen axis to a 3μm finish.

Hardness was measured using Vickers indentation, ASTM E 384-99 (2000). The indentations were made using a Zwick hardness tester fitted with a United Kingdom Accreditation Service (UKAS) 0441 calibrated diamond indent tool. using a load of 20N maintained for 30 seconds. The instrument was calibrated using an Asahi test block, returning values within certification. The indentations where measured using a Nikon Eclipse ME600 optical microscope and digital imaging system. The fracture toughness (K_{1c}) values were derived using the Vickers crack propagation method as per Anstis *et al*. [5].

The modulus of rupture values were gathered from bars of dimensions 3x4x55mm, using the four-point bending method, ASTM method C1161-94 (1996). The values obtained during the MOR testing were tabulated and a Weibull Modulus determined.

Images for grain sizing were obtained using a Philips XL30 SEM. The grain size was determined using the Abrams' three circle method from ASTM E-112. Fracture surfaces from the MOR test bars were also examined using SEM.

Specimens were selected for microstructural analysis utilising either a JEOL 3000F TEM or a JEOL 2011 TEM. The samples were prepared for transmission electron microscopy by hand polishing 3.05mm discs, dimple grinding and ion beam milling to electron transparency using a Gatan PIPS operating at 4-5 keV.

X-ray diffraction (XRD) patterns of the samples were obtained using a Siemens D500 diffractometer with Bragg-Brentano optics, using Cu Kα radiation. XRD patterns of the powder were collected from 3-120°2θ and of the pellet from 20-120°2θ with step size 0.02°. Phase analysis of the patterns was conducted using MDI Jade version 6.0.3 analytical software [6]

3. RESULTS

The results of the chemical analysis of the powder prior to sintering (Table 1), show that the material contained 14.0 wt% or 8.2 mol % Y_2O_3. The data for silicon (<20 ppm), sodium (<20ppm) aluminium (<10ppm) and calcium (<10ppm) collected using ICP – OES indicated that there are no impurities present in the product within the limits of detection. The N_2-BET specific surface area was 8.06 m^2/g and the particle size range determined by laser particle-sizing instrument was d_{10} 0.107, d_{50} = 0.350 and d_{90} = 1.613 μm.

Table 2 reports the physical properties of the precursor powder and the mechanical properties and densities (green and fired) of the final ceramic. The values given in brackets represent the error in the least significant figure, described by one standard deviation. This differs however, for the measured grain size, where two standard deviations are reported in order to remain consistent with established literature.

Table 1. Results of chemical analysis of powder.

Test	Result
XRF	
wt% Y_2O_3	14.0
(mol% Y_2O_3**)**	**(**8.2)
ICP	
Si (ppm)	<20
Na (ppm)	<20
Al (ppm)	<10
Ca (ppm)	<10

Table 2. Results of Mechanical Testing.

Test	Result
Powder	
Particle Size (μm)	
d50	0.350
d90	1.613
d10	0.107
BET Specific Surface (m^2g^{-1})	8.06
Final Product	
Hardness (GPa)	11.9(4)
Toughness (MPa $m^{1/2}$)	1.3(1)
MOR (MPa)	262(27)
Weibull Modulus	10.1
Linear Shrinkage %	20.5(2)
Green Density (gcm^{-3})	2.99(1)
Sintered Density (gcm^{-3})	5.87(1)
Grain Size (μm)	2.6(2)

The XRD pattern of the powder, shown in Figure 1, demonstrates that the powder consists of only cubic phase material. The XRD pattern obtained from the sintered pellet (Figure 2) also contained only cubic material, and indicates that no phase change occurred due to thermal cycling experienced during sintering. The dilatometry curve (Figure 3) supports this with smooth shrinkage being displayed with a single maximum change of 22% obtained at close to the maximum sintering temperature of 1500°C. The 22% shrinkage from dilatometry agrees with the linear shrinkage value of 20.5 % (Table 2).

The sintered sample density achieved was 98.3% of the theoretical density of the 8 mol% $Y_2O_3 – ZrO_2$ reported by Ingel and Lewis [7]. SEM analysis (Figure 4) shows a number of small pores present in the material which was also confirmed using TEM. Porosity is also demonstrated by the edge highlighting seen in the SEM images. The porosity was calculated by determining the number of pixels observed as pores in several micrographs; the area-weighted result was converted to a volumetric result of around 1.1%, close to the 1.7% determined from the density measurements.

