GeO$_2$-doping Dependence of High Temperature Superplastic Behavior in 3Y-TZP

Kenji Nakatani$^1$, Hitoshi Nagayama$^1$, Hidehiro Yoshida$^2$, Takahisa Yamamoto$^{1,*}$ and Taketo Sakuma$^1$

$^1$Department of Advanced Materials Science, Graduate School of Frontier Science, The University of Tokyo, Tokyo 113-8656, Japan
$^2$National Institute for Materials Science, Tsukuba 305-0047, Japan

Superplastic behavior in a fine-grained, GeO$_2$-doped 3 mol% yttria-stabilized tetragonal zirconia polycrystal (3Y-TZP) with the dopant level of 0.2–3 mol% was examined at 1400°C under an initial strain rate of $1.3 \times 10^{-4}$ s$^{-1}$. Microstructure and chemical composition at the grain boundaries was examined by high-resolution electron microscopy (HREM) combined with an X-ray energy dispersive spectrometer (EDS). No secondary phase was observed along the grain boundaries, though EDS analysis indicated the segregation of Ge cations along the grain boundaries. The Ge content at the grain boundaries tends to increase with increasing the total amount of GeO$_2$ addition, but saturate over the doping level of 2 mol%. Dependence of flow stress reduction on the total amount of GeO$_2$ addition has a good correlation with Ge content at the grain boundaries. This fact indicates that the GeO$_2$-doping effect on the flow stress in 3Y-TZP is caused mainly from the grain boundary segregation of Ge cations.

(Received March 1, 2004; Accepted July 8, 2004)

Keywords: tetragonal zirconia polycrystal, superplasticity, grain boundary segregation, transmission electron microscopy

1. Introduction

Superplastic behavior in fine-grained, yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) has been extensively examined by many researchers. In most of the previous reports, a logarithmic relationship between strain rate $\dot{\varepsilon}$ and flow stress $\sigma$ in Y-TZP has been analyzed in detail, and rate-controlling mechanism for the superplastic flow has been discussed based on the deformation parameters such as the strain rate sensitivity $m$ and the grain size exponent $p$. For example, Jiménez-Melendo et al. reported that the superplastic flow in Y-TZP is dominated mainly by Zr$^{4+}$ lattice diffusion, and that transition behavior of log $\dot{\varepsilon}$-log $\sigma$ relationship is changed by the presence of residual impurities. However, there is no description about what type of impurities are responsible for the transient behavior, and the origin of the doping effect on the superplastic behavior has not been clarified yet.

In our previous reports, it has been revealed that the superplastic flow in 3Y-TZP is significantly affected by the doping of 0.2 mol% cations. High-resolution electron microscope (HREM) observation and an X-ray energy dispersive spectrometer (EDS) analysis using an incident beam size of about 1 nm suggest that the dopant cations tend to segregate along the grain boundaries. However, dependance of the superplastic flow on the amount of dopant cations has not been systematically investigated. The present study therefore aims to examine dependence of the superplastic behavior on the amount of dopant cations in 3Y-TZP. The superplastic behavior and microstructure in 0.2-3 mol% GeO$_2$-doped 3Y-TZP were extensively examined in order to reveal the relationship between the high temperature superplastic flow and the segregation behavior of the dopant cations.

2. Experimental Procedure

The materials used in this study were tetragonal ZrO$_2$-3 mol%Y$_2$O$_3$ polycrystal (3Y-TZP) and either 0.2 mol%, 0.5 mol%, 1 mol%, 2 mol% or 3 mol% GeO$_2$-doped 3Y-TZP. The starting materials were 3Y-TZP powders (TZ-3Y; Tosoh, Japan) and germanium oxide (purity > 99.99%, Rare Metallic). The impurity level of 3Y-TZP powders is very low; for example, Al$_2$O$_3$ < 0.005 mass%, SiO$_2$ < 0.005 mass%, Fe$_2$O$_3$ < 0.002 mass%. The powders were mixed, ball milled in polyurethane container with ethanol and zirconia balls for 24 h. The mixed powders were dried in argon, sieved, pressed into bars at 33 MPa, and then cold isostatically pressed under a pressure of 100 MPa in a rubber tube. The green bodies were sintered at 1400°C for 2 h in air. The density of the sintered bodies was measured by Archimedes method. An average grain size of the present materials was measured from a scanning electron micrograph (SEM, JEOL JSM-5200) using the linear intercept method. Table 1 shows sintering condition and initial grain sizes in the present materials. High temperature mechanical testing was carried out using Instron Type tensile testing equipment (AG-5000C, SHIMAZU) at 1400°C in air and an initial strain rate of $1.3 \times 10^{-4}$ s$^{-1}$.

