Structure and chemistry of grain boundaries in SiO₂-doped TZP

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Abstract

The addition of glass phase can control the grain boundary structure and hence the mechanical properties of tetragonal zirconia polycrystals (TZP). To reveal the effect of the glass dopant on the high-temperature deformation behavior of TZP, SiO₂-doped TZP, (SiO₂-Al₂O₃)-doped TZP, (SiO₂-MgO)-doped TZP and undoped TZP were prepared and their grain boundary structure, chemical composition and chemical bonding state were investigated by high resolution electron microscopy (HREM), energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) using a field-emission-type transmission electron microscope (FE-TEM). It was found that no amorphous film was formed along the grain boundaries in any of the specimens examined, but amorphous pockets formed at multiple grain boundary junctions in three kinds of glass-doped specimens. In the glass-doped specimens, the segregation of yttrium, silicon and the added metal ions (Al⁴⁺ or Mg²⁺) was observed over a width of several nm across the grain boundaries. The addition of pure SiO₂ much enhanced the ductility in TZP, although further addition of a small amount of Al₂O₃ or MgO to SiO₂ phase resulted in a marked reduction in the tensile ductility of SiO₂-doped TZP. EELS measurements and molecular orbital (MO) calculations using a cluster model revealed that the ductility of TZP was related to the bond overlap population (BOP) at the grain boundaries, which was influenced by the kinds of segregated dopants. That is, the presence of Si⁴⁺ increases the BOP, strengthening the grain boundary bonding strength and thus preventing cavity formation, but Al⁴⁺ and Mg²⁺ decrease the BOP, enhancing the grain boundary cavitation and thus reducing the ductility. Furthermore, the dynamic behavior of SiO₂ in TZP was observed using a TEM in situ heating technique, and the results supported the fact that Si segregates along the grain boundaries. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There has been considerable expectation surrounding the use of structural ceramics in high-temperature technical applications; however, their poor machinability and formability have limited these applications. However, superplasticity can be obtained if the grain size is very fine. The idea of fine-grained superplasticity in ceramics dates back to 1970 [1], and then several researchers started to study the superplasticity in ceramics [2–5]. Subsequently, intensive investigations began only after Wakai et al. reported in 1986 that fine-grained tetragonal zirconia polycrystal (TZP) showed a superplasticity of more than 100% even in a high-temperature tensile test [6]. Since then, the goal of research in this field has been to fabricate ceramics that show high superplasticity, and tensile ductility has always been thought to be a key factor in superplasticity in ceramics. In 1988, Nieh and Wadsworth [7] reported a superplasticity of 350% in TZP, and later Ma and Langdon reported a superplasticity of 355% in TZP [8]. After Wakai and Kato [9] reported that a superplasticity of 200% can be obtained in 20% Al₂O₃–TZP, Nieh and Wadsworth [10] reported a superplasticity of 625% in the same materials, and Kajihara et al. reported a superplasticity of 1083% in SiO₂-doped TZP [11], the highest reported elongation for TZP based ceramics. Recently, Suzuki et al. reported a superplasticity of 995% for 0.2 wt% Al₂O₃-doped TZP fabricated by colloidal processing [12].

The mechanism of superplasticity in ceramics has also been studied by many researchers. It has been generally accepted that superplasticity in fine-grained ceramics mainly occurs by grain boundary sliding. Grain boundary sliding is considered to be rate-controlled by the accompanied accommodation process due to stress concentration at the grain boundary ledges or junctions [13]. Several models
have been proposed for this mechanism, including: (i) the diffusion accommodated grain switching model [14,15]; (ii) dislocation model [16,17]; and (iii) core and mantle model [18]. These models have been discussed in detail in comparison with the experimentally obtained results [19–22]; however, it is still unclear which model is the most suitable in the case of ceramics. The grain boundary structure must first be characterized to clarify the mechanism of superplasticity in ceramics because the presence or absence of grain boundary amorphous film is directly related to grain boundary sliding. For this purpose, the grain boundary structure of TZP has been intensively studied by high resolution electron microscopy (HREM) [22–26]. However, concerning the presence of an amorphous phase at the grain boundaries in TZP, there has been a lack of agreement in the reported results. Although the nature of an amorphous phase has not yet been clarified, Primdahl et al. [22] have reported that the formation of an amorphous phase in TZP can be attributed to impurities; that is, an amorphous phase is present in low-purity TZP but absent in high-purity TZP. In contrast, Ikuhara et al. [27] and Chokshi et al. [28] reported that there is no amorphous film at the grain boundaries, irrespective of the impurities in TZP. On the other hand, Wakai [29] proposed the mechanism based on the presence of amorphous film, and this model explained the deformation parameter by the solution-precipitation phenomena in the amorphous film. These results all indicate that further investigation is required to understand the nature and role of the grain boundary for superplasticity in ceramics.

In this study, we characterized the grain boundaries in undoped TZP and glass-doped TZP in order to clarify their role in the mechanism of superplastic deformation. How impurities affect the grain boundary structure and properties is also important; therefore we selected three kinds of glass: i.e. SiO2; (SiO2–Al2O3); and (SiO2–MgO) and systematically investigated the effects of these impurities.

