Effects of Temperature and Chemical Composition of Intergranular Glass on Dihedral Angle of Glass-Doped 3Y-TZP

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ガラス添加 3Y-TZP の二面角に及ぼす粒界ガラス組成と温度の影響

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The distribution and the morphology of glass phase in polycrystals are affected by the dihedral angle and the volume fraction of the glass phase. The effects of temperature and chemical composition of intergranular glass on dihedral angle of glass-doped 3-mol%-yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) were studied by transmission electron microscopy (TEM). The intergranular glass was either SiO₂ (melting point of 1700°C) or Y₂O₃-Al₂O₃-SiO₂ eutectic glass (YAS glass; melting point of 1350°C). The average dihedral angles of SiO₂-doped and YAS-doped 3Y-TZP, which were sintered at 1300°C, were found to be 70° and 50°, respectively. The dihedral angle in YAS-doped 3Y-TZP decreased to 25° after annealing at 1500°C, whereas that in SiO₂-doped 3Y-TZP remained constant. From the relationship between the dihedral angle and the ratio of grain boundary energy to solid/glass interface energy (γ_{SS}/γ_{SL}), it was suggested that γ_{SS}/γ_{SL} increased at elevated temperatures higher than the melting point of glass.

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1. Introduction

Ceramics often contain a glass phase at grain boundaries. The residual glass phase results from the liquid phase sintering with metal oxides as additives. A very small amount of liquid-forming impurities in the starting powder also forms a glass phase in some ceramics.^(1,2) The glass phase promotes mass transport at elevated temperatures, and as such reduces the flow stress. The presence of glass phase affects the deformation behavior of ceramics.^(3,4) 3-mol%-yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) is one of the most typical ceramics that shows superplasticity at elevated temperatures.⁽⁵⁾ The effects of additional glass on superplasticity of Y-TZP have been studied to improve the ductility^{(6)–(11)} Yoshizawa et al.⁽⁶⁾ and Gust et al.⁽⁷⁾ reported that the additional silicate glass was present not only at multiple junctions as glass pocket but also at two-grain junctions as thin film. However, Ikuhara et al.⁽⁹⁾ revealed that intergranular glass film did not exist in SiO₂-doped Y-TZP. No intergranular glass film was present in barium silicate glass doped Y-TZP, and borosilicate glass doped Y-TZP also.⁽¹¹⁾ Zirconia grains in this material, as well as those in undoped Y-TZP,^{(12)–(14)} were directly bonded atomically at grain boundaries.

The distribution and the morphology of glass phase in polycrystals are determined by solid/glass interface energy (γ_{SL}), solid/solid interface energy (grain boundary energy: γ_{SS}), and volume fraction of glass phase.^{(15)–(17)} The equilibrium relationship between γ_{SL} , γ_{SS} , and dihedral angle (ϕ) can be expressed by the following equation⁽¹⁸⁾ (Fig. 1)

$$\frac{\gamma_{SS}}{\gamma_{SL}} = 2 \cos \frac{\phi}{2} \quad (1)$$

According to Eq. (1), if the ratio γ_{SS}/γ_{SL} is equal or greater than 2, $\phi=0$, and the faces of all grains are completely covered by the glass phase. If the ratio γ_{SS}/γ_{SL} is less than 2 (ϕ

Fig. 1. Dihedral angle (ϕ) in multiple pocket of glass-containing ceramic (YAS-doped 3Y-TZP). γ_{SS} is the grain boundary energy, and γ_{SL} is the interface energy between grain and glass.

>0), the grains are partly covered by the glass phase and uncovered grain boundaries are formed. This uncovered area fraction increases with increasing the dihedral angle ϕ . Zhao et al.⁽¹⁹⁾ reported that the dihedral angle in SiO₂-doped Y-TZP decreased with increasing temperature. The dihedral angle in glass-doped Y-TZP will be dependent not only on temperature but also on composition of glass phase. In this report we studied the effect of temperature and chemical composition of glass on the dihedral angle in glass-doped 3Y-TZP.

2. Experimental procedure

2.1 Materials preparation

The materials were prepared from a high-purity 3Y-TZP powder (TZ-3Y, Tosoh Co.) containing 3 mol% Y₂O₃. The impurities in 3Y-TZP powder were <0.005 mass% Al₂O₃,

Fig. 2. TEM micrographs of as-sintered (a) undoped 3Y-TZP, (b) SiO₂-doped 3Y-TZP, and (c) YAS-doped 3Y-TZP.