Microstructure was examined by transmission electron microscopy (TEM). TEM specimens were prepared by standard technique involving mechanical grinding to a thickness of about 0.1 mm, dimpled to a thickness of 20 µm and ion beam milling to electron transparency at about 4 kV. HREM observation was performed to analyze the grain

<table>
<thead>
<tr>
<th>Material</th>
<th>Sintering condition</th>
<th>Initial grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Y-TZP</td>
<td>1400°C for 2 h</td>
<td>0.38</td>
</tr>
<tr>
<td>0.2 mol%GeO$_2$-doped TZP</td>
<td>1400°C for 2 h</td>
<td>0.39</td>
</tr>
<tr>
<td>0.5 mol%GeO$_2$-doped TZP</td>
<td>1400°C for 2 h</td>
<td>0.41</td>
</tr>
<tr>
<td>1 mol% GeO$_2$-doped TZP</td>
<td>1400°C for 2 h</td>
<td>0.43</td>
</tr>
<tr>
<td>2 mol%GeO$_2$-doped TZP</td>
<td>1400°C for 2 h</td>
<td>0.50</td>
</tr>
<tr>
<td>3 mol% GeO$_2$-doped TZP</td>
<td>1400°C for 2 h</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 1 Sintering condition and initial grain size in undoped and 0.2-3 mol% GeO$_2$-doped 3Y-TZP.
boundary structure with H-9000 NAR (Hitachi, 300 kV). Chemical analysis was carried out by EDS attached to Topcon 002BF (200 kV) field-emission type TEM with a probe sizeless than 1 nm. EDS analysis was performed for ten individual grain boundaries and the center of the grains in 0.2 mol%, 1 mol%, 2 mol% and 3 mol% GeO$_2$-doped 3Y-TZP. Ge cation content was quantitatively estimated from Ge-K$_\alpha$, Zr-K$_\alpha$ and Y-K$_\alpha$ peaks by Cliff-Lorimer method based on the thin-foil criterion; the analyzed points were thin enough to obtain HREM lattice image.

3. Results and Discussion

Figure 1 shows stress-strain curves in the present materials at 1400°C and an initial strain rate of 1.3 × 10$^{-4}$ s$^{-1}$. Superplastic behavior in 3Y-TZP is sensitively affected by the small amount of GeO$_2$-doping. The flow stress decreases, and the elongation to failure increases with increasing the dopant content. In 2 mol% or 3 mol% GeO$_2$-doped 3Y-TZP, the flow stress is about 20 MPa lower than that in 3Y-TZP and the elongation to failure is increased to be more than 400%. The improvement in the elongation to failure in Ge-doped TZP seems to be explained from reduction in the flow stress; as reported earlier, lower flow stress usually provides a larger value of the superplastic ductility in ceramics.

Figure 2 shows the flow stress for the grain size of 0.5 μm and the elongation to failure against GeO$_2$ composition in the present materials. The flow stress flattens out over the content of 2 mol%. The leveling off behavior of the elongation corresponds to that of the flow stress. As mentioned above, the improvement in the elongation to failure can be explained from the reduction in the flow stress. In order to examine GeO$_2$-doping dependence of the flow stress, microstructure and chemical composition was investigated in the present materials as follows.

Figure 3(a) shows a HREM image of a grain boundary in 1 mol% GeO$_2$-doped 3Y-TZP. As seen in the high-resolution image, no second phase particle or amorphous phase was observed along the grain boundary. Chemical composition at the grain boundary and the grain interior was examined by EDS analysis using an incident beam size of about 1 nm. Figures 3(b) and (c) show the EDS spectra taken from the center of the grain and the grain boundary, respectively. Ge cations exist both in the grain interior and at the grain boundary, but the peak intensity of Ge is higher at the grain boundary than in the grain interior. This fact indicates that the dopant cation segregates in the vicinity of the grain boundaries.