For characterizing the grain boundary, transmission electron microscopy (TEM), and in particular, high-resolution electron microscopy (HREM) is one of the most useful techniques for studying the atomic structure of grain boundaries. In recent years, HREM has been used to investigate various kinds of grain boundaries in superplastic ceramics [22–24]. Analytical electron microscopy (AEM) can reveal the element distribution and the chemical bonding state with a spatial resolution of nanometer order [30,31], and recent improvements to the field emission gun enable investigators to employ energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) with a spatial resolution of less than 1 nm [30,31].

In this study, we used HREM, EDS, and EELS to characterize the microstructure of (SiO2–, SiO2–Al2O3), and (SiO2–MgO)-doped TZP with high spatial resolution and compared the results with the microstructure of undoped TZP in order to understand the superplastic behavior in these materials at the atomic level. Theoretical calculations are needed for quantitative analysis of the electron energy near edge structure (ELNES) and to understand the nature of chemical bonding at the grain boundary. We used a first principle molecular orbital (MO) calculation using the discrete-variational (DV)-Xα method [32]. In addition, the high-temperature behavior of TZP and SiO2 was directly observed in TEM in order to confirm the chemical reaction and therefore the segregation behavior at high temperatures in glass-doped TZP.

2. Experimental procedure

2.1. Sample preparation

SiO2–, (SiO2–Al2O3), and (SiO2–MgO)-doped TZP and undoped TZP were prepared as follows. A small amount of Al2O3 and MgO were added to the starting colloidal silica to investigate the impurity effects [33]. The starting materials were based on 2.5 mol% Y2O3-stabilized TZP powders with an average grain size of 25 nm (Tooh) and colloidal silica (Nissan Chemical Industry). The glass compositions were 100 wt%-pure SiO2, 98 wt.%SiO2–2 wt%MgO and 98 wt.%SiO2–2 wt.%Al2O3, and a 5 wt% of each glass was mixed with TZP powders in a ball mill for 24 h. The total amount of the impurity (MgO or Al2O3) was therefore in the order of 1000 ppm. The powders were then granulated by #60 mesh, pressed into bars in a cemented carbide die under a pressure of 33 MPa, and cold-isostatically pressed under a pressure of 100 MPa to obtain green compacts. The glass-doped TZP compacts were then sintered for 2 h in air at 1300°C, whereas that without SiO2 was sintered at 1450°C to make the grain sizes the same in all specimens [11]. The bulk density of the sintered specimens was measured by the Archimedes’ method, and it was confirmed that fully dense sintered bodies were obtained for all materials by the sintering.

2.2. High-temperature tensile test

Specimens for tensile tests were cut from the sintered bodies and ground with a diamond wheel to a final size of 2 × 2 × 13.5 mm3. High temperature tensile tests were carried out for each material at a strain rate of 1.3 × 10−4 or 6.2 × 10−4 s−1 and at a temperature of 1400 or 1500°C in air by using an Instron type mechanical testing machine (Shimazu AG-5000C).

2.3. TEM characterization

Thin pieces were cut off from the sintered bodies to prepare TEM specimens. Specimens were obtained using a standard technique involving mechanical grinding to a thickness of 0.1 mm, dimpling to a thickness of 20 mm and ion beam milling to electron transparency at about 4 kV. HREM observations were performed using a Topcon 002BF field emission microscope with a point-to-point
resolution of 0.18 nm. EDS for chemical analysis was carried out with a Noran Voyager system in the Topcon microscope with a probe size of less than 0.5 nm. EELS was obtained using a Gatan PEELS spectrometer (model 666) in the Topcon microscope with an energy resolution of 0.7–0.8 eV.

For high-temperature in-situ observations, the powders after mixing in the ball mill were sprinkled onto a tungsten wire in the side entry-type specimen holder in a TEM (Hitachi H-9000NAR, 300 kV) [34]. The mixed powders were heated to 1400°C by passing current through the tungsten wire. Details of this particular specimen holder are described elsewhere [35]. The dynamic behavior of SiO$_2$ and TZP at high temperatures was recorded using a video system connected to a CCD camera in the TEM.

Image simulations were performed using the Tempas program developed by Kilaas [36]. The MO calculations for interpreting the change in ELNES were made by the discrete-variational (DV)-X$\alpha$ method developed by Adachi [32].

