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Microwave sintering of zirconia–yttria electrolytes and measurement of their ionic conductivity

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Abstract

Yttria–zirconia electrolytes of 3 and 8 mol% Y_2O_3 nominal content have been prepared by sintering in a microwave furnace under several different conditions to obtain crack-free high density specimens. The ionic conductivity of both compositions has been investigated with a four-probe DC technique as a function of temperature over the 400°–1000°C range and as a function of time at the normal fuel cell operating temperature of 1000°C. Impedance spectroscopy has been used to separate the grain boundary contribution to the total resistivity. The results have been compared with conventionally sintered (radiant heat) materials.

Keywords: Microwave sintering; Ion conductivity; Zirconia-yttria electrolytes

1. Introduction

Microwave sintering is a relatively new technique employed for sintering of ceramics. It is a faster method and high densities can be achieved over a shorter period of sintering time compared with conventional pressureless radiant heat sintering techniques. Microwave sintering also has the potential to produce ceramics with better microstructures due to more uniform heat distribution leading to lower thermomechanical stresses [1–3]. This method is of interest for preparing possibly stress-free ceramic components for use in solid oxide fuel cells, an environmentally friendly power generation technology, and other similar electrochemical devices. In this study, investigations have been performed on microwave sintered specimens of two potential electrolyte compositions representing extremes in ionic conductivity and mechanical properties in the zirconia–yttria electrolyte system. The 8 mol% Y_2O_3–ZrO_2 composition has the highest conductivity, reported at 1000°C and it is a factor of three higher than that for 3 mol% Y_2O_3–ZrO_2 [4]. However, at room temperature its mechanical strength is about a factor of three lower than the 3 mol% Y_2O_3–ZrO_2 composition. In a previous preliminary investigation results of microwave sintered specimens which had developed cracks during sintering or had a low density were reported [5]. In this study crack-free, high density specimens have been obtained with microwave sintering and the conductivity results of these specimens

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have been compared with conventionally (radiant heat) sintered electrolyte compositions.

2. Experimental procedures

The zirconia–yttria powders of 3 (TZ3Y) and 8 (TZ8Y) mol% (nominal) Y_2O_3 content were used in this work (Tosoh, Japan). Bars were pressed from the as-received powders (without any prior milling or other treatment) in a uniaxial rectangular die 50 mm long and 5 mm wide at a pressure of ~20 MPa. Specimen bars were then isostatically pressed at a pressure of 210 MPa. Two types of firing conditions were adopted. Conventional pressureless sintering (C#-1) involved heating the green samples at 1500°C (4 h) in air (heating and cooling rate: 300 C° h^{-1}). The second method used was microwave sintering (M#-n). The detailed procedures for this technique have been described in previous publications [2,3]. In summary, a 1.2 kW, 2.45 GHz multimode microwave oven was used with continuously variable control over the power output. The control over the sintering cycle was provided by controlling the power output (with a computer) from the microwave oven (as % of the maximum available). The temperature was measured and controlled with a type R thermocouple (to within ±4°C) located in the furnace cavity. For initial heating of samples, silicon carbide rods were used as susceptors. Six different microwave sintering conditions were used. Specimen preparation details and measured densities are given in Table 1.

Details of DC conductivity and impedance measurements have been described in a previous publication [6]. In summary, four-probe DC conductivity measurements were made on selected specimens (C3-1, M3-1, M3-4, C8-1, M8-1 and M8-4) over the temperature range 400–1000°C and as a function of time at 1000°C. Impedance measurements were made over the temperature range of 300–450°C on all specimens as well as on DC conductivity specimens after annealing at 1000°C for 5000 min. All sintering and conductivity measurements were performed in air. Microstructures of polished and etched specimens were examined with both scanning electron and optical microscopes.

3. Results and discussion

All specimens prepared by both conventional and microwave sintering had a density close to the theoretical (Table 1) except for specimens (M#-4) sintered for only 10 min at 1500°C which had somewhat lower density. In a previous study [5]

