JOURNAL OF MATERIALS SCIENCE 25 (1990) 2805–2808

Electrical conductivity of tetragonal stabilized zirconia

O. YAMAMOTO, Y. TAKEDA, R. KANNO, K. KOHNO
Faculty of Engineering, Mie University, Tsu 514, Japan

The electrical conductivity change on annealing for tetragonal stabilized zirconia (TZP) was studied with the help of a.c. impedance dispersion analysis techniques. The dependences of the conductivity on annealing time at 1000° C and on temperature cycling between room temperature and 1000° C were investigated. A decrease in conductivity of about 30% at 1000° C of TZP with 3 mol % Y_2O_3 was observed during the first 200 h of annealing at 1000° C, and no change was observed during further annealing. A similar result was observed for TZP with 2.9 mol % Sc_2O_3. For TZP with 3.0 mol % Yb_2O_3, the conductivity decreased gradually during an annealing time of over 2000 h. The impedance dispersion analysis at lower temperature suggested that the decrease in electrical conductivity by annealing at 1000° C could be attributed to the increases of both grain boundary and intragrain resistance. No monoclinic phase was observed for the samples annealed at 1000° C for 2000 h. On the other hand, a trace of a monoclinic phase was found for TZP with 3 mol % Y_2O_3 after the 50th temperature cycling, but no significant decrease in conductivity was observed with the cycling.

1. Introduction

Stabilized zirconia is a promising material for technologicaly useful devices such as oxygen sensors and solid oxide fuel cells. Until recently, fully stabilized (FSZ) or partially stabilized (PSZ) zirconia has been used for these devices [1, 2]. FSZ has the cubic fluorite structure and high oxide ion conductivity at elevated temperatures [2], while PSZ generally consists of a cubic and tetragonal phase mixture and has good mechanical strength and toughness [3]. The ionic conductivity of PSZ is rather poor compared to that of FSZ. FSZ has been used as an electrolyte in solid oxide fuel cells, and PSZ in oxygen sensors for exhaust gas from automobiles. Recently, a third type of stabilized zirconia consisting of a pure tetragonal phase (TZP) has been developed [4]. TZP has a high mechanical strength and toughness. In the previous paper, we have reported that polycrystalline tetragonal zirconia doped with 3 mol % Y_2O_3, 2.9 mol % Sc_2O_3 and 3 mol % Yb_2O_3 was found to have a high electrical conductivity of about 10^{-1} S cm^{-1} at 1000° C [5]. TZP is extremely attractive because it is available as an electrolyte for solid oxide fuel cells of planar configuration and honeycomb structure [6]. Several previous studies, however, have shown that the use of the system ZrO_2–Y_2O_3 is accompanied by substantial deterioration of electrical conductivity by annealing [7–9]. It is important to study these changes when prolonged use is anticipated. The influence of annealing on the electrical conductivity of TZP has been reported for the system ZrO_2 with 2 mol % Y_2O_3 at 200° C by Kuwabara *et al.* [10]. No detailed result has been reported for the conductivity change of TZP by high-temperature annealing. In this study, the ageing effects on the electrical conductivity of tetragonal zirconia doped with M_2O_3 (M = Sc, Y, Yb) have been studied in view of the application to solid oxide fuel cells. These cells are usually designed to operate in the temperature range 900 to 1000° C [6].

2. Experimental procedures

Yttria-stabilized zirconia powder with 3.0 mol % Y_2O_3 (3Y–TZP) was obtained from To-So, Japan. Scandia-stabilized zirconia powder with 2.9 mol % Sc_2O_3 (2.9Sc–TZP) and ytterbia-stabilized zirconia powder with 3.0 mol % Yb_2O_3 (3Yb–TZP) were purchased from Osaka Cement, Japan. These powders were prepared by the co-precipitation method from mixtures of $ZrOCl_2$ and MCl_3 (M = Y, Sc, Yb). The samples for the conductivity measurements were prepared by uniaxial pressing followed by isostatic pressing at 200 MPa and sintering at 1450° C for 3 h. The phases presented in the sintered specimens were studied by X-ray diffection (XRD). 3Y–TZP, 2.9Sc–TZP and 3Yb–TZP showed only the diffraction lines due to the tetragonal phase. The densities of the sintered samples were more than 95% of the calculated ones, except 2.9Sc–TZP, which was about 90%. The mean grain sizes of as-sintered samples were about 0.3 μm.