2.4. Theoretical calculations

DV-X$\alpha$ MO calculations were performed to evaluate the chemical bonding state at the grain boundaries. Fig. 1 shows the (Y$_2$Zr$_{15}$O$_{50}$)$^{8-}$ cluster, which represents the structure of Y-TZP [37]. The cluster is composed of 108 ions and includes up to the 12th nearest neighbor from the Zr ions located at sites C(1) or C(2) indicated by the arrows. In the cluster, two Y$^{3+}$ ions are replaced with Zr$^{4+}$ ions at the third nearest neighbor site from Zr$_{C(1)}$. An oxygen vacancy is thus introduced at the second nearest neighbor site from the two Y$^{3+}$ ions [38] to maintain electrical neutrality. Similarly, two Y$^{3+}$ ions are located at the third nearest neighbor sites from Zr$_{C(2)}$ and an oxygen vacancy is introduced at the second nearest neighbor site from the two Y$^{3+}$ ions. The cluster size was confirmed to be large enough to reproduce the actual electronic state by comparing the calculated results with the experimental data obtained by EELS [37]. For the grain boundary models in which Si segregates, a (Si$_{7.5}$Y$_{0.5}$Zr$_{15}$O$_{50}$)$^{8-}$ cluster was constructed for the present calculation, and a (SiMg$_{0.5}$Y$_{0.5}$Zr$_{15}$O$_{50}$)$^{8-}$ cluster was constructed for the grain boundary in which Si and Mg co-segregate. Table 1 shows the location of Zr, Si, and Mg for each cluster and the name of the cluster. All clusters were put into a field of a Madelung potential composed of about 6000 point charges. Bond overlap population (BOP) and net charge (NC) were calculated from these clusters to evaluate the chemical bonding state at the grain boundaries. The BOP represents the degree of covalency of a bond, while the NC corresponds to the effective ionicity of an ion in a crystal. The product of NCs is thus expected to describe the strength of an ionic bond. In the DV-X$\alpha$ MO calculation, the electronic structures of ions at the edge of a cluster are very much affected by dangling bonds. To remove this influence, it is necessary to examine the electronic structure near the center of a cluster. We analyzed the bonding states around the ions located at C(1) and C(2).

3. Results and discussion

3.1. Morphology of microstructure

Fig. 2 shows bright-field transmission electron micrographs of (a) TZP and (b) SiO$_2$-doped TZP in the as-sintered state. Both materials are highly dense and their grain sizes are about 0.2 μm. The grains in TZP are faceted and have straight grain boundaries. Most of the grains in SiO$_2$-doped TZP, in contrast, are rounded at the grain corners, and glass pockets are formed at grain boundary multiple junctions. The dihedral angles between grain boundaries and glass pockets look homogeneous irrespective of the type of grain boundaries, as shown in Fig. 3(a). Fig. 3(b) shows the distribution of dihedral angles at the multiple junctions of SiO$_2$-doped TZP. The dihedral angles are clearly distributed around an average angle of approximately 80°.

| Cluster models, ion located at C(1) and C(2), and name of the clusters | (Y$_2$Zr$_{15}$O$_{50}$)$^{8-}$ | (Si$_{7.5}$Y$_{0.5}$Zr$_{15}$O$_{50}$)$^{8-}$ | (Si$_{7.5}$Y$_{0.5}$Zr$_{15}$O$_{50}$)$^{8-}$ | (SiMg$_{0.5}$Y$_{0.5}$Zr$_{15}$O$_{50}$)$^{8-}$ |
|---|---|---|---|---|
| C(1) | Zr | Si | Si | Mg |
| C(2) | Zr | Zr | Si | Si |
| Name | 3Y–TZP | 3Y–1Si | 3Y–2Si | 3Y–MgSi |
This suggests that grain boundary energy does not depend on grain boundary orientation.

The equilibrium relationship between dihedral angle $\phi$, grain boundary energy $\gamma_{gb}$, and solid/liquid interface energy $\gamma_d$ can be expressed by the following equation [39]

$$\cos(\phi/2) = 1/2(\gamma_{gb}/\gamma_d).$$

(1)

According to this equation, the ratio of $\gamma_{gb}/\gamma_d$ is between 1 and $\sqrt{3}$ for $\phi$ values between 60 and 120°. In this range, the liquid phase partially penetrates at the triple junction, but does not penetrate along whole grain boundaries. Since the observed angle of 80° is in this range, the boundary energy is considered to be low enough for TZP grains to join without an amorphous phase, which usually reduces grain boundary energy.

3.2. High-temperature plastic deformation

The superplastic elongation in TZP is greatly improved by the addition of SiO$_2$ [11]. Fig. 4 shows the stress--strain curves of TZP and SiO$_2$-doped TZP obtained at a strain rate of $1.3 \times 10^{-4}$ s$^{-1}$ at 1400°C in air. As can be seen, SiO$_2$ doping reduces the flow stress and enhances the tensile ductility of TZP. The tensile elongation is 1100% in SiO$_2$-doped TZP, whereas under the same conditions it is only 123% in TZP. Fig. 5 shows (a) the flow stress and elongation and (b) photographs of specimen of pure SiO$_2$-doped TZP, (SiO$_2$-2 wt%MgO)-doped TZP, and (SiO$_2$-2 wt%Al$_2$O$_3$)-doped TZP tensiled to failure at a strain rate of $6.2 \times 10^{-4}$ s$^{-1}$ at 1500°C. As shown in the figures, the high ductility of pure SiO$_2$-doped TZP is significantly reduced.
by the addition of other oxides into the SiO$_2$ phase. The amount of glass phase was kept at 5 wt\% in the three materials. Note that the amount of additional oxide additives is only in the order of 1000 ppm in the (SiO$_2$–2 wt\%MgO)- and (SiO$_2$–2 wt\%Al$_2$O$_3$)-doped samples, but the flow stress and, in particular, the tensile ductility drastically change with the additives. The addition of Al$_2$O$_3$ decreases the flow stress to 4.4 MPa, but the elongation is only one fourth of that of SiO$_2$-doped TZP. On the other hand, the addition of MgO increases the flow stress, whereas the elongation is 255\%. The enhancement of superplasticity has been explained in terms of the reduction of flow stress [40] and the suppression of grain growth by SiO$_2$ doping [11]. The grain growth behavior in the pure SiO$_2$-doped TZP during deformation at high-temperature has been reported elsewhere [11], showing that the grain growth in SiO$_2$-doped TZP is pretty sluggish [41]. The grain growth behavior of two other samples was also checked, but there was no difference in comparison with the present three materials. The results shown in Fig. 5 thus indicate that tensile ductility is not directly related to decreases in flow stress. The origin of the superplastic ductility in glass-doped TZP is in the chemical bonding state in the grain boundaries, which will be discussed in the following sections.