Table 1
Sintering conditions for conventional and microwave sintered specimens

Specimen code	Sintering temperature (time)	Heating Rate* C° h^{-1}	Density (theoretical) (g cm^{-3}) 3 mol%	8 mol%
C#-1	1500°C (4 h)	300	6.08 (99.6)	5.98 (99.5)
M#-1	1500°C (4 h)	300	6.08 (99.6)	5.98 (99.5)
M#-2	1500°C (1 h)	300	6.07 (99.4)	5.97 (99.4)
M#-3	1500°C (1 h)	1500	6.04 (99.0)	5.85 (97.4)
M#-4	1200°C (1 h)	1800 to 200°C 3000 to 300°C 4200 to 400°C 6000 to 1200°C	5.96 (97.6)	5.81 (96.7)
	1500°C (10 min)	3000 to 1500°C		
M#-5	1200°C (1 h)	1500 to 1200°C	6.03 (98.8)	5.95 (99.0)
	1500°C (10 min)	3000 to 1500°C		
M#-6	1200°C (1 h)	1500 to 1200°C	6.04 (99.0)	5.91(98.4)
	1400°C (2 h)	1500 to 1400°C		

#Refers to 3 or 8 mol% Y_2O_3 nominal composition (actual 2.9 and 7.6 mol% respectively).
* All microwave sintered specimens (except M#-1) were allowed to cool in the furnace after switching the power off at the maximum sintering temperature. Conventionally sintered and M#-1 specimens were cooled at the rate of 300C° h^{-1}.

where control over microwave sintering conditions was poor, even relatively dense specimens showed two distinct regions with varying degrees of porosity. The outer core of specimens had very little porosity but it increased towards the centre (Fig. 1). Cracks running through the denser outer region of specimens were commonly observed and were very pronounced in some specimens. No such behaviour was observed for specimens in this study prepared with a modified microwave sintering furnace [3].

Fig. 2 compares microstructures of some microwave and conventionally sintered specimens. The specimens of 3 mol% Y_2O_3 composition had a much smaller grain size, compared with the 8 mol% Y_2O_3 composition, with very few and uniformly distributed pores. In general, the grain size in microwave

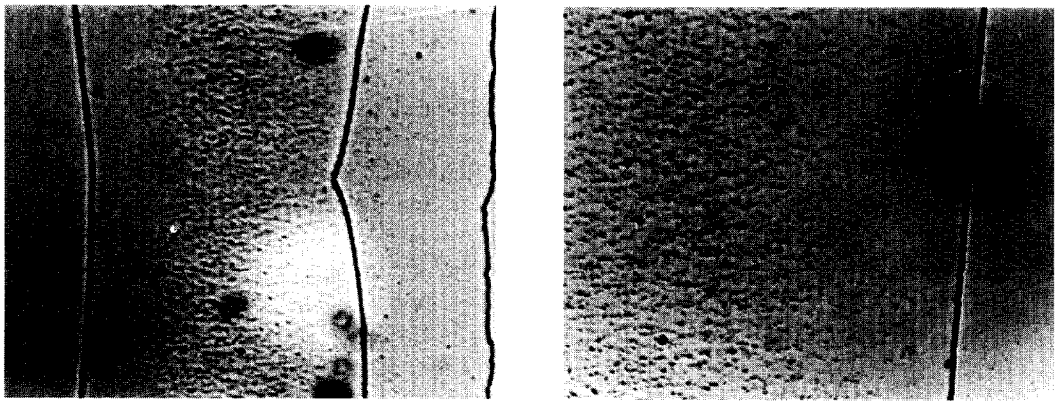

Fig. 1. Low magnification optical micrographs of polished surfaces of a microwave sintered (TZ3Y) specimen from the previous study [5].