<0.005 mass% SiO₂, <0.002 mass% Fe₂O₃, and 0.023 mass% Na₂O. Two different glasses were used as additives, which had different melting points (m.p.): one a SiO₂ glass (m.p. of 1700°C) and the other Y₂O₃-Al₂O₃-SiO₂ eutectic glass (YAS glass: m.p. of 1350°C²⁰). The chemical composition of YAS glass was 42 mass% Y₂O₃, 25 mass% Al₂O₃, and 33 mass% SiO₂. Two kinds of materials were prepared: (1) 5 mass% (12 vol%) SiO₂-doped 3Y-TZP, (2) 5 mass% (9 vol%) YAS glass-doped 3Y-TZP. Colloidal silica (Nissan Chemical Industries Ltd.) was used as SiO₂ glass. The Y₂O₃-Al₂O₃-SiO₂ eutectic glass (YAS glass)²¹ was prepared from Y₂O₃ powder (Shin-Etsu Chemical Co.), Al₂O₃ powder (AKP-50, Sumitomo Chemical Co.), and SiO₂ powder (Kojundo Chemical Lab., Co.). The homogeneous starting powder mixture of YAS glass was melted in a platinum crucible at 1600°C for 2 h and quenched in air. The obtained glass batch was ground in a Y-TZP pot with Y-TZP balls and anhydrous ethanol for 10 h at a speed of 250 r.p.m. using a planetary ball-mill. The 3Y-TZP powder was mixed with 5 mass% glass powder in a ball mill for 24 h, and dried. The mixed powders were pressed into bars under a pressure of 30 MPa, and then, cold isostatically pressed under a pressure of 200 MPa to obtain green bodies. The compacts were sintered at 1300°C for 2 h in air. Archimedes method was used for measuring densities of sintered bodies and YAS glass batches. The true densities of glasses were 2.3 g/cm³ for SiO₂, and 3.5 g/cm³ for YAS. Bulk densities of the samples were found to be 5.58 g/cm³ for SiO₂-doped 3Y-TZP, and 5.56 g/cm³ for YAS-doped 3Y-TZP. All the samples used in this study had final densities higher than 97% of the theoretical value. In order to study the effects of annealing on microstructures, the sintered bodies were heated in the temperature range from 1300°C to 1500°C for 2 h in air, and cooled rapidly at a rate of 200°C/min to below 900°C.

2.2 Microstructural characterization

Scanning electron microscopy (SEM) was used to characterize the microstructures of the as-sintered samples. For SEM observation, samples were mechanically polished and then thermally etched at 1250°C for 10 min in air. The average grain size was measured by using the mean linear intercept method. Samples for transmission electron microscopy (TEM) were prepared using a standard technique. Sintered bodies were cut and mechanically ground to get disks of 3 mm diameter. They were subsequently ground to a thickness of 50 μm, dimpled to a thickness of 10 μm, and ion-milled to electron transparency at 5 kV. These samples were clipped by copper grids with carbon coating. Observations were done at a voltage of 200 kV on a JEM-2000EX (JEOL).

Fig. 3. Cumulative distribution function of the observed dihedral angles in as-sintered glass-doped 3Y-TZP. The average dihedral angle (ϕ_m) are 70° for SiO₂-doped 3Y-TZP, and 50° for YAS-doped 3Y-TZP.

3. Results and discussion

Figure 2(a) shows a typical TEM micrograph of undoped 3Y-TZP sintered at 1400°C for 2 h in air. The average grain size was measured to be 0.35 μm. Figures 2(b) and (c) show TEM micrographs of the glass-doped 3Y-TZP, i.e., SiO₂-doped 3Y-TZP and YAS-doped 3Y-TZP, respectively. The average grain sizes obtained from the SEM photographs of the as-sintered bodies were 0.25 μm for SiO₂-doped 3Y-TZP, and 0.35 μm for YAS-doped 3Y-TZP. All zirconia grains in the three samples were equiaxed. The grains in undoped 3Y-TZP were faceted with sharp triple junctions. However, the grains in glass-doped 3Y-TZP were rounded in their corners, and glass pockets were found at the multiple junctions.