3.3. Grain boundary atomic structure

As mentioned before, there is a discrepancy in the reported results regarding the presence of an amorphous phase at grain boundaries in TZP. These results were mainly obtained by HREM [22–26], but HREM images frequently include a strong diffraction contrast and the small size of TZP grains make the interpretation of HREM images ambiguous [42]. Thus, one of the reasons for the discrepancy may be due to investigators having different interpretations of the HREM images. In order to characterize grain boundary structure accurately by HREM, grain boundary planes should be set parallel to the incident electron beam [43]. In addition, two grains adjacent to a grain boundary must satisfy the Bragg reflection condition so that lattice images of both can be observed without overlapping. In superplastic ceramics, however, there are very few grain boundaries that satisfy these conditions because they have fine grains and the grain boundary planes are mostly curved. Furthermore, a strong diffraction fringe appearing parallel to a grain boundary often forms a white contrast, which looks like an amorphous phase along the boundary. As a result, the observed lattice images often contain such artifacts as image overlapping and diffraction contrast in the vicinity of the grain boundaries. In addition, grain boundary grooving during ion milling may show an amorphous-like contrast.

![Fig. 5](image)

Fig. 5. (a) Flow stress and elongation of (SiO$_2$–2 wt\%Al$_2$O$_3$)-doped TZP, (SiO$_2$–2 wt\%MgO)-doped TZP and pure SiO$_2$-doped TZP tensile at a strain rate of 6.2 × 10$^{-4}$ s$^{-1}$ at 1500°C, and (b) the corresponding tensile specimens after fracture.

![Fig. 6](image)

Fig. 6. High resolution electron micrograph of a grain boundary in (a) undoped TZP and (b) SiO$_2$-doped TZP, indicating that no amorphous phase is formed along the grain boundaries in both cases.
along grain boundaries in HREM micrographs. The following results were thus obtained under the edge-on condition so the images were without these artifacts.

Fig. 6 is a high resolution electron micrograph of a typical grain boundary in (a) undoped and (b) SiO$_2$-doped TZP. In the grain boundary of the undoped TZP, the (110) planes are connected to the boundary, and no amorphous phase is observed along the grain boundary. In the boundary of the SiO$_2$-doped TZP, the {200} and the {111} lattice planes are seen in each grain. Note that there is no amorphous phase at the grain boundary even in the SiO$_2$-doped samples. More than 20 grain boundaries satisfying the edge-on condition were observed, and none of them revealed the presence of an amorphous phase, irrespective of grain boundary orientations. As mentioned in Section 3.2, an amorphous phase is present only at grain boundary multiple junctions.

Fig. 7 is a high-resolution electron micrograph of another grain boundary in the SiO$_2$-doped TZP. The observed direction is parallel to the [001] for both the adjacent grains. The orthogonal set of {100} planes can be seen in each grain, and the misorientation angle around [001] is 28.07° to form a [001]Σ17a coincidence site lattice (CSL) boundary. The grain boundary plane is (410) for both grains to form a symmetric CSL boundary. As shown in the micrograph, no amorphous phase is observed at the grain boundary. However, white contrasts, which reflect the channel structures at the grain boundary, are observed periodically along the boundary. This white contrast has a periodicity with a spacing of 1.1 nm as indicated by the arrows in Fig. 8(c), which is a magnified section of Fig. 7. A possible structure of the grain boundary in Fig. 8(c) is illustrated in Fig. 8(a) where the oxygen atoms correspond to small circles and the zirconium atoms large ones. The model is constructed by simply removing closer atoms at the boundary, and neither the presence of solute atoms nor the structure relaxation is taken into account. The atoms at the boundary are removed when the bond length is shortened to within 0.05 and 0.097 nm for O–O and Zr–Zr bonds, respectively. The parameters of the supercell in the calculations were 3.298 × 3.298 × 0.4 nm with 796 atoms. The calculations were performed over a range of thickness from 2 to 20 nm, and a range of defocus from 0 to −80 nm. The best match was obtained at a thickness of 5 nm and defocus of −42 nm as shown in Fig. 8(b). In the simulated image, large white circles and peanuts-like contrast are alternately observed along the grain boundary. This periodicity is 1.1 nm, which agrees well with that observed in the experimental image in Fig. 8(c). Although the grain boundary model is not perfect, the agreement between the experimental and simulated images suggests that the grain boundary is set at the edge-on condition and the periodic

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**Fig. 7.** High resolution electron micrograph of Σ17a CSL boundary, in which two adjacent grains have a misorientation angle of 28.07° around the [001] axis. Note that white dots are observed periodically along the grain boundary.
channel-structure is actually formed along the boundary as shown in Fig. 8(a). The strained contrast in the vicinity of the grain boundary is considered to be due to the solution of silicon atoms, which will be discussed in Section 3.4.

