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Microstructural design and high temperature tensile deformation behaviour of 8 mol% yttria stabilized cubic zirconia (8YCSZ) with SiO_2 additions

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Abstract

In the present study, the microstructural evolution and high temperature deformation behaviours of 8 mol% Y_2O_3 stabilized cubic zirconia (8YCSZ) containing up to 10 wt% SiO_2 is investigated. The experimental results show that the SiO_2 doped specimens sintered at 1400 °C contain only the cubic crystalline phase and SiO_2 has the very limited solubility of 0.3 wt% in cubic zirconia. This suggests that only small part of the SiO_2 dissolves in the cubic zirconia and the rest of SiO_2 segregates at grain boundaries and multiple junctions as amorphous (glassy) phase. This glassy phase prevents the grain growth by minimizing grain boundary energy and mobility, which results from solute segregation at the grain boundary and its drag. The deformation of the undoped 8YCSZ is characterized by large strain hardening with limited elongation. This is mainly due to severe grain growth during high temperature deformation. The addition of the SiO_2 results in a decrease in strain hardening and enhanced tensile elongation. These effects have been further improved with the increase of the SiO_2 addition reaching the elongation to failure of 152% for 10 wt% SiO_2 doped specimen in tension at a temperature of 1400 °C and strain rate of $1.3 \times 10^{-4}\ s^{-1}$. The decreased strain hardening and increased ductility in the SiO_2 doped specimens are due to the segregation of amorphous glassy phase to the grain boundaries, thus hindering grain growth and facilitating grain boundary sliding, which is the primary mechanism of deformation in fine grained materials at high temperatures.

Keywords: A. Grain growth; Cubic zirconia; Silica; High temperature deformation

1. Introduction

High temperature deformation in ceramics was first reported in tetragonal zirconia [1] and so far extensive improvements have been achieved using this material due to its grain size stability during high temperature deformation [2]. Although the crystal structure of cubic zirconia is close to that of tetragonal zirconia [3], the elongation to failure for the former is very limited due to strain hardening from both static and dynamic grain growth [4]. Ceramics such as cubic zirconia may often undergo high temperature deformation with a grain size sufficiently small to exhibit high temperature deformation. However, the amount of static and dynamic grain growth, which occurs at sintering and test temperatures, soon exceeds the requisite slowing strain rate values causing high strain hardening. As a consequence, the ceramic powder loses its nanocrystalline character. In order to preserve the nanocrystalline character of such ceramics, the grain growth must be inhibited. Improvement of high temperature ductility in zirconia ceramics has been considered to be associated with a number of contributing factors, including the presence of a low viscosity grain boundary phase or doping with transition metal oxides [4–8]. These additives possibly play a multiple role as sintering aids, grain growth inhibitors and modifiers of grain boundary strength and grain boundary chemistry. Conventionally, reducing the strain rate or increasing the test temperature also promotes larger elongations at lower stress levels. High deformation rates, high ductility and low forming temperatures are primary forming requirements for industrial applications of ceramics.

Eight molar percent yttria-stabilized cubic zirconia is a promising solid-state electrolyte material and has been applied

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to many devices, such as solid oxide fuel cells, oxygen sensors, thermal barrier and oxygen pumps, because of its high oxygen ionic conductivity and chemical stability over a wide range of temperatures and oxygen partial pressure [9]. However, the cubic zirconia has poor mechanical properties at room and high temperatures, high thermal expansion and low thermal shock resistance. These drawbacks would limit its use as electrolyte, because it may fracture due to thermal stresses, mechanical stresses during operation, lack of transformation toughening and severe grain growth [10]. Therefore, an improvement of room and high temperature mechanical properties of cubic zirconia is needed.

In the present study, the effect of SiO_2 addition with various amounts on microstructure and high temperature deformation behaviour of 8 mol% Y_2O_3 stabilized cubic zirconia (8YCSZ) has been investigated.