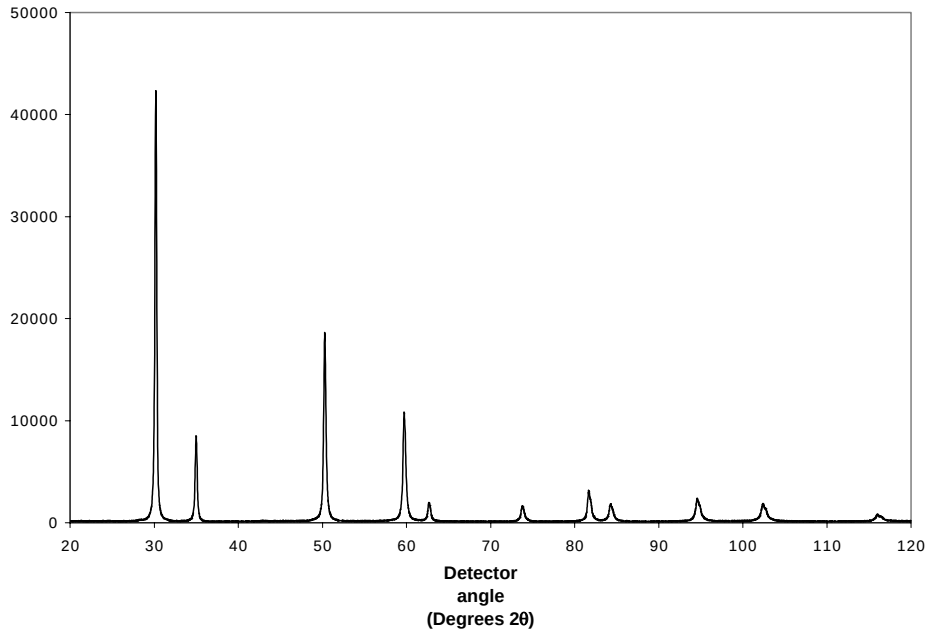

Figure 1. X-ray diffraction pattern of ZY8 powder showing a fully cubic system.

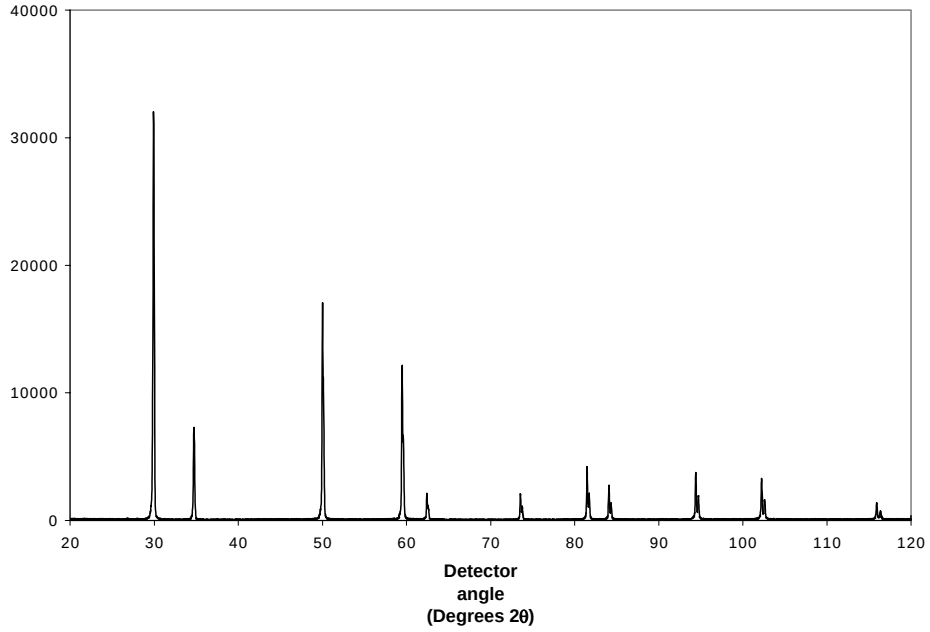

Figure 2. X-ray diffraction pattern of sintered ceramic showing a fully cubic system.