The conductivity measurements were carried out with cylindrical samples of ~ 0.5 cm in diameter and 3 cm long, and with discs of ~ 1.0 cm in diameter and 0.2 cm long. The a.c. conductivity was measured using a frequency-response analyser (Solartron FRA-1250) over a frequency range of 10^{-2} to 6.5×10^4 Hz with an applied potential of 0.2 V and a temperature range 250 to 1000° C with platinum paint electrodes sintered at 1000° C for 1 h. All measurements were performed in air.

0022-2461/90 $03.00 + .12

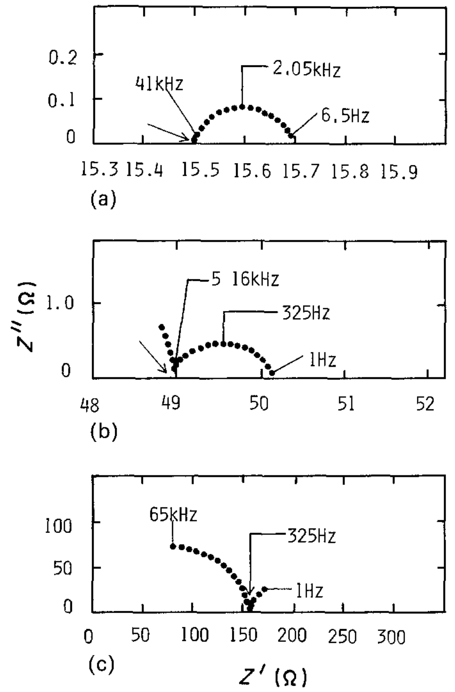

Figure 1 Complex impedance plane plots for 3Y–TZP at (a) 1000; (b) 800; (c) 600° C.

3. Results and discussion

In Fig. 1, complex impedance plane plots for the cylindrical sample of 3Y–TZP are shown. Generally, complex impedance plane plots of polycrystalline solid ionic conductors show three semicircles, corresponding to intragrain, grain boundary and electrode interfaces [11, 12]. But, at a higher temperature, such as 1000° C, only a semicircle due to electrode interfaces was observed. Kleitz *et al.* [12] have reported that, as a rule, the observable range shifts from the left (high frequency) to the right (low frequency) of the complex resistivity diagram as the temperature of the sample increases. The resistance was estimated from the interceptions of the arcs in the real axis at higher frequency for higher temperatures, and at lower frequency for the first arc at lower temperatures, which are indicated by arrows in the figure. The resistances estimated by this manner are comparable to those of d.c. measurements [5]. In this study, the electrical conductivity at 1000° C was estimated from the complex impedance plane plots using cylindrical samples. The conductivity measurements on cylindrical samples allow no dominating correction for the sample holder resistance above 1000° C [13].

Fig. 2 shows the conductivity changes of 3Y–TZP, 2.9Sc–TZP and 3Yb–TZP on annealing at 1000° C in air. The ageing process for stabilized zirconia was first investigated by Carter and Roth [7] for the ZrO_2–CaO system, and it was concluded that defect ordering processes must be taking place. A square-root law for the conductivity change of FSZ with 8 mol % Y_2O_3 at 875° C was found by Kleitz *et al.* [12], indicating a diffusion-controlled process for the segregation of oversaturated impurities at the grain boundaries. Moghadam and Stevenson [14] have reported the influence of annealing on the conductivity of 4.5 mol % Y_2O_3 in ZrO_2. At 1000° C there was a 10% decrease in conductivity during the first 24 h of annealing, and a further 10% decrease between 80 and 100 h. The initial decrease was attributed to precipitation of tetragonal zirconia from the cubic matrix. The second decrease was attributed to ordering in the cubic phase. However, the initial conductivity of 1.5×10^{-2} S cm^{-1} is quite low compared to that of 8.0×10^{-2} S cm^{-1} measured by us. The discrepancy may be due to the difference of the grain size of sintered material. The grain size of Moghadam's samples was 1 to 2 μm, in contrast to 0.3 μm for our samples.

Fig. 3 shows the conductivity dependence on annealing time at 1000° C for 3Y–TZP. As shown in Fig. 3a, the dependence exhibits a good square-root law during the first 60 h, and during prolonged annealing does not obey the square-root law. Schouler [15] has found an exponential law for the conductivity change for a single crystal of FSZ with Y_2O_3. This would correspond to a reorganization of the crystal, associated with partial ordering of the cations. In Fig. 3b the relation between log $(\sigma - \sigma_\infty/\sigma_0 - \sigma_\infty)$ and annealing time is also shown, where σ_0 and σ_∞ are the conductivities of annealing time at 60 h and 2000 h, respectively, and the annealing time is counted after 60 h. The curve shows a good linearity. These results suggest that there may be two processes contributing to the ageing mechanism of TZP with 3 mol % Y_2O_3: the segregation of impurities and/or non-conductive second phase, and the ordering in the tetragonal phase.

