Local Bonding States of Titanium and Germanium-doped Tetragonal Zirconia Polycrystal and Their Correlation to High Temperature Ductility

Akihide Kuwabara 1, *, Syu Yokota 1, *, Yuichi Ikuhara 2 and Taketo Sakuma 3

1 Department of Materials Science, School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan
2 Engineering Research Institute (PRESTO, Japan Science and Technology Corporation), The University of Tokyo, Tokyo 113-8656, Japan
3 Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, Tokyo 113-8656, Japan

The chemical bonding states of GeO 2 and/or TiO 2 -doped tetragonal zirconia polycrystal (TZP) are calculated by a first principle molecular orbital method using model clusters. It is clarified that Ge 4+ and Ti 4+ ions, which are substituted into a lattice of TZP, have a high covalent bond with oxygen ions rather than Zr–O bond. Covalency of TZP is more increased by solution of germanium ions than that of titanium ones. In superplastic deformation of TZP, an addition of GeO 2 or TiO 2 enhances tensile ductility of TZP. Germanium ion is more effective to improve ductility than titanium. The increment of covalency is in a good agreement with the improvement of elongation to failure in doped TZP. Dopant cations segregate at grain boundaries and form no secondary phase. Assuming that a dopant effect on chemical bonding states in grain boundaries is similar to that in grain interior, segregation of germanium or titanium ion increases covalent bonding strength nearby grain boundaries. Such increasing of covalency is likely to enhance cohesion of grain boundaries. The enhancement of grain boundary cohesion suppresses intergranular failure during tensile deformation at elevated temperatures. This must be the reason why an addition of GeO 2 and TiO 2 is effective to improve the high temperature ductility of TZP. Our calculation suggests that the covalency nearby grain boundaries have a critical role in the tensile ductility of TZP.

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1. Introduction

Superplasticity in fine-grained ceramics has been widely examined by many researchers. Improvement of tensile ductility in superplastic ceramics depends not only on stable grain size, but also on flow stress. Kim et al. reported that elongation to failure in fine-grained ceramics is decreased with increasing of Zener-Hollomon (Z-H) parameter, \( \dot{\epsilon} \exp(\frac{Q}{RT}) \). Since Z-H parameter is proportional to flow stress under a condition of constant grain size, their analysis means that elongation to failure increases with reduction of flow stress. However, there are several results which show that the changes in ductility of TZP cannot be explained only from the flow stress. Figure 1 shows results of tensile test in TZP-5 mass%SiO 2 and TZP-5 mass%SiO 2 containing 2 mass% other oxides. As shown in the figure, the elongation to failure sensitively changes with an addition of small amount of oxides although the level of flow stress does not change drastically among three specimens including SiO 2 . The change in ductility is explained from difference in chemical bonding states around grain boundaries due to segregation of dopants.

Recently, an interesting phenomenon is reported in GeO 2 and/or TiO 2 doped TZP by Sasaki et al., as shown in Fig. 2. GeO 2 -doped TZP has a special feature that flow stress increases obviously in the latter stage of deformation. The increment of flow stress is likely to result from concurrent grain growth. It should be noted that the ductility of GeO 2 or TiO 2 doped-TZP is not simply in inverse proportion to its flow stress. The flow stress of 3Y-TZP with 2 mol%GeO 2 and 2 mol%TiO 2 (3Y-2Ge2Ti) exceeds that of 3Y-TZP with 2 mol%GeO 2 (3Y-2Ge) in the latter part of deformation. However, 3Y-2Ge2Ti has higher ductility than 3Y-2Ge. Until now, an origin of extensive ductility in GeO 2 and TiO 2 co-doped TZP has not been clearly understood yet. A purpose of this paper is to make clear effects of GeO 2 and TiO 2 on the tensile ductility of TZP from the viewpoint of chemical bonding state using first principle calculations.

2. Computational Procedure

Electronic structures are calculated by the discrete variational (DV)-Xα method employing the computer code SCAT. In this method, an electronic structure of a model cluster is obtained self-consistently by solving a one-electron

Fig. 1 Stress-Strain curves obtained for SiO 2 -doped TZP (SiO 2 -2 mass%MgO)-doped TZP, and (SiO 2 -2 mass%TiO 2 )-doped TZP at a strain rate of 1.3 × 10^{-4} s^{-1} at 1400°C