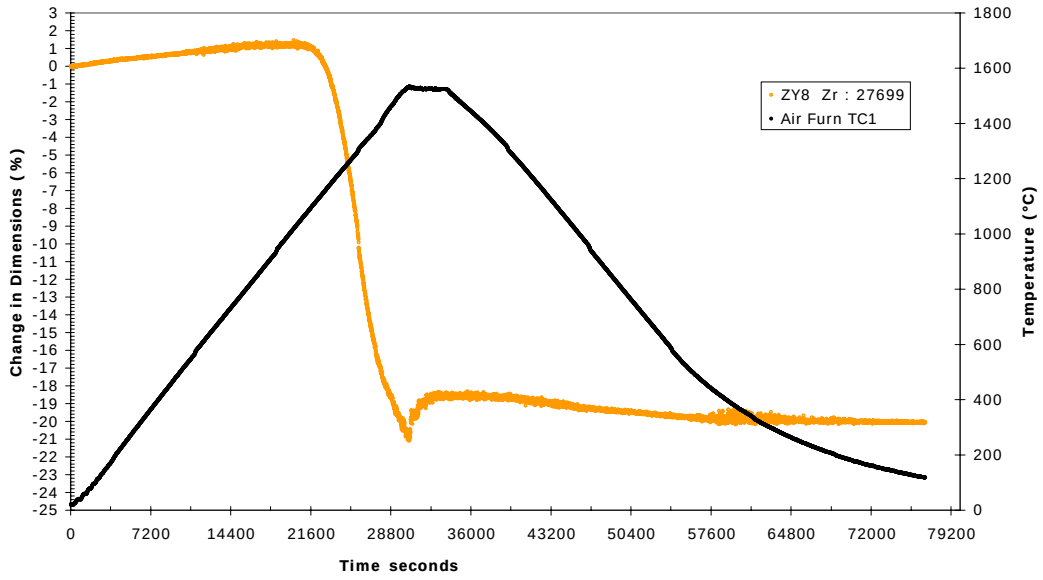

Figure 3. Dilatometry curves for sintering of ZY8.