Tegragonal stabilized zirconia with Y_2O_3 is thermodynamically unstable below the eutectoid transformation point ($\approx$490° C) [16]; tetragonal zirconia solid solution decomposes into monoclinic zirconia solid solution and cubic solid solution. Degradations of the

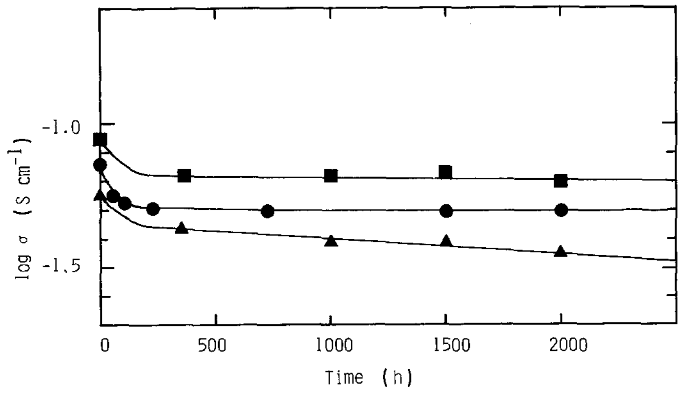

Figure 2 Conductivity change of TZP on annealing at 1000° C in air. ■, 2.9 mol % SC_2O_3 TZP; ●. 3.0 mol % Y_2O_3 TZP; ▲, 3.0 mol % Yb_2O_3 TZP.

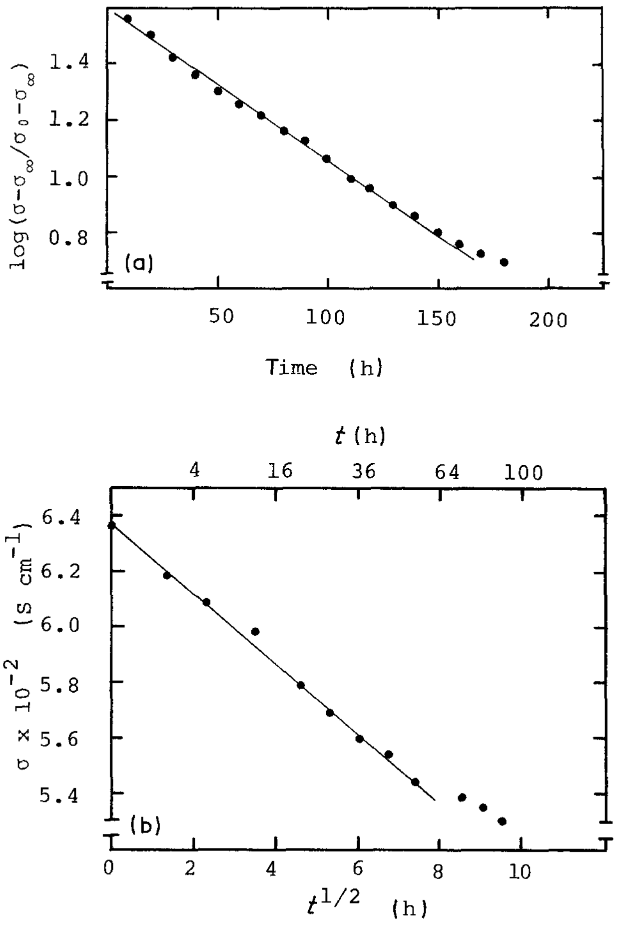

Figure 3 Conductivity change of 3Y–TZP on annealing at 1000° C in air.

electrical conductivity of ZrO_2 with 5 mol % Y_2O_3 [17, 18] have been observed after annealing at 200 and 300° C. The degradation was attributed to the formation of the poor conductivity monoclinic phase. In view of the application of TZP as a fuel cell, the stability of TZP after temperature cycling between 1000° C and room temperature is very important. In Fig. 4, the change of conductivity of 3Y–TZP at 1000° C is shown as a function of temperature cycling. The pattern of heating and cooling temperature cycling