The surprising finding here is that there is no amorphous phase at the grain boundaries of SiO₂-doped TZP containing a large amount of intentionally doped SiO₂. This differs from previously published results [24–26]; however, it is consistent with the fact that the average dihedral angle between grain boundaries in SiO₂-doped TZP is about 80°. One theory of the equilibrium thickness of the intergranular glass phase in ceramics has been proposed by Clarke [44], and this has been successfully applied to the grain boundary glassy phase of the Si₃N₄/SiO₂ system [45,46]. According to the theory, the equilibrium thickness for the TZP/SiO₂ system should be about 0.7 nm if the grain boundary is wetted by an amorphous phase [44]. However, the present result is contrary to this.

3.4. Grain boundary composition

Fig. 9(a) and (b) are typical EDS profiles obtained from a grain interior and grain boundary in TZP, respectively. The electron probe size used for the analysis was about 0.5 nm. The concentration of yttrium is higher at the grain boundary than within the grain. Fig. 9(c) and (d) show EDS profiles obtained from a grain interior and grain boundary in SiO₂-doped TZP, respectively. These spectra were taken from the areas shown in Fig. 7. As shown in the figures, silicon as well as yttrium is detected at the grain boundary.

Fig. 10(a) and (b) show profiles of element distribution across the boundaries in TZP and SiO₂-doped TZP, respectively. The profiles were obtained by normalizing the X-ray intensity for each element by the intensity of Zr–Kα. Since the specimens for the analysis were thin enough for HREM image to be observed, the concentrations of Y₂O₃ and SiO₂ could be calculated by using the theoretical K factor derived from the thin foil approximation [30]. As shown in the profiles, yttrium ions segregate at grain boundaries over a width of about 10 nm in both TZP and SiO₂-doped TZP. In addition, silicon ions co-segregate with yttrium ions at the boundary over a width of about 10 nm in SiO₂-doped TZP. The amount of segregated yttrium is more than twice as large as that of the grain interior in both TZP and SiO₂-doped TZP, but the amount in TZP is slightly higher than that in SiO₂-doped TZP. This difference may be associated with the co-segregation of silicon in SiO₂-doped TZP. The observed results also indicate that silicon ions are dissolved into tetragonal zirconia in the vicinity of grain boundaries, even though the solubility of SiO₂ into ZrO₂ is reported to be almost negligible [47].

McLean [48] proposed the following equation for the strain energy due to solute misfit:

\[ W = 24 \pi K G r_1 \left( r_1 - r_2 \right) \left[ \frac{1}{3} + 4 \frac{r_1}{r_2} \right], \]

where \( K \) is the bulk modulus of the solute, \( G \) the shear modulus of the solvent, and \( r_1 \) and \( r_2 \) are the ionic radii of the solute ions. Accordingly, the strain energy should be 25 kJ mol⁻¹ when silicon is dissolved into the ZrO₂ lattice. This strain energy will accumulate near the grain boundary.
and distort the ZrO₂ lattice, where silicon is dissolved. The change in contrast in the vicinity of the boundary in Fig. 7 is likely to reflect such a localized strain. In this case, the total energy of this system is reduced at the grain boundary, even though strain energy accumulates along the boundary. Thus it can be concluded that the grain boundary energy of SiO₂-doped TZP is low enough to allow for an increase of strain energy at the boundary.

3.5. Effect of impurities

Fig. 11 shows typical transmission electron micrographs of (a) pure SiO₂-doped TZP, (b) (SiO₂–MgO)-doped TZP and (c) (SiO₂–Al₂O₃)-doped TZP in the as-sintered state. All materials have a density of about 99% of theoretical density. The grains are nearly equiaxed and there are no elongated grains in any of the materials. Most of the grains have rounded corners. Amorphous glass pockets were visible at the grain boundary multiple junctions. The average grain size is 0.21 μm in pure SiO₂-doped TZP, 0.27 μm in (SiO₂–MgO)-doped TZP and 0.23 μm in (SiO₂–Al₂O₃)-doped TZP. Note that the morphology of the microstructure is almost the same regardless of the kind of doped glass.

Fig. 12 shows HREM images of a grain boundary in (a) (SiO₂–Al₂O₃)-doped and (b) (SiO₂–MgO)-doped TZP.

Fig. 11. Bright field images of (a) pure SiO₂-doped TZP, (b) (SiO₂–MgO)-doped TZP and (c) (SiO₂–Al₂O₃)-doped TZP in as sintered state, indicating that microstructural morphology is similar among all of specimens.

Fig. 12. High-resolution electron micrograph of a grain boundary in (a) (SiO₂–Al₂O₃)-doped TZP and (b) (SiO₂–MgO)-doped TZP, indicating that no amorphous phase is formed along the grain boundaries in either cases.

In the (SiO₂–Al₂O₃)-doped TZP, the (110) lattice planes in each grain run into the grain boundary. This figure clearly indicates the absence of any amorphous phase along the grain boundary. We observed 11 grain boundaries in this material, and no amorphous phase was present in any. In the (SiO₂–MgO)-doped TZP, the lattice fringes of adjacent grains again indicate that no amorphous phase is present along the grain boundary. This tendency was the same for seven other grain boundaries examined in the specimen.