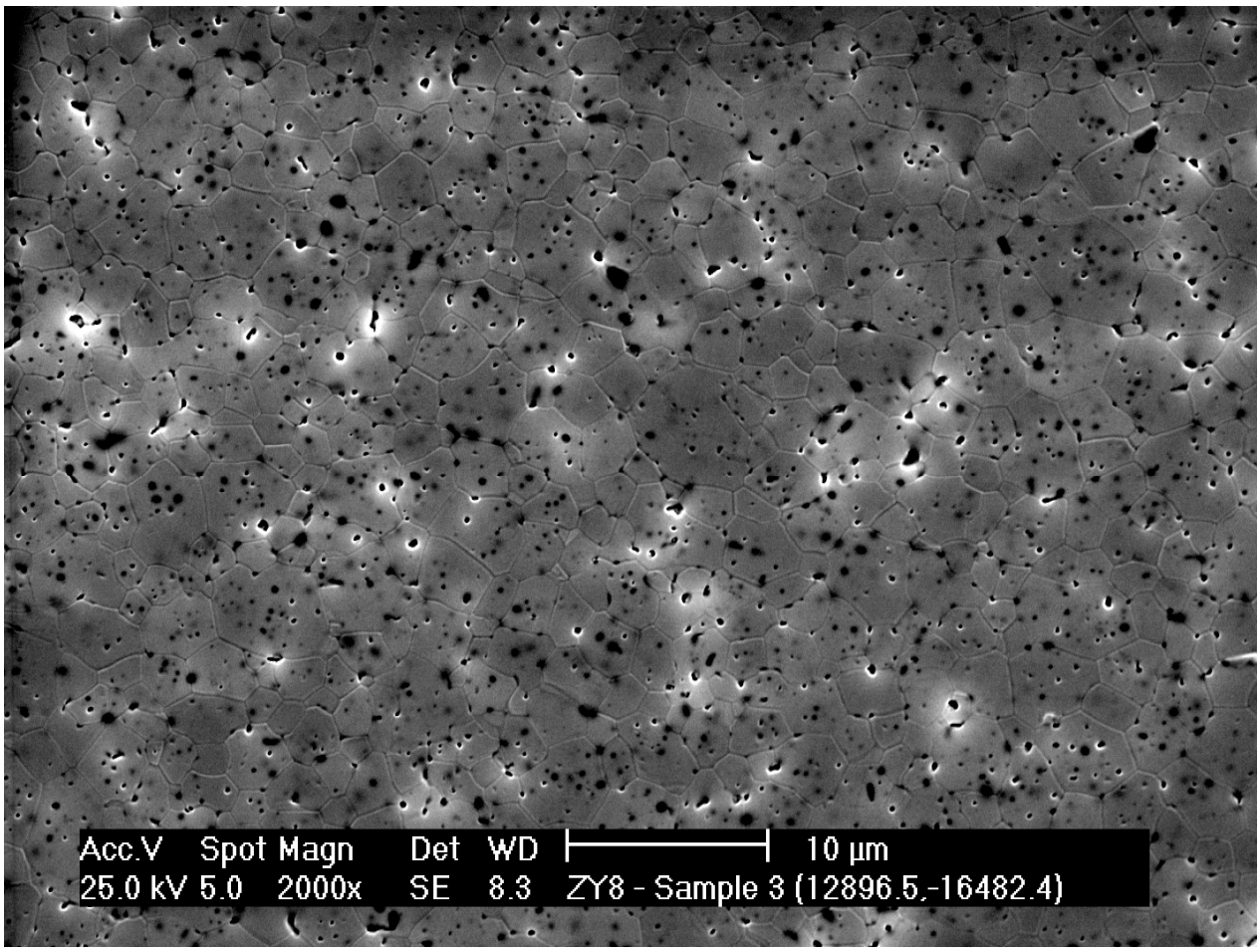

Figure 4. SEM micrograph showing small grain size and even particle size distribution and porosity of DSC-ZY8 ceramic.

The Vickers hardness value of 11.9 GPa is slightly lower than literature values for other 8 mol% Y_2O_3 ceramics containing no alumina which are typically around 13-14.5GPa [8]. This may be due to the small amount of porosity present. The fracture toughness (K_{1c}) value of 1.3 MPa $m^{1/2}$ is similar to those of other 8 and 10 mol % Y_2O_3 ceramics containing no alumina, indicative of a fully cubic ZY8 system [4]. A typical Vickers indent is shown in Figure 5.

The value obtained for the modulus of rupture of 262 MPa, is consistent with values quoted by Badwal *et al.* of between 250-300 MPa [2]. The Weibull modulus (Figure 6), developed from the MOR testing was 10.1, and is similar to those of other ceramic materials.

Typical SEM images as shown in Figure 4 were used to determine the grain size. The grain size of 2.6(2) µm obtained here is relatively small. The grain size for YSZ materials with less than 8.5 mol% yttria is usually larger than 5µm [2], almost twice the grain size measured here. The small grain size can also be seen in the TEM images (Figure 7). The TEM images also show strain at the edges of the grains within the ceramic, which is thought to be due to the small grain size, with the grains not having grown sufficiently to relieve all of the strain. This strain may also be a contributor to the lower than expected Vickers hardness value.