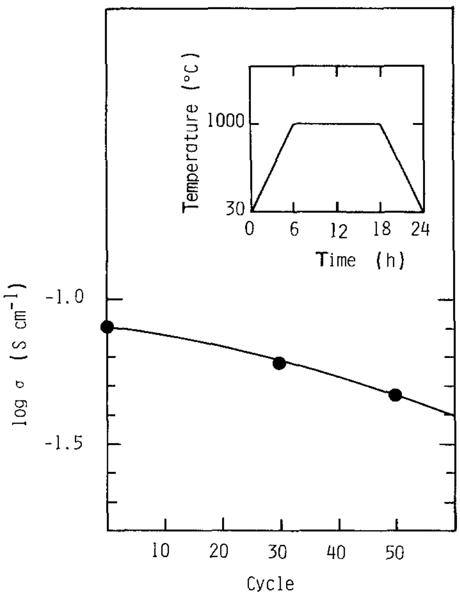

Figure 4 Conductivity change of 3Y–TZP on temperature cycling.

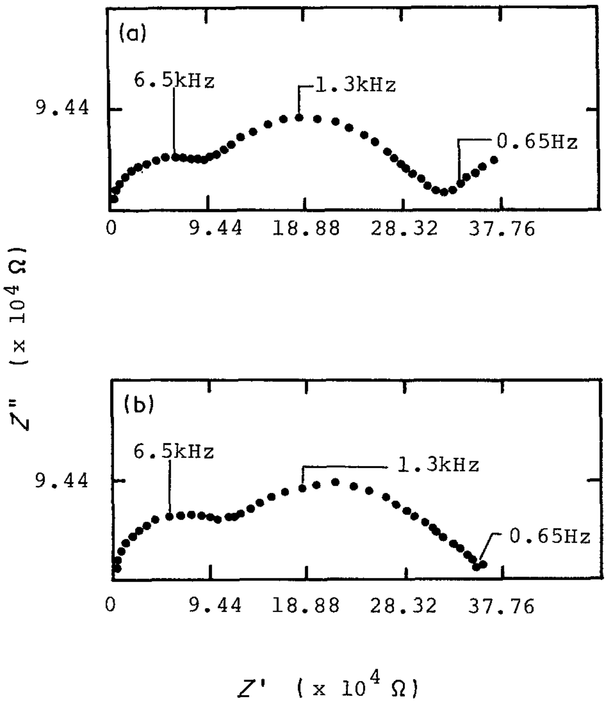

Figure 5 Complex impedance plane plots for 3Y–TZP annealing at 1000° C. Annealing time (a) 0 h; (b) 500 h.

is indicated in this figure. The conductivity decreases linearly with temperature cycling. After the 50th cycling, the conductivity decrease is about 40%, and a small amount of the monoclinic phase (about 1%) was observed. The temperature cycling on the conductivity brings about formation of the poor conductivity monoclinic phase. However, the decrease in conductivity and trace formation of the monoclinic phase is not so serious, because fifty cycles are enough for practical applications as solid oxide fuel cells.

Complex impedance plane plot analysis is quite useful to separate the intragrain and grain boundary contributions of conductivity. As shown in Fig. 1, however, the plot at 1000° C shows only a semicircle corresponding to the electrode interfaces in the frequency range examined. At a low temperature such as 250° C. two semicircles corresponding to intragrain and grain boundary were observed. Here disk-type samples were used for the measurements because of the high resistance and high sample-holder capacity to grain-boundary capacity ratio in the bar type samples at low temperatures. In Fig. 5, complex impedance plane plots at 250° C for 3Y–TZP as-sintered at 1450° C and annealed at 1000° C for 500 h are shown. On annealing at 1000° C for 500 h, the intragrain resistivity increase is about 30%, and the increase of grain boundary resistivity is only 6%. Fig. 6 also shows complex impedance plane plots at 250° C for 3Y–TZP after the 50th temperature cycle. The increase in intragrain resistivity (about 25%) is comparable to that for the sample annealed at 1000° C. On the other hand, a more significant increase in grain boundary resistance (about 11%) is observed. The increase in resistance may be due to the segregation of the poor conductivity monoclinic phase at the grain boundary. The conductivity change at 1000° C is not estimated straightforwardly by the impedance analysis, but we could conclude that the successive decrease of conductivity with