Fig. 13 shows the profile of element distribution across the grain boundaries in (a) pure SiO₂-doped, (b) (SiO₂–MgO)-doped, and (c) (SiO₂–Al₂O₃)-doped TZP. The probe size and separation for the EDS analysis were about 0.5 and 1 nm, respectively. The X-ray intensity of each element was normalized by the intensity of Zr–Kα. As shown in the figures, Y³⁺ and Si⁴⁺ ions segregate at the
grain boundary faces but partially penetrates along the grain multiple junctions as mentioned previously. This is in agreement with the present result that no amorphous layer is present along the grain boundaries in any of the materials.

Judging from the observed microstructural features and dihedral angle, the grain boundary energy in glass-doped TZP is expected to be so low that the amorphous phase forms pockets in the multiple grain junction rather than an intergranular film along the grain boundaries.

In this study, it was found that yttrium, silicon and additive cations segregate at grain boundaries in glass-doped TZP. Two factors may contribute to the segregation of these ions in the grain boundaries of oxide ceramics. One is the strain energy relaxation that results from the size mismatch between the solute and matrix ions, and the other is electrostatic charge compensation [49]. The size mismatch can be approximated in terms of the misfit value $\epsilon$ as follows:

$$
\epsilon = (r_1 - r_2)/r_1,
$$

where $r_1$ and $r_2$ are the ionic radii of solvent and solute ions [48]. The strain energy relaxation is the principal driving force for the segregation, when the misfit value is large. The misfit value is about 0.21 for $Y^{3+}$ and 0.14 for $Mg^{2+}$. These values are not large enough for the segregation to be accounted for by the strain energy relaxation alone. The charge difference between $Zr^{4+}$ and $Y^{3+}$ or $Mg^{2+}$ ions must be considered.

The ionic radii of $Si^{4+}$ and $Al^{3+}$, on the other hand, are too small to be dissolved into zirconia [50]. Their misfit values are 0.52 and 0.36, respectively. These values are in accordance with reports indicating that $SiO_2$ and $Al_2O_3$ are insoluble in $ZrO_2$ [47,51,52]. The presence of $Si^{4+}$ and $Al^{3+}$ ions in the vicinity of grain boundaries may result from the co-existence of $Y^{3+}$ ions.

The important point clarified in this study is that the segregation of additive cations in the vicinity of grain boundaries must be the origin of the marked reduction in tensile ductility in SiO$_2$-doped TZP. As mentioned previously, the tensile ductility of glass-doped TZP is considered to depend on both flow stress and chemical bonding at the grain boundaries. These factors correspond to an accommodation process for grain boundary sliding and a cavitation mechanism, respectively. Stress accommodation due to grain boundary sliding is thought to take place in the amorphous phase formed at multiple junctions, which is related to the viscosity in the amorphous phase and hence the flow stress in the glass-doped specimens. Cavitation correlates with chemical bonding at the grain boundaries. The chemical bonding is considered to be high in the order of pure SiO$_2$-doped > (SiO$_2$–MgO)-doped > (SiO$_2$–Al$_2$O$_3$)-doped specimens, while the flow stress would be large in the order of (SiO$_2$–MgO)-doped > pure SiO$_2$-doped > (SiO$_2$–Al$_2$O$_3$)-doped specimens. The balance of flow stress and chemical bonding must determine the tensile ductility in

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**Fig. 13.** Profile of element distribution at every 1 nm across a grain boundary in (a) pure SiO$_2$-doped TZP, (b) (SiO$_2$–MgO)-doped TZP and (c) (SiO$_2$–Al$_2$O$_3$)-doped TZP.
3.6. Grain boundary chemical bonding state

EELS is a powerful technique for evaluating the chemical bonding state in narrow region such as grain boundaries. This is because the near edge structure of core-loss peaks in an EELS spectrum (electron energy loss near edge structure, or ELNES) is sensitive to the structural and chemical environment of the atoms. The ELNES of the O-K-edge was obtained across the boundary in both TZP and SiO$_2$-doped TZP in order to evaluate the bonding state at the respective grain boundaries. Fig. 14 shows the ELNES of the O-K-edge taken with a probe size of about 1 nm at (a) a grain boundary and (b) the grain interior in SiO$_2$-doped TZP. In the spectra, the main peak of the O-K-edge appears at around 535 eV in both the grain boundary and grain interior. In the grain boundary spectrum, however, there are three additional shoulder peaks, indicated by arrows, which do not appear in the grain interior spectrum. Similar shoulders were also seen for other grain boundaries examined, although there was a small difference in their fine structure around the main peak. The small difference probably reflects a dependence on the atomic structure of the grain boundary. The formation of the three additional peaks suggests that the chemical bonding state is influenced by the silicon segregation at the grain boundary.

To interpret the appearance of the additional peaks, we carried out theoretical calculations for the ELNES features using model clusters. It has been reported that a first principles MO calculation using the DV-Xα cluster method was useful for interpreting ELNES in a number of ceramic materials [53]. The calculation does not require any adjustable parameters, and the results are directly interpretable in terms of chemical bonds. However, since the calculation treats all electrons included in the cluster, the number of atoms that can be treated with presently available computers is limited to a few hundred. In the present study, we obtained theoretical O-K-edge ELNES spectra for perfect crystalline ZrO$_2$ for a grain interior model and Si containing ZrO$_2$ for a grain boundary model in order to understand the spectral features that were observed experimentally. The model clusters used for this calculation were Zr$_{14}$O$_{36}$ and SiZr$_{12}$O$_{56}$ (Fig. 15), which are embedded in the Madelung potential generated by the point charges.