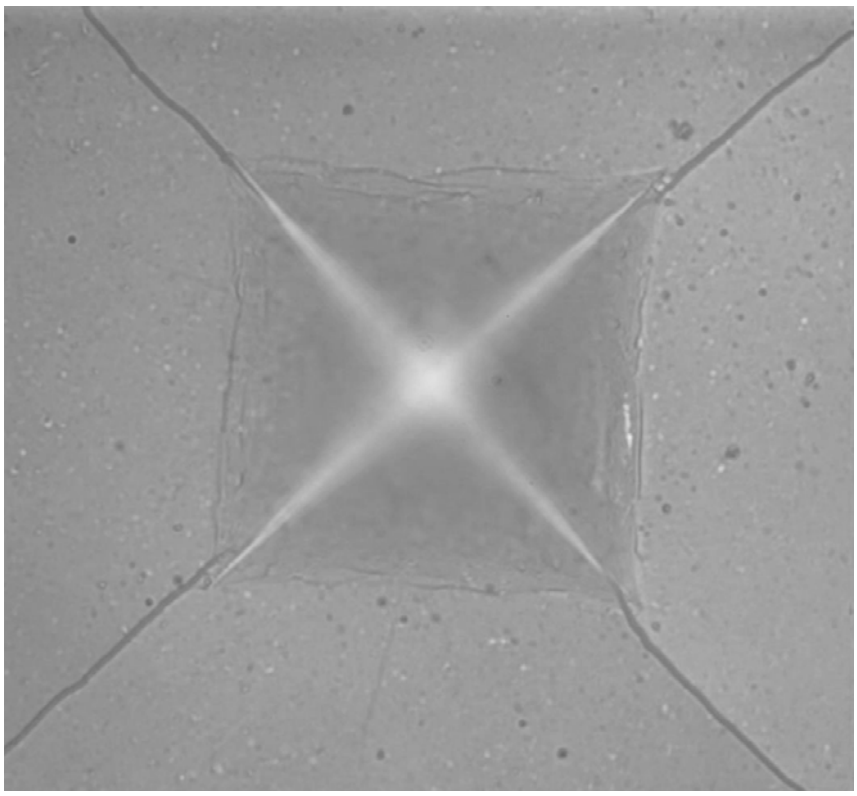

Figure 5. Optical micrograph of a typical Vickers indent at 100 times magnification.