2. Experimental procedure

As starting materials, nanoscale 8 mol% yttria-stabilized cubic zirconia powders (8YCSZ, Tosoh, Japan) and colloidal silica (Nissan Chemical Industry Co. Ltd., Japan) were used. The average particle sizes were 0.3 μm for 8YCSZ and about 0.1–0.2 μm for colloidal silica. The chemical composition of 8YCSZ was 13.6 wt% Y_2O_3 (equivalent to 8 mol%), 85.9 wt% ZrO_2, and the following impurities (in wt%), Al_2O_3 0.25, SiO_2 0.10, TiO_2 0.12, Fe_2O_3 0.003, Na_2O 0.002 and CaO 0.02. The 8YCSZ powders were doped by adding different amounts of SiO_2 up to 10 wt% and then ball-milled in ethanol for 24 h by using zirconia balls. The as-prepared slurries were dried in air, sieved through an 60 μm sieve, pressed into cylinders and bars by uniaxial pressing at 30 MPa in a steel die and then cold isostatically pressed (CIP) under a pressure of 100 MPa in a rubber tube. The specimens were sintered at 1400 °C for 1 h. The densities of as-sintered specimens were measured using the Archimedes method in distilled water.

After sintering, the specimens were sectioned, ground, polished to 1 μm surface finish and thermally etched in air for 30 min at a temperature 50 °C lower than the sintering temperature. Finally, the specimens were chemically etched in HF acid for 5 s to reveal the grain boundaries more clear. Scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) attachment was used to characterize the microstructure of as-sintered specimens. Grain sizes were measured by the mean linear intercept method. An average grain size was obtained by multiplying 1.78 to average intercept lengths over 1000 grains.

Tensile tests were carried out to investigate the high temperature deformation behaviour of different amount of SiO_2 doped 8YCSZ. For tensile tests, specimens 2 mm × 2 mm in cross-section and 13.5 mm in gauge length were cut and ground from sintered bars. High temperature tensile tests were conducted at a strain rate of $1.3 \times 10^{-4}\ s^{-1}$ and at a temperature of 1400 °C in air using an Instron type mechanical testing machine (Shimadzu Ag-5000C) equipped with a high temperature furnace and SiC jigs. The furnace was heated to the test temperature within 3 h and then held there for 10 min to reach the equilibrium state before the test. The testing temperature was measured by a Pt-PtRh thermocouple attached to the specimen. X-ray diffraction patterns (XRD) of the specimens were obtained using a Siemens D-5000 diffractometer and monochromated high intensity Cu Kα radiation. A scan speed of 0.02° 2θ (s^{-1}) was employed.

3. Results and discussion

X-ray diffraction data indicated that all specimens contained only fluorite structure and that there were no diffraction peaks of second phases for all specimens. Fig. 1 shows the variation of the average lattice parameter of the 8YCSZ with various SiO_2 contents. The average lattice parameter of 8YCSZ linearly decreases with increasing SiO_2 content up to 0.3 wt% and the parameter becomes constant with further increase in the SiO_2 content. This linearity shows that the solid solubility limit of the SiO_2 in 8YCSZ is about 0.3 wt%. The lower values of the lattice parameter found for the SiO_2 doped 8YCSZs could be due to the dissolution in the cubic phase of some SiO_2 and to the substitution of smaller Si^{4+} ions for Zr^{4+} and Y^{3+} ions in the cubic lattice (the ionic radii of Si^{4+}, Y^{3+} and Zr^{4+} for eight-fold coordination are 0.4, 1.015 and 0.84 Å, respectively). As the solubility limit of the SiO_2 in 8YCSZ is ~0.3 wt%, the SiO_2 can hardly form a solid solution with 8YCSZ. Therefore, the SiO_2 mostly segregates around the 8YCSZ particles and at grain boundaries.

Fig. 2 shows representative microstructures of the specimens with various SiO_2 contents up to 10 wt%, sintered at 1400 °C for 1 h in air. The grains of the undoped 8YCSZ were faceted and straight grain boundaries were often seen (Fig. 2a). The grains in the SiO_2 doped 8YSCZs were rounded and a darker phase was located along the grain boundaries and at grain boundary triple points (Fig. 2b–d). EDS analyses showed that the darker phase is an amorphous glassy phase enriched with Si. The change in microstructure with the addition of the SiO_2 can be explained as follows. For a small amount of the SiO_2 addition, less than 0.3 wt%, the SiO_2 dissolves in the 8YCSZ lattices so that no amorphous phase is found. For a further