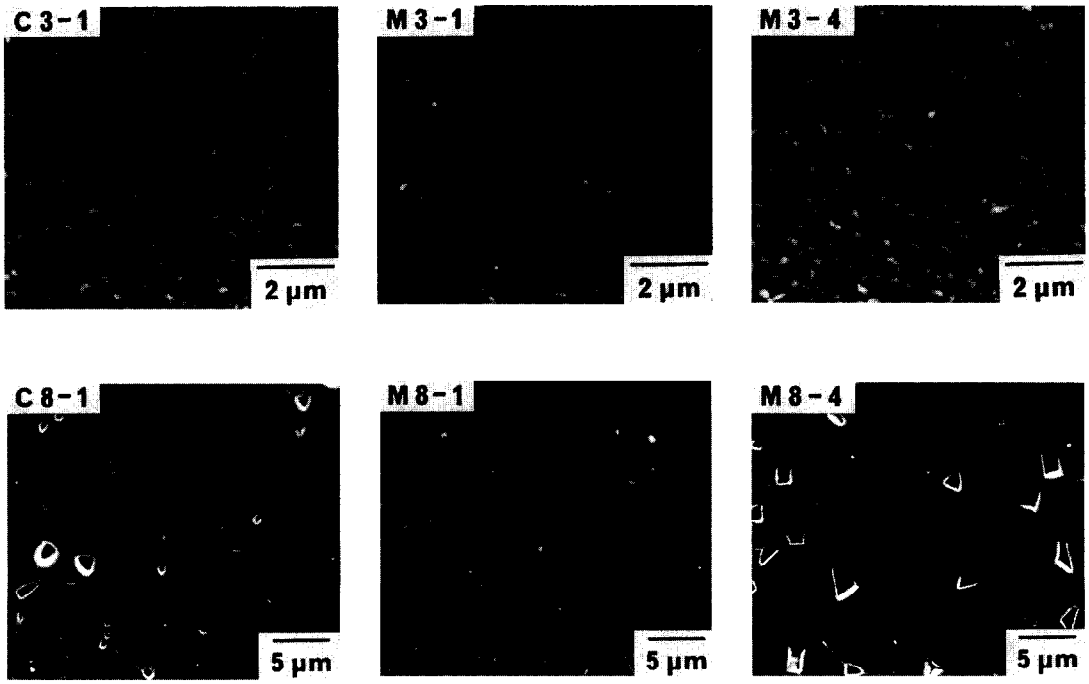

Fig. 2. Scanning electron micrographs of conventionally and microwave sintered specimens.

specimens was slightly larger than that in conventionally sintered (under similar conditions (C#-1 and M#-1)) specimens. The grain size of specimens sintered for only 10 min at 1500°C in a microwave was smaller with more uniform grain size distribution.

For C8-1, large pores were present at both grain boundaries and within the grains. In the microstructure of M8-1, only a small number of pores were present which were evenly distributed within the grains. For M8-4, sintered only for 10 min at 1500°C, large irregular shaped pores were present mainly along grain boundaries indicating that the sintering process had not been completed.

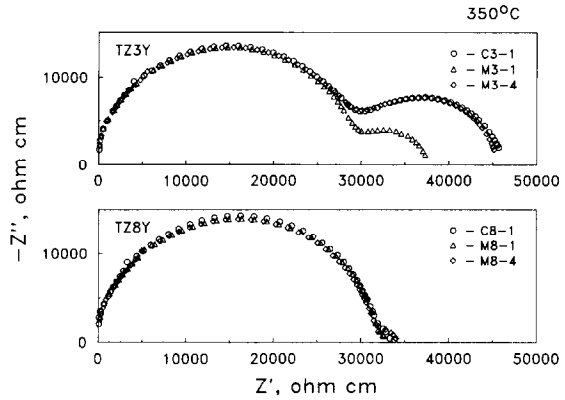

Fig. 3. Impedance diagrams at 350°C for conventionally and microwave sintered specimens. ○, C3-1, C8-1; △, M3-1, M8-1; ◇, M3-4, M8-4.

The results of impedance measurements at 350°C for conventionally sintered and high density microwave sintered specimens of 3 and 8 mol% Y_2O_3–ZrO_2 compositions are shown in Fig. 3. In these impedance diagrams, the circular arc on the right side is due to grain boundaries and the arc on the left side (next to Y-axis) is due to oxygen-ion migration within grains (bulk or volume resistivity). The difference of intercepts of each arc on the real (or X)-axis gives grain boundary (intergrain) or volume (intragrain) resistivity. Table 2 gives results of impedance measurements at 350°C. For specimens of both 3 and 8 mol% Y_2O_3–ZrO_2 composition, the differences observed in the volume resistivity were small and mainly related to minor variations in the microstructure or phase assemblage produced by different sintering conditions. Both compositions are in the two phase field and such minor variations are not unexpected. For the 8 mol% Y_2O_3–ZrO_2 composition, in general, the contribution of the grain boundary resistivity was small and the error in separating the contributions of intra and inter grain resistivities was too large to draw any significant conclusions. For the 3 mol% Y_2O_3–ZrO_2 composition, it is clear from Table 2 that all microwave sintered specimens had a lower grain boundary resistivity in comparison with the conventionally

Table 2
Impedance (350°C) and four-probe DC conductivity (1000°C) results

Specimen identification	Resistivity ($k\Omega$cm) Impedance results at 350°C			Resistivity (Ωcm) Four-probe DC at 1000°C	
	Total	Intragrain	Intergrain	10 min	5000 min
C3-1	46.29	29.07	17.22	17.57	19.49
M3-1	37.68	29.39	8.29	17.01	18.82
M3-2	38.78	27.55	11.23		
M3-3	39.81	27.65	12.16		
M3-4	45.79	29.14	16.65	17.44	19.42
M3-5	42.17	28.17	14.00		
M3-6	42.44	27.21	15.23		
C8-1	33.38	32.25	1.13	5.49	5.91
M8-1	33.13	32.25	0.88	5.37	5.80
M8-2	32.51	30.63	1.88		
M8-3	33.01	32.13	0.88		
M8-4	34.38	32.13	2.25	5.90	6.31
M8-5	32.38	30.63	1.75		
M8-6	33.26	31.63	1.63		