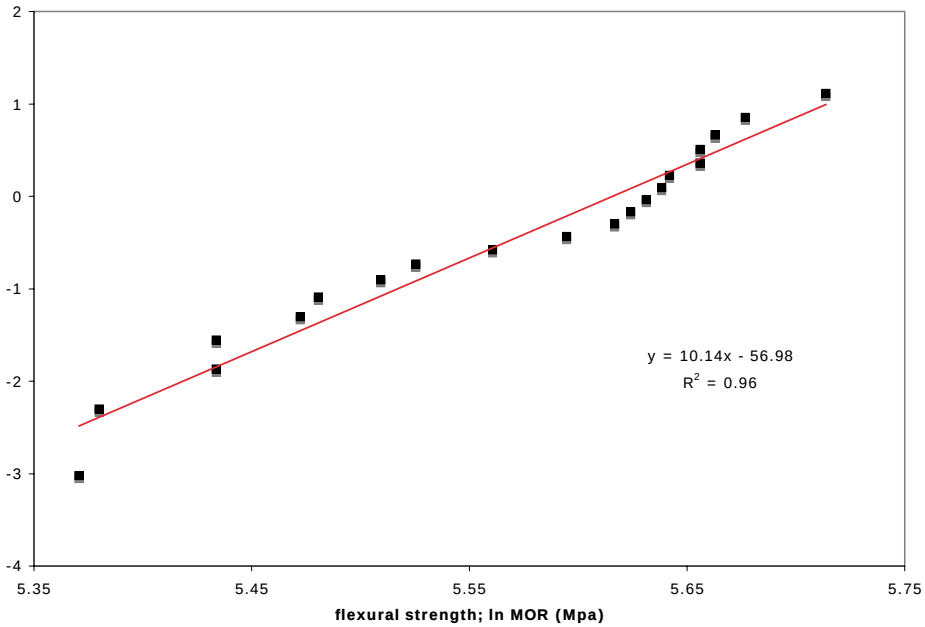

Figure 6. Weibull modulus developed from MOR testing of DSC-ZY8

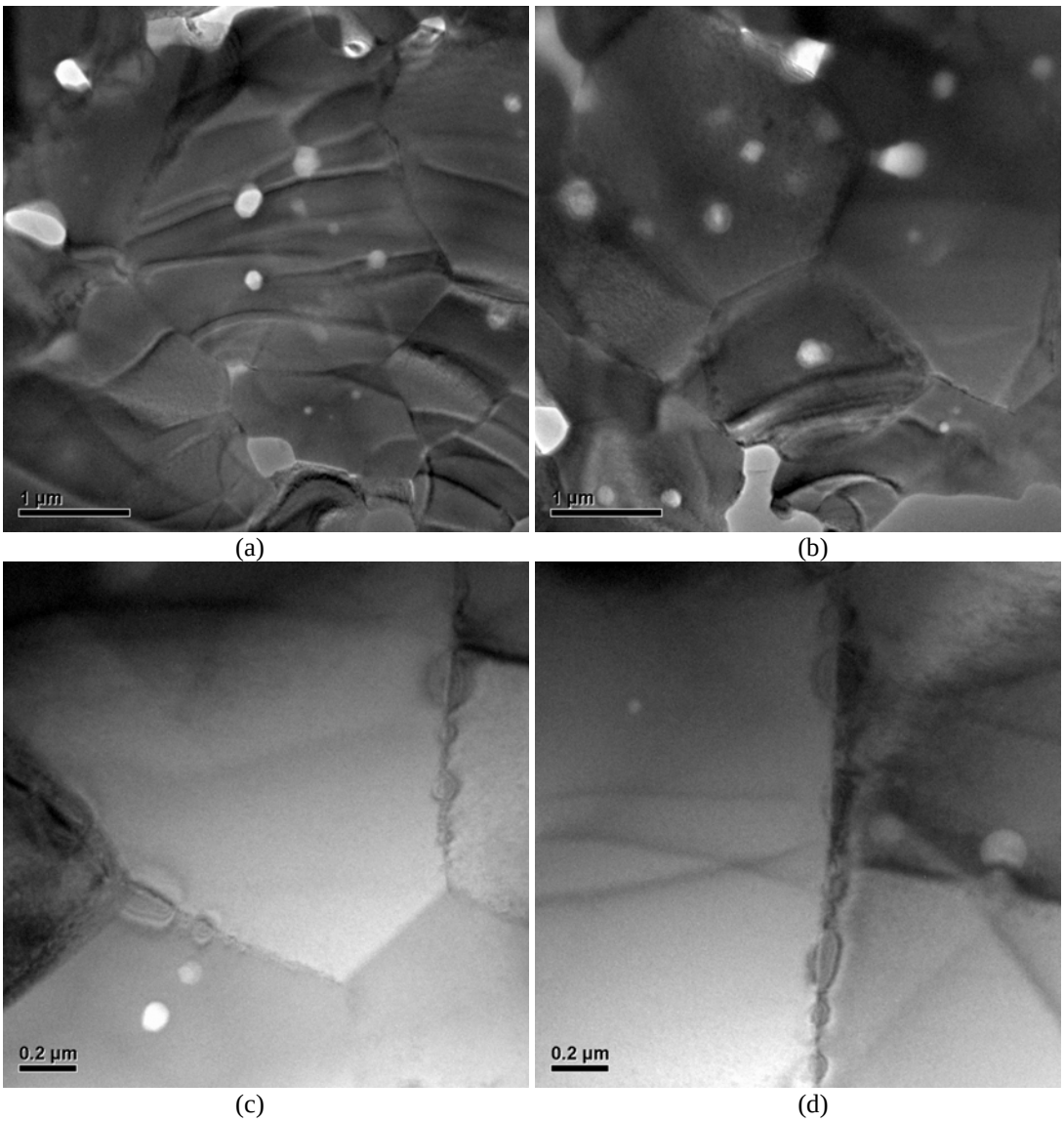

Figure 7. TEM micrographs showing; (a, b) small grain size, (c, d) grain boundary strain.

A combination of scanning TEM and energy dispersive spectroscopy was used to map the elements present in the samples. Generally the mapping (Figure 8) shows that only yttria (Y_2O_3) and zirconia (ZrO_2) are present and that the light coloured areas are pores and do not contain alumina or silica, or other low atomic number elements. A linescan showing the relative X-ray counts for the elements Si, Y and Zr across the area (figure 9) shows that the counts from all of the elements decrease in the pores. Also importantly the Y:Zr ratio is constant. The absence of Al and Si impurities was also confirmed by EDS point analysis of the pores. Si was observed in a single grain boundary triple point, Figure 7. The grain boundaries were also free of impurities, although they often show areas of strain (Figure 7).