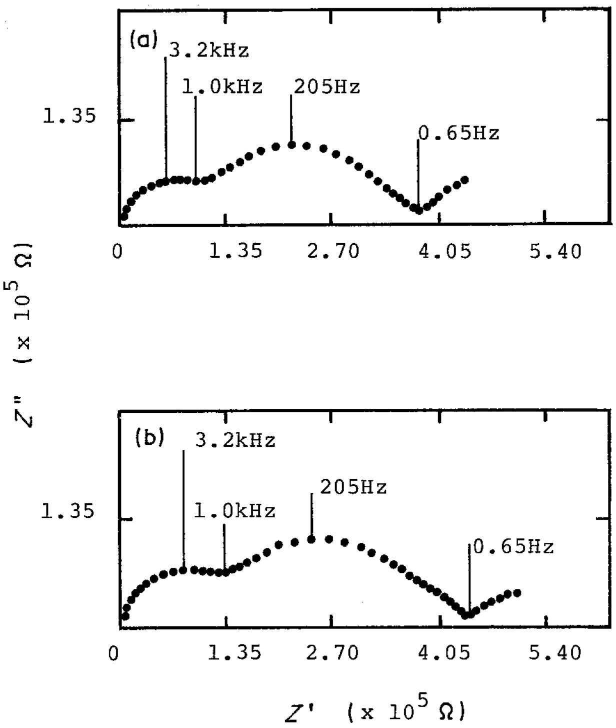

Figure 6 Complex impedance plane plots for 3Y-TZP after temperature cycling. (a) 0th cycle; (b) 50th cycle.

temperature cycling is attributed to the formation of the monoclinic phase at the grain boundary.

4.Conclusion

The conductivity change on annealing at 1000° C and on temperature cycling between 1000° C and room temperature for tetragonal stabilized zirconia with Y_2O_3, Sc_2O_3 and Yb_2O_3 has been studied from the viewpoint of application to solid oxide fuel cells. The electrical conductivities after annealing at 1000° C for 2000 h are 5×10^{-2} S cm^{-1} for 3Y-TZP, 6.5×10^{-2} S cm^{-1} for 2.9Sc-TZP and 3.6×10^{-2} S cm^{-1} for 3Yb-TZP. Consequently, tetragonal zirconia is a promising electrolyte for solid oxide fuel cells, because of its excellent mechanical properties and long-term conductivity stability.

References

1. T. L. MARKIN, R. J. BONES and R. M. DELL, in "Superionic Conductors", edited by G. D. Mahn and W. L. Roth (Plenum, New York, 1973) p. 15.
2. T. H. ESTELL and S. N. FLENGAS, *Chem. Rev.* **70** (1970) 339.
3. K. KOBAUASHI, H. KAWAJIMA and T. MASAKI, *Solid State Ionics* **3/4** (1981) 489.
4. T. K. GUPTA, *et al., J. Mater. Sci.* **12** (1977) 2421.
5. O. YAMAMOTO *et al., J. Mater. Sci. Lett.* **8** (1988) 198.
6. B. C. H. STELLE, "Ceramic Electrochemical Reactors" (Ceramionics, London, 1987).
7. R. E. CARTER and W. L. ROTH, in "EMF Measurements in High Temperature Systems", edited by C. B. Alock (Institute of Minerals and Metallurgy, London, 1968) p. 125.
8. E. SCHOULER, G. GIROUND and M. KLEITZ *J. Chim. Phys. Physiochim. Biol.* **70** (1973) 1309.
9. Y. SUZUKI and K. SUGIYAMA, *J. Ceram. Soc. Jpn.* **95** (1987) 480.
10. M. KUWABARA, *et al., J. Mater. Sci. Lett.* **5** (1986) 7.
11. J. E. BAUERLE, *J. Phys. Chem. Solids* **30** (1969) 2657.
12. M. KLEITZ, *et al.*, in "Advances in Ceramics", edited by A. H. Heuer and L. W. Hobbs (American Ceramic Society, Columbus, Ohio, 1981) p. 310.
13. J. J. BENTZEN, *et al., Solid State Ionics* **28–30** (1988) 550.
14. F. K. MOGHADAM and D. A. STEVENSON, *J. Amer. Ceram. Soc.* **65** (1982) 213.
15. E. SCHOULER, PhD Thesis, Grenoble, 1979.
16. C. PASCUAL and P. DURAN, *J. Amer. Ceram. Soc.* **66** (1983) 23.
17. K. KOBAYASI, H. KUWAJIMA and T. MASAKI, *Solid State Ionics* **3/4** (1981) 489.
18. M. KUWABARA *et al., J. Mater. Sci. Lett.* **5** (1986) 7.

Received 1 March
and accepted 30 August 1989