The computational procedures have been described elsewhere [32,53]. The electric-dipole selection rule allows a transition from the O-1s orbital to the unoccupied 2p orbital in the case of the O-K-edge ELNES. As a result, the unoccupied density of states (PDOS) of O-2p corresponds to the O-K-edge ELNES. Fig. 16(a) shows the O-2p PDOS for the ZrO$_2$ (grain interior model) and silicon containing

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Fig. 14. ELNES of the O-K-edge taken with a probe size of about 1 nm at (a) a grain boundary and (b) the grain interior in SiO$_2$-doped TZP. Note that three additional shoulders appear as indicated by the arrows around the main peak.

Fig. 15. Cluster model for (a) grain interior (Zr$_{14}$O$_{36}$) and (b) grain boundary (SiZr$_{12}$O$_{56}$). The location of Si atom in the grain boundary is indicated by the arrow in (b).

Fig. 16. Theoretical O-2p unoccupied PDOSes for the grain boundary model and grain interior model in Fig. 15, which correspond to the O-K-edge ELNES. Three shoulders, which reflect the level structures due to the Si segregation shown in (b), are observed around the main peak only in the spectra of the grain boundary model.
ZrO$_2$ (grain boundary model). Comparing the two profiles, we can see three shoulder peaks as indicated by the arrows in the grain boundary model. On the other hand, no shoulders can be seen in the spectra from the grain interior model. Fig. 16(b) shows level structures due to the presence of silicon. The energies at the shoulder peaks in the grain boundary model are coincident with the energies of the level structures. This result agrees well with the experimental spectra in Fig. 14, and confirms the segregation of silicon in the SiO$_2$-doped TZP. The nature of chemical bonding will be discussed later.

3.7. High-temperature behavior

To observe the reaction between SiO$_2$ and TZP directly, and hence to understand the segregation behavior of Si at high temperatures, the mixed powders were placed in the high-temperature TEM holder. In the TEM stage, amorphous SiO$_2$ particles (colloidal silica) were well dispersed on the grains of ZrO$_2$. The average grain sizes of SiO$_2$ were about 0.01 μm.

It was found that most amorphous SiO$_2$ particles were absorbed into a ZrO$_2$ grain at about 1300°C. When the SiO$_2$ particles were relatively large, some amount of SiO$_2$ particle remained on the surface of the ZrO$_2$ grain, forming a curved interface due to the wetting of SiO$_2$. This suggests that there is a limit to the solubility of SiO$_2$ in ZrO$_2$, even at 1300°C. Fig. 17 shows (a) ZrO$_2$ grains held at 1300°C, which have clean surfaces after absorbing SiO$_2$ particles and (b) the same grains after the temperature was reduced from 1300 to 400°C. A thin film with weak contrast is seen around the entire surface of the grains. The thickness of the film is about 4 nm as indicated by the arrows. Film such as this gradually formed on all of the ZrO$_2$ grains from 500 to 400°C when the powders were cooled from 1300°C. Fig. 18(a) shows a thin film formed on the ZrO$_2$ grain, and (b) and (c) show the EDS spectra obtained from 2 nm areas in the thin film and the grain interior, respectively. Comparing the two spectra, it is obvious that the thin film is composed of silicon. The micro-diffraction pattern revealed that the thin film was in the amorphous state, so we concluded that the film was amorphous SiO$_2$ phase. The SiO$_2$ thin film is thought to be formed by a precipitation process from a super-saturated SiO$_2$–ZrO$_2$ solid solution during cooling from a high temperature. This solution-precipitation behavior was found to be reversible; that is, the SiO$_2$ thin film was absorbed in the ZrO$_2$ grain when the temperature was raised to 1300°C, and SiO$_2$ was re-precipitated around the ZrO$_2$ grain as a thin film when the powders were cooled from that temperature. However, no such film was formed at the grain boundary, as indicated by the triangle in Fig. 17. This suggests that Si could not form the film, but does segregate at the boundary because the adjacent grains are tightly bonded, which is consistent with the experimental results obtained by EDS and EELS.

3.8. Electronic structure

In t-ZrO$_2$ (tetragonal zirconia), there are two types of Zr–O bond, i.e. a long bond and a short bond, because oxygen atoms alternately shift along the c-axis. The long Zr–O bond and the short bond are denoted as Zr–O(l) and Zr–O(s), respectively. Similarly, other bonds between cation and oxygen ion can be denoted as, e.g. Si–O(s) and
Fig. 19. Calculated BOPs of Zr–O bonds in the cluster of 3Y–TZP, and Zr–O and Si–O bonds of 3Y–1Si.

Fig. 20. Calculated BOPs of Zr–O bonds of 3Y–TZP, Si–O bonds of 3Y–2Si, and Mg–O and Si–O bonds in 3Y–MgSi.