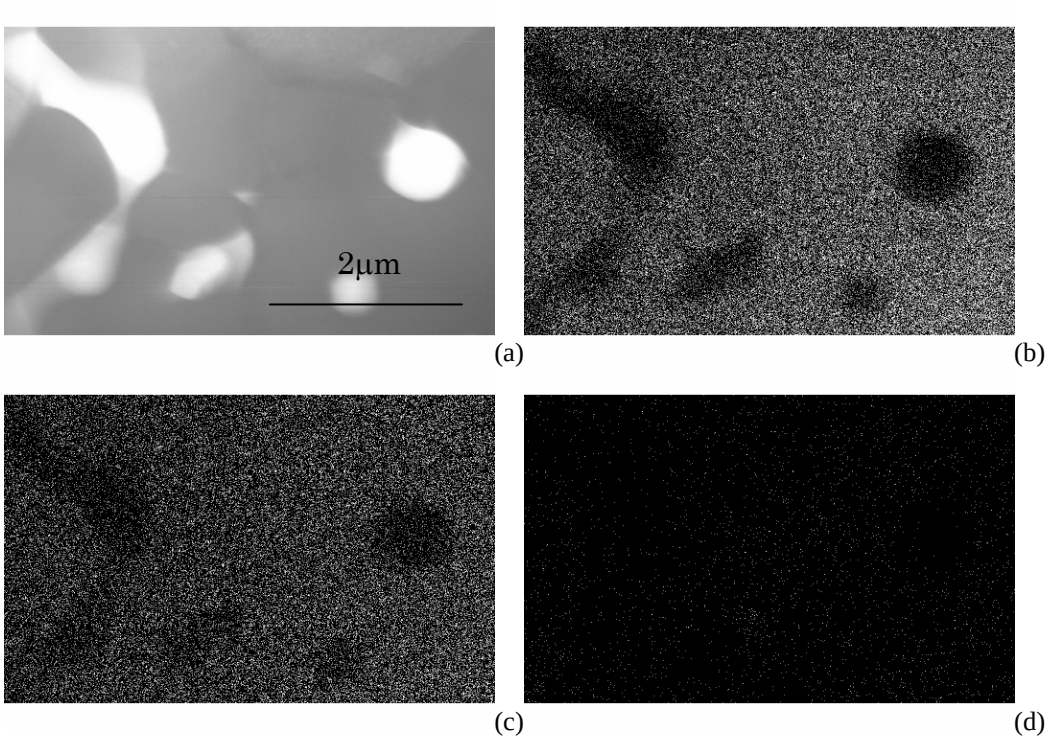

Figure 8. Image (a) and STEM-EDS maps of (b-d), Zr, Y and Si distribution

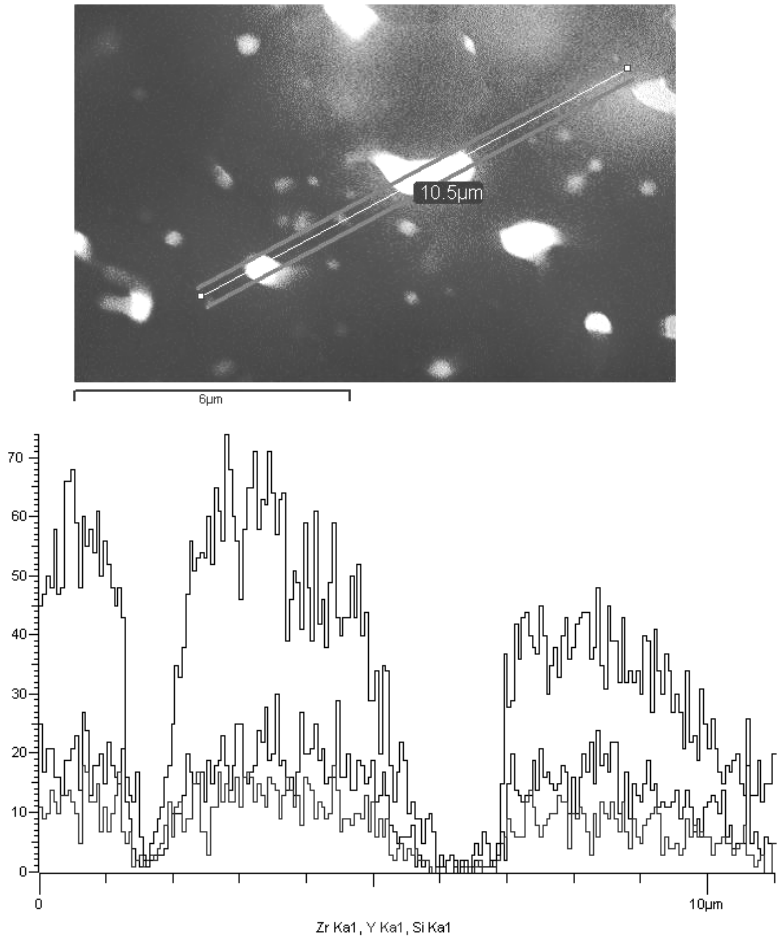

Figure 9. Linescan across map area showing counts for Zr, Y and Si. All counts rise and fall simultaneously indicating concentration changes are due to thickness changes (i.e. pores) across sample.