In order to measure dihedral angles ϕ in glass-doped 3Y-TZP, tangential lines were drawn at a glass pockets as illustrated in Fig. 1.^{22,23} More than 100 dihedral angles were measured in each sample. **Figure 3** shows the cumulative distribution function of the dihedral angles in glass-doped 3Y-TZP which were sintered at 1300°C. The average dihedral angles (ϕ_m) were defined as the dihedral angle of 50% point on the cumulative distribution function, and they were found to be 70° and 50° for SiO₂-doped 3Y-TZP and YAS-doped 3Y-TZP, respectively. When a small amount of the second phase, i.e., glass phase, is present in a polycrystalline microstructure, its distribution amongst the primary grain is critically dependent on the dihedral angle.^{15–18} When the dihedral angle is smaller than 60°, a small amount of liquid forms a

Fig. 4. Plot of average dihedral angle as a function of annealing temperature. (□ as-sintered SiO₂-doped 3Y-TZP, ■ annealed SiO₂-doped 3Y-TZP, ○ as-sintered YAS-doped 3Y-TZP, ● annealed YAS-doped 3Y-TZP, ▼ Zhao's results on SiO₂-doped 3Y-TZP¹⁹⁾).

continuous skeleton along the grain edges.¹⁸⁾ The average dihedral angle in YAS-doped 3Y-TZP was less than 60°, then the intergranular YAS glass can be an interconnected each other.

While no significant grain growth was observed in SiO₂-doped 3Y-TZP after annealing at 1500°C for 2 h, the average grain size of YAS-doped 3Y-TZP increased from 0.35 μm to 0.64 μm. It is supposed that the diffusion through interconnected glass phase can enhance the grain growth of YAS-doped 3Y-TZP. The constituent atoms in glass phase, i.e., Y,^{13),14)} Si^{9),24)} and Al^{24),25)} segregate at grain boundaries of Y-TZP. The segregated atoms affects grain boundary diffusion and the grain boundary energy (γ_{ss}). No significant grain growths were found in YAS-doped 3Y-TZP after annealing at temperatures lower than 1400°C for 2 h.

Figure 4 shows the relationship between the average dihedral angles and the annealing temperature. The vertical axis on the right hand shows the ratio γ_{ss}/γ_{sl} . In the temperature range from 1300°C to 1500°C, the average dihedral angles in SiO₂-doped 3Y-TZP remained constant at about 70°, whereas those in YAS-doped 3Y-TZP decreased with increasing temperature. The average dihedral angle in YAS-doped 3Y-TZP decreased to about 25° at 1500°C, which was higher than the melting point of YAS glass. Zhao's results on 5 mass% SiO₂-doped Y-TZP¹⁹⁾ were also shown in Fig. 4 for comparison. The average dihedral angle of SiO₂-doped 3Y-TZP decreased to 30°–40° at 1800°C, which was higher than the melting point of SiO₂. According to Eq. (1), the dihedral angle ϕ depends on the ratio γ_{ss}/γ_{sl} . The temperature dependence of the average dihedral angle suggests that γ_{ss}/γ_{sl} increases at temperatures higher than the melting point of intergranular glass. Since the effect of temperature on grain boundary energy is smaller than that on solid/liquid interface energy,²⁶⁾ the increase of γ_{ss}/γ_{sl} is probably due to the decrease of γ_{sl} at temperatures higher than the melting point.

The dihedral angle changes with increasing temperature in other liquid-containing oxides and metals also. Gambino et al.²⁷⁾ studied the effect of annealing on the dihedral angle of Bi-rich intergranular phase in ZnO varistor. The dihedral angles were decreased with the rise in annealing temperature. Above the eutectic point in the Bi₂O₃-ZnO system (about 780°C), the dihedral angle became zero, and all ZnO grains

were completely covered by the second phase. The increase of ZnO concentration in the second phase caused the decrease of the dihedral angle with increasing temperature. Ikeuye and Smith²⁸⁾ also reported the decrease in dihedral angle with increasing temperature in Al-Sn and Cu-Pb systems. According to those reports, γ_{sl} decreased around the eutectic point because of chemical composition changes in the second phase. Cheng and Thompson²⁹⁾ reported that the zirconia solubility in Y₂O₃-Al₂O₃-SiO₂ glass increased with increasing temperature. Therefore, we conclude that the increase in zirconia concentration in the glass phase decrease the γ_{sl} in YAS-doped 3Y-TZP at temperatures higher than the melting point of the glass.

4. Conclusions

The effect of temperature and chemical composition of intergranular glass on dihedral angle of glass-doped 3Y-TZP were studied by transmission electron microscopy. The following results were obtained:

- (1) The average dihedral angle of YAS-doped 3Y-TZP was 50°, and that of SiO₂-doped 3Y-TZP was 70°.
- (2) The grain size of YAS-doped 3Y-TZP increased from 0.35 μm to 0.64 μm after annealing at 1500°C for 2 h, while no significant grain growth was observed in SiO₂-doped 3Y-TZP.
- (3) The dihedral angle of YAS-doped 3Y-TZP decreased to 25° at 1500°C. It was suggested that γ_{ss}/γ_{sl} increased at elevated temperature higher than the melting point of glass.

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