Si–O(l). Fig. 19 shows the calculated BOPs of the Zr–O bonds in the cluster of 3Y–TZP, and the Zr–O and Si–O bonds of 3Y–1Si. As can be seen, the BOPs of the two clusters of Zr–O bonds are not very different, but the BOPs of the Si–O bonds are larger than those of the Zr–O bonds. The BOP of the Si–O(s) bond is about three times larger than those of the Zr–O bonds. This indicates that Si ions in SiO₂-doped TZP have a higher covalent bonding with O ions in comparison with the Zr ions. Fig. 20 compares the BOPs of the Zr–O bond of 3Y–TZP, Si–O bond of 3Y–2Si, and Mg–O and Si–O bonds in 3Y–MgSi. The difference in the BOPs of Si–O between 3Y–MgSi and 3Y–2Si does not seem to be large. This suggests that an additional dopant such as Mg²⁺ does not influence the chemical bonding state of Si–O in SiO₂-doped TZP.

As discussed in Section 3.7, the tensile ductility of SiO₂-doped TZP is likely to be related to the chemical bonding state at the grain boundaries. Experimental results indicate that the elongation to failure in glass-doped TZP is greatly enhanced by the segregation of Si¹⁺ ions, but is deteriorated by further addition of a small amount of cations such as Mg²⁺. As shown in Fig. 19, Si ions in TZP have a higher covalent bonding with oxygen ions in comparison with Zr ions. The grain boundaries in SiO₂-doped TZP must be strengthened by the increase in covalency with the segregated Si ions, which would increase the resistance to grain boundary cavitation. In (SiO₂–MgO)-doped TZP, however, the BOP of the Mg–O bonds in 3Y–MgSi is almost the same as that of the Zr–O bonds in 3Y–TZP. This indicates that MgO is not very effective in increasing the covalency at the grain boundary. Fig. 21 shows the relationship between the elongation to failure and (a) the product of NC, and (b) the total BOP in 3Y–TZP, 3Y–2Si and 3Y–MgSi. As shown in the figure, the elongation cannot be described by the product of NC, which corresponds to the strength of the ionic bond, while the elongation has a good relationship with the covalency of the bonds. It is thus concluded that the covalency is one of the key factors in determining the ductility of glass-doped TZP. The amorphous glass phase located at the multiple junctions accommodate the stress concentration caused by grain boundary sliding, while the covalency at the grain boundaries plays an important role in keeping the connection of adjacent grains stable during deformation. Grain boundary cavitation and resultant fracture may be suppressed by the formation of strong grain boundaries.

Fig. 21. Relationship between the elongation to failure and (a) the product of NC, and (b) the total BOP in 3Y–TZP, 3Y–2Si and 3Y–MgSi, indicating that the total BOP is related to the elongation.
4. Conclusions

In order to understand the mechanism of superplasticity in glass-doped TZP, the atomic structure, chemical composition, and chemical bonding state at grain boundaries in undoped TZP and three kinds of SiO$_2$-doped TZP were investigated using HREM, EDS, and EELS with high spatial resolution. In addition, the high-temperature behavior of SiO$_2$-doped TZP was directly observed by TEM in situ heating experiments to investigate the chemical reaction of SiO$_2$ and TZP. A first principles MO calculation using the DV-Xα method was performed to interpret the ELNES from the grain boundaries in SiO$_2$-doped TZP and to understand the nature of the chemical bonding state at the boundaries. The results of these investigations are summarized as follows.

1. The addition of SiO$_2$ greatly enhanced the tensile ductility of TZP, but the subsequent addition of a small amount of Al$_2$O$_3$ or MgO markedly reduced ductility. This result is due to the segregation of Al$^{3+}$ or Mg$^{2+}$ at the grain boundaries, which change the chemical bonding state at the boundaries.

2. HREM studies revealed that there was no amorphous film along the grain boundaries in TZP and the three kinds of glass-doped TZP. However, the amorphous phase formed glassy pockets at multiple grain junctions.

3. The average dihedral angle between grain boundaries in the three kinds of glass-doped TZP was distributed from 80 to 90°, which agreed well with the fact that there was no glass phase at the grain boundaries. This result indicates that the grain boundary energy is relatively low in all glass-doped specimens.

4. Yttrium segregated in the vicinity of the grain boundaries in both TZP and the three kinds of SiO$_2$-doped TZP. In the glass-doped specimens, Si$^{4+}$ and doped Al$^{3+}$ or Mg$^{2+}$ segregated over a width of several nm along the grain boundaries. The segregation is related to the ductility of glass-doped TZP.

5. Most SiO$_2$ particles dissolved into ZrO$_2$ grains above 1300°C, but the SiO$_2$ phase re-precipitated in the form of a thin layer around ZrO$_2$ grains during cooling from high temperature. This dynamic phenomenon well explains the segregation behavior of Si at the grain boundaries in SiO$_2$-doped TZP.

6. The O-K-edge ELNES obtained from the grain boundaries in SiO$_2$-doped TZP was interpreted using MO calculation. The theoretical results agreed well with the experimentally obtained results, and confirmed the segregation of Si at the grain boundaries in SiO$_2$-doped TZP.

7. Theoretical calculations suggest that the covalency at the grain boundaries plays an important role in keeping the connection of adjacent grains stable during deformation. Grain boundary cavitation and resultant fracture would be suppressed by the formation of strong grain boundaries. On the other hand, the amorphous glass phase located at the multiple junctions would effectively work to accommodate the stress concentration caused by grain boundary sliding.

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