4. DISCUSSION

Ionic conductivity is directly affected by the presence of impurities and silica is particularly detrimental to fuel cell operation. Grain boundary impedance is increased by SiO_2 content as it congregates at grain boundaries and triple points to form glassy phases causing a constriction of the intergranular ion flow thus increasing the ohmic resistance and decreasing the mechanical strength of the material. [9] This process is one of the factors contributing to ageing, the decrease in the conductivity of a fuel cell over time. The repeated thermal cycling of SOFCs allows the impurities in the system to migrate intergranularly, but this is less likely to occur if few impurities are present. Badwal *et al.* (2004) reported that specimens with below 20ppm SiO_2 yield the best conductivity results [10], the SiO_2 concentration of DSC-ZY8 is below 20 ppm. Therefore the chemical purity of the material studied here was sufficient that grain boundary phases present in the sintered material, or their formation during SOFC applications, should be minimal.

The most significant factor contributing to conductivity in SOFC is the phase constitution of the electrolyte. The zirconia phase providing the greatest ionic conductivity is cubic [2]. Any transformation from cubic to tetragonal phase during SOFC operation will result in a degradation of the conductivity. It is for this reason that 10 mol% YSZ is usually preferred to 8 mol% YSZ, as an 8 mol% composition usually contains some tetragonal phase and is much closer to the tetragonal/cubic phase boundary [3]. Analysis of the XRD pattern shown in Figure 1 demonstrates that the powder consists of only cubic material. Examination of the XRD pattern obtained from the sintered pellet, Figure 2, also reveals only cubic material. This indicates that the ionic conductivity of the ceramic will be high when compared to similar compositions containing mixtures of tetragonal and cubic materials, a result that is demonstrated in Bellon *et.al.*[4]. Furthermore, this indicates that there is no effect on the phase of the material when pressed and fired under these conditions. This is also supported by the dilatometry results, which show a smooth densification with a single maximum.

The small grain size obtained for the DSC-ZY8 ceramic is a significant advantage for this material. Starting with a low grain size obtained for this material (2.6μm) enables manufacturers to manipulate the sintering time in order to achieve the desired result. A large grain size is likely to contribute to a lower ohmic resistance, due to fewer grain boundaries per unit area, but at the detriment of mechanical strength. A small grain size however, is likely to improve the 'flatness' of the sheets for use in SOFC stacks as investigated by Bellon *et al.* [4]. Furthermore, grain size has been linked with phase transformation; materials containing a high yttria dopant level are less likely to undergo a phase change when they have small grain size [2]. Fine grained ceramics with uniform grain size have superior mechanical properties [2]. The presence of strain indicated in the grain boundaries can probably be manipulated by increasing the grainsize, and is not seen as a large impediment.

The authors have previously shown that ceramics manufactured from similarly synthesised precursor powders were very homogenous in their yttria and zirconia distribution in powder form and as sintered ceramics [11]. This even distribution prevents local inhomogeneities and thus development of tetragonal or other phases in the ceramic during SOFC operation [12]. Mapping of the yttria concentration in these ceramics demonstrates that yttria was evenly distributed in the powder and sintered materials.

The Vickers hardness value of 11.9 GPa and fracture toughness (K_{1c}) value of 1.3 MPa $m^{1/2}$ are consistent with the values obtained for other fully cubic 8 and 10 mol % Y_2O_3 ceramics containing no alumina [4]. The value obtained for the modulus of rupture of 262 MPa, and a Weibull modulus of 10.1, is also similar to those of other ceramic materials. These values suggest that the mechanical strengths of SOFC made from DSC-ZY8 material will be similar to those of the other materials.

5. CONCLUSIONS

The 8 mol% zirconia-yttria material (DSC-ZY8) was found to be fully cubic in powder form as well as after pressing, sintering and grinding. This is a significant improvement on the tetragonal/cubic mix found in most $ZrO_2(Y_2O_3)_{0.08}$ ceramics. The mechanical strength (MOR) of the material was within the range predicted by Badwal *et al.* [2] and the hardness (Vickers) and toughness (K_{1c}) values are consistent with existing ZY8 compositions [4]. The major difference this compound introduces is a much smaller grain size, almost half that of current formulations. Thus the material represents a potentially significant enhancement to the SOFC manufacturing industry.

Acknowledgements

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