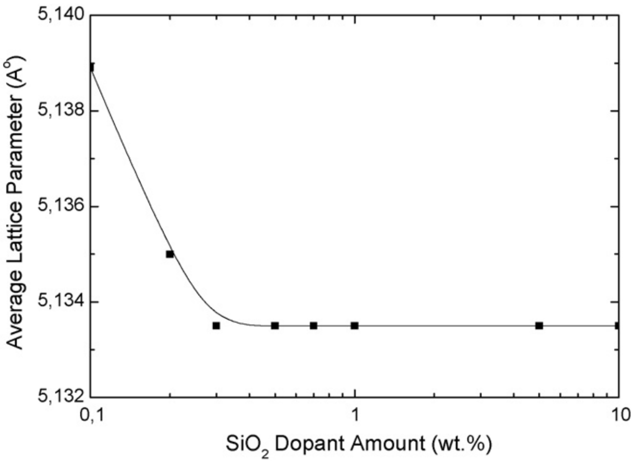

Fig. 1. Average lattice parameter change as a function of SiO_2 amount.

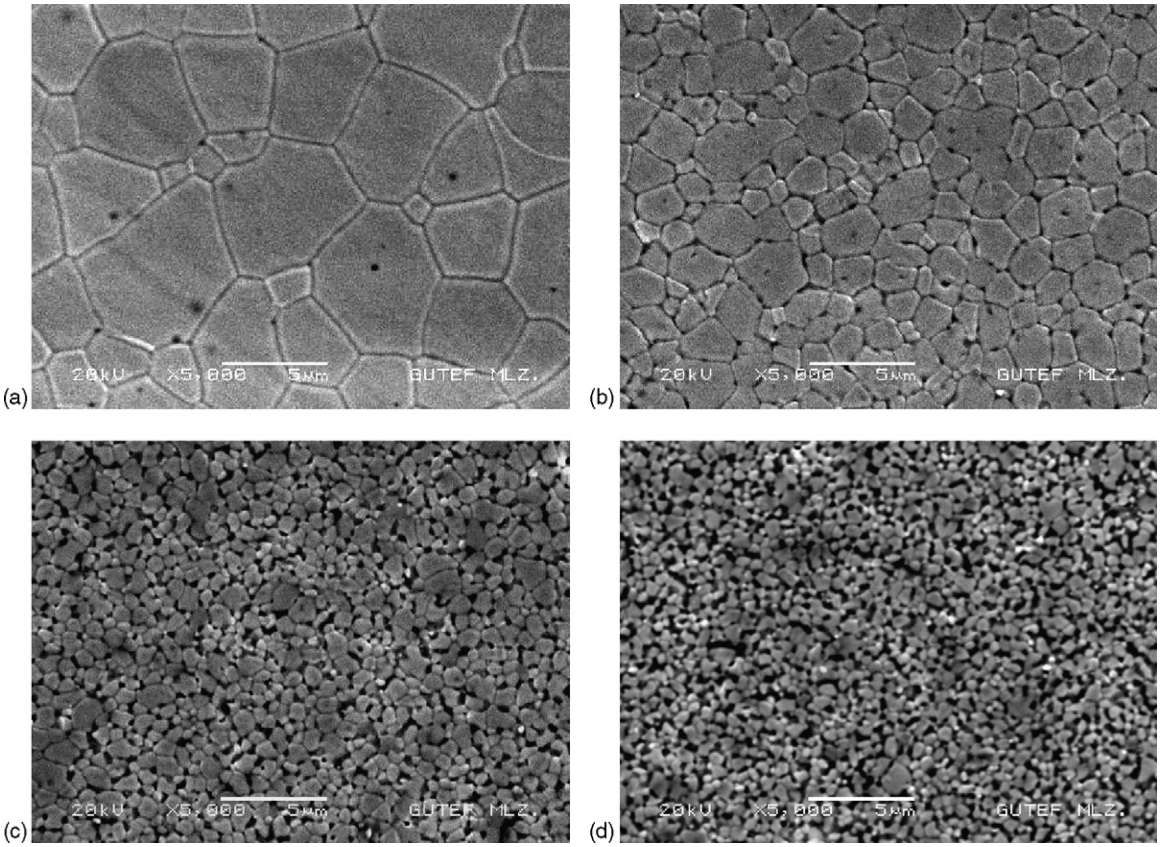

Fig. 2. The changes in microstructure with SiO_2 addition: (a) undoped, (b) 1 wt% SiO_2, (c) 5 wt% SiO_2 and (d) 10 wt% SiO_2.