sintered specimens. The notable difference in the grain boundary resistivity is between specimens C3-1 and M3-1, both of which were sintered at 1500°C for 4 h with heating and cooling rates of 300 $C° h^{-1}$. These differences may be due to somewhat larger grain size (small grain boundary surface area) and better microstructure of the microwave sintered specimens. For all other microwave sintered specimens (i.e. M#-2 to M#-6), the cooling rate is much larger ($>>300$ $C° h^{-1}$) at least during the initial stages compared with conventionally sintered specimens for which the cooling rate was controlled at 300 $C° h^{-1}$. In a previous publication it has been reported that the cooling rate has a marked effect on the grain boundary resistivity [7], and the lower value of the grain boundary resistivity in these specimens is consistent with the reported data. The differences in the value of the grain boundary resistivity (although still lower than that of conventionally sintered specimens) in these fast-cooled microwave sintered specimens of 3 mol% Y_2O_3 content appears to be related to shorter times at the maximum sintering temperature of 1500°C (1 h for M3-2 and M3-3, and 10 min for M3-4 and M3-5) or a lower maximum sintering temperature (1400°C for M3-6).

The four-probe DC resistivity results for the various microwave and conventionally sintered specimens at 1000°C before (10 min) and after annealing for 5000 min are given in Table 2 and Arrhenius plots for selected compositions are shown in Fig. 4. All specimens showed a change in the slope with

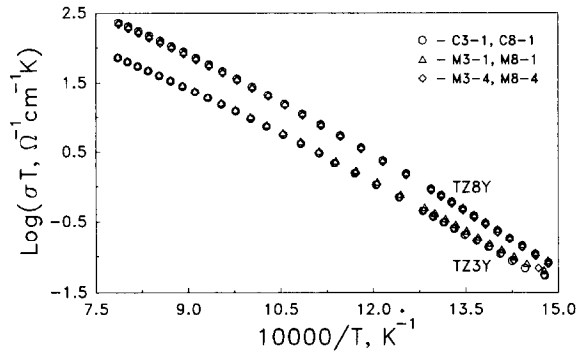

Fig. 4. Arrhenius plots for conventionally and microwave sintered specimens (four-probe DC data) of both 3 (TZ3Y) and 8 (TZ8Y) mol% Y_2O_3 compositions.

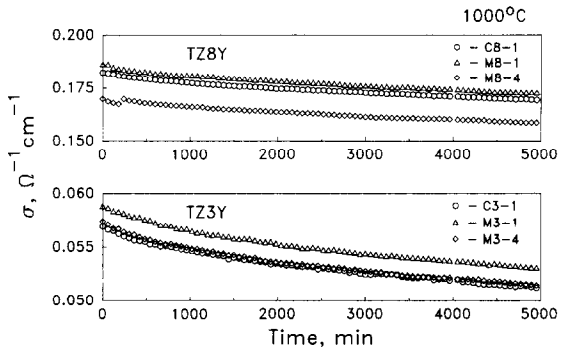

Fig. 5. Ageing behaviour at 1000°C for conventionally and microwave sintered specimens of both 3 and 8 mol% Y_2O_3 compositions.

increasing temperature as reported previously [7]. As expected no major differences in the activation energies were observed between conventionally or microwave sintered specimens.

Most ceramics showed an increase (7–12%) in the resistivity as a result of annealing at 1000°C (Fig. 5) irrespective of the preparation method used and this is mainly related to both compositions being in the two phase field at the annealing temperature. Impedance measurements in the temperature range 300–450°C after these anneals at 1000°C for 5000 min showed an increase in both the grain boundary and the volume resistivity for all specimens. Some disproportionation of sintered phases occurs at 1000°C as dictated by the phase equilibrium requirements, leading to the precipitation of less conducting phases [7] and is the cause of resistivity increase.

4. Conclusions

High density specimens have been produced by the microwave sintering technique over a much shorter time compared with conventional sintering. It has been demonstrated that the ionic conductivity of microwave sintered specimens is comparable with or lower than that of conventionally sintered specimens and microstructure is more uniform. No major differences were observed in the behaviour of either the grain boundary or the volume resistivity following annealing at 1000°C for 5000 min for microwave or conventionally sintered ceramics.

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