Figure 4 is a plot of Ge content at the grain boundaries and the grain interiors estimated from the EDS analysis against the total amount of GeO$_2$ addition. The Ge content is defined as the atomic ratio for all cations in Ge-doped TZP. The Ge content along the grain boundary increases with increasing total amount of GeO$_2$ addition, but saturates over the doping level of 2 mol%. On the other hand, Ge content in the grain interior increases almost linearly with increasing in GeO$_2$ addition. In 0.2 mol% GeO$_2$-doped TZP, Ge content is about 1.4 mol% at the grain boundaries, nevertheless Ge content is almost zero in the grain interiors. This result indicates that dopant cations segregate preferentially along the grain boundaries with the dopant level of less than 0.2 mol%, and that the segregation content has a limitation of about 7 mol%.

An X-ray diffractionmetry (XRD) analysis revealed that 0.2–3 mol% Ge-doped TZP shows no significant amount of cubic phase, and consists of tetragonal phase. The Ge-doping has no effect on apparent microstructure in TZP with the doping level of 0.2–3 mol%. On the other hand, the present results of
Figs. 3 and 4 indicate the grain boundary segregation of Ge cations, which must be the origin of GeO$_2$-doping dependence of the flow stress. It should be also noted that the dependence of Ge content along the grain boundary on the total amount of Ge addition correlates well with the flow stress change in Ge-doped TZP; the Ge content increases, and the flow stress decreases with increasing of the total amount of Ge addition, but both the Ge content and the flow stress become constant over the doping amount of 2 mol%. This result indicates that the flow stress in Ge-doped TZP is dominantly affected by the segregated Ge cations rather than Ge cations inside grains. As previously reported, Ge-doping probably enhances diffusivity in TZP as an accommodation process of the superplastic flow. The segregated Ge cations are supposed to enhance the grain boundary diffusivity in TZP, and the superplastic flow stress is consequently reduced in the present materials.

Figure 5 shows the relationship between log $\dot{\varepsilon}d^2$ and log $\sigma$ at 1400°C in high-purity and low-purity TZP. The stress exponent increases with decreasing of the strain rate in high-purity TZP, though such a transition behavior does not appear in low-purity TZP. The low-purity TZP contains Al$_2$O$_3$ or SiO$_2$ as impurity with the amount of more than 0.1 wt%, which is supposed to be equivalent to 0.1–0.2 mol%. The present data are also plotted in Fig. 5 for comparison. The present data in undoped 3Y-TZP shows good agreement with the previous data. The decline of the flow stress due to Ge-doping seems to agree with the previous data. However, the present study revealed that the flow stress depends on the dopant content, though the previous paper reported that log $\dot{\varepsilon}d^2$-log $\sigma$ relationship in low-purity TZP can be described by a single straight line regardless of content and type of impurity. Since the small amount of dopant cation tends to segregate along the grain boundaries, it seems reasonable that the grain boundary diffusivity is affected by the segregation of the doped cation with the dopant level of less than 2 mol%. Therefore, one can conclude that the change in the flow stress is caused by difference in the grain boundary diffusivity due to the doped cations’ grain boundary segregation. The origin
of the Ge-doping dependence can be explained from the segregation behavior of dopant cation.

4. Conclusion

Superplastic behavior in GeO$_2$-doped 3Y-TZP was examined with the dopant level in a range of 0.2–3 mol%. The flow stress decreases with increasing the amount of GeO$_2$ addition, however, the flow stress reduction is almost saturated over the doping level of 2 mol%. HREM-EDS analysis revealed the segregation of Ge cations along the grain boundaries. The content of Ge cations at the grain boundary tends to increase with increasing the total amount of GeO$_2$ addition, but tends to saturate over the doping level of 2 mol%. On the other hand, Ge content in the grain interiors increases almost linearly with increasing in GeO$_2$ addition. The dependence of the Ge content along the grain boundary on the total amount of Ge addition correlates well with the change in the flow stress in GeO$_2$-doped 3Y-TZP. The grain boundary segregation of Ge cations probably dominates the superplastic flow stress in small amount of GeO$_2$-doped 3Y-TZP.

Acknowledgements

We wish to express our thanks to the Ministry of Education, Culture, Sports, Science and Technology Japan and Japan Society for the Promotion of Science for the financial support by Grant-in-Aid for Scientific Research and Grant-in-Aid for Encouragement of Young Scientists. We also wish to express our thanks to Nippon Sheet Glass Foundation for Materials Science of Engineering for their financial aid.

REFERENCES