increase in the SiO_2 addition, the 8YCSZ matrix is saturated with SiO_2 and hence the excess amount of the SiO_2 is preferentially segregated along the grain boundaries and at multiple grain junctions as glass pocket. This glassy phase wets the 8YCSZ grains and forms rounded grains. The thickness of this glassy phase increases with increasing SiO_2 content, and the rounded grains are formed due to minimizing interfacial energy between glass and 8YCSZ grains. The microstructural investigations also showed that the specimens with a solubility limit up to 0.3 wt% were very dense and free from porosities in the grain interiors. This suggests that the small amount of SiO_2 addition located at the grain boundaries of 8YCSZ is sufficient for improving densification. However, in the specimens with higher amount of SiO_2 additions, there is much porosity in the grain interior and along the grain boundaries. The comparison of the grain size of the specimens at the same heat treatment indicated that grains were larger in the undoped 8YCSZ than in the SiO_2 doped 8YCSZs. Also, the grain size decreased with increasing SiO_2 content (Fig. 3). To inhibit the grain growth, the grain boundary mobility and energy should be reduced for example by impurities, dopants or particles of a second phase. In polycrystalline materials, it has been shown that particles of a second phase with limited solubility are especially effective in pinning grain boundaries and thus minimizing static and dynamic grain growth [11]. The grain boundary mobility decreases with increasing the grain boundary width. Additives and dopants that increase grain boundary width may be effective in minimizing grain growth. Also, the additives that decrease grain boundary energy have an additional effect on minimizing grain growth. A reduction in grain boundary energy occurs when intergranular phases wet the grain boundaries. In the present study, the addition of SiO_2 to the 8YSCZ resulted in limiting grain growth by segregation of solute cations to grain boundaries and by wetting the grain boundary at high temperature. The SiO_2 has a higher viscosity and a lower diffusivity at high temperatures. Hence, the grain growth was limited by Zenner pinning of the grain boundaries and by

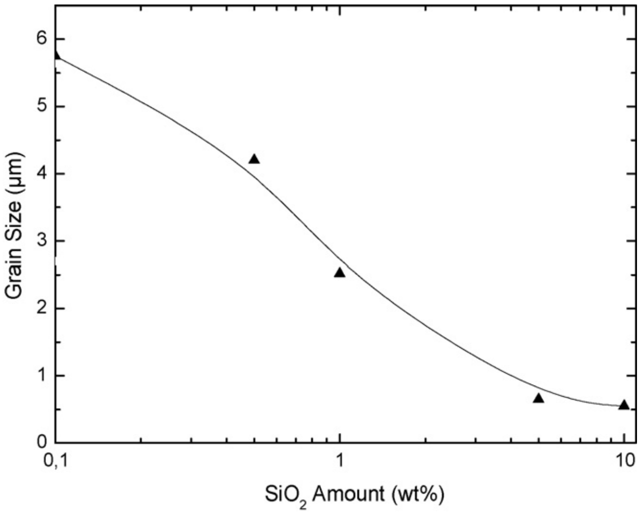

Fig. 3. Grain size variation with SiO_2 content.

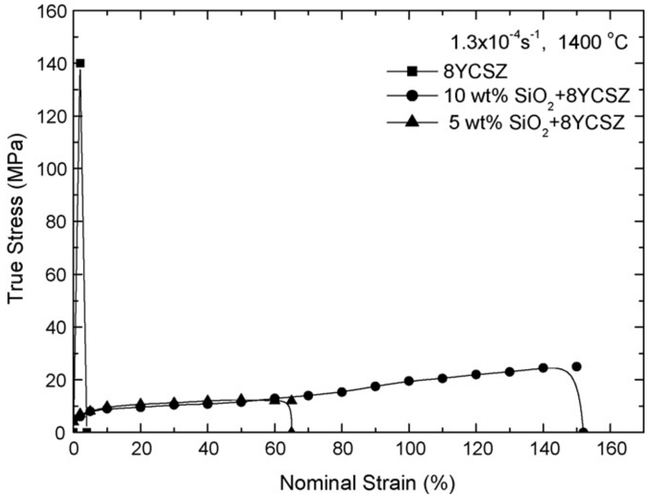

Fig. 4. True stress-strain curves for undoped and SiO_2 doped 8YCSZ specimens tested at 1400 °C and an initial strain rate of $1.3 \times 10^{-4}\ s^{-1}$. Undoped 8YCSZ data is from Ref. [12].

reducing the driving force for grain growth in the presence of the lower energy liquid/ceramic interface. In addition, the grain boundary mobility with respect to grain growth decreased by increasing the effective grain boundary width, as liquid phase distributed along the grain boundaries.

To investigate the effect of SiO_2 addition on high temperature deformation behaviour of 8YCSZ, sintered specimens with various SiO_2 amounts were tested in tension at $1.3 \times 10^{-4}\ s^{-1}$ and 1400 °C. The stress–strain curves for the undoped and SiO_2 doped 8YCSZs are shown in Fig. 4. True stress–true strain curve of the undoped 8YCSZ is characterized by extensive strain hardening followed by early fracture at a limited strain of about 4% after reaching a peak stress of about 140 MPa. The cause of low ductility and high strain hardening can be related to extensive grain growth, which reduces grain boundary sliding causing early fracture. The SiO_2 doped 8YCSZs showed less strain hardening and larger elongations. With the addition of 5 and 10 wt% SiO_2, the flow curves showed a less strain hardening and the flow stresses slightly increased with tensile straining. The maximum flow stress was about 12 MPa for 5 and 25 for 10 wt% SiO_2 doped 8YCSZ. Also the SiO_2 addition vastly improved the elongation to failure of 8YCSZ. As shown in Fig. 4, 5 and 10 wt% SiO_2 doped 8YCSZ demonstrated an elongation to failure of 65% and 152% under tension, respectively. The ductility increase is probably due to the effect of intergranular silica on the grain boundary mobility, ease of grain boundary sliding and grain size stability during sintering and high temperature deformation. It has been suggested that in order to enhance grain boundary diffusivity and to lower the deformation resistance in zirconia ceramics, additives that segregate to the grain boundary and form a low melting phase could be effective. This grain boundary phase would act to reduce the friction between grains, promoting grain boundary sliding and allowing an enhancement in strain rate. In the present study, high viscosity and low solubility amorphous second phase at grain boundaries and grain boundary triple points of the SiO_2 doped 8YCSZ enhanced tensile elongation by (a) limiting grain growth by decreasing grain to grain contact of the same phase, (b) promoting grain boundary sliding and rotation, (c) accommodating stresses arising from grain boundary sliding and (d) inhibiting cavitation during high temperature deformation. Large elongation to failure, however, have not been observed in undoped 8YCSZ due to extensive grain growth in single phase system during deformation.

4. Conclusions

1. XRD results show that SiO_2 has the very limited solubility of 0.3 wt% in the cubic lattice. This suggests that only a small part of SiO_2 is dissolved in 8YCSZ and the rest of SiO_2 is segregated at grain boundaries or multiple junctions.
2. The comparison of the grain size of the specimens indicates that grains are larger in the undoped 8YCSZ than in the SiO_2 doped 8YCSZ, and that the grain size decreases with increasing SiO_2 content.
3. The achievement of extensive elongation in the SiO_2 doped 8YCSZ is explained by the combination of hindrance of grain growth by the intergranular silica phase and the decrease of flow stress.

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References

[1] F. Wakai, S. Sagaguchi, Y. Matsuno, Adv. Ceram. Mater. 1 (1986) 259–263.
[2] K. Kajihara, Y. Yoshizawa, T. Sakuma, Acta Metal. Mater. 43 (1995) 1235–1242.
[3] U. Messerschmidt, D. Baither, B. Baufeld, M. Bartsch, Mater. Sci. Eng. A 233 (1997) 61–74.
[4] S. Tekeli, T.J. Davies, Mater. Sci. Technol. 17 (2001) 109–112.
[5] A.A. Sharif, M.L. Mecartney, Acta Mater. 51 (2003) 1633–1639.
[6] R.P. Dillon, S.S. Sosa, M.L. Mecartney, Script. Mater. 50 (2004) 1441–1444.
[7] Y. Kitano, K. Yamada, E. Tanabe, M. Oka, K. Nagao, J. Electron. Microsc. 51 (Suppl.) (2002) s135–s141.
[8] A.A. Sharif, M.L. Mecartney, J. Eur. Ceram. Soc. 24 (2004) 2041–2047.
[9] H. Inaba, H. Tagawa, Solid State Ionics 83 (1996) 1–16.
[10] T. Zhang, Z. Zeng, H. Huang, P. Hing, J. Kinler, Mater. Lett. 57 (2002) 124–129.
[11] D. Turnbull, Trans. AIME 191 (1951) 78.
[12] H. Yoshida, A. Kubo, H. Ito, H. Nagayama, T. Sakuma, Script. Mater. 52 (2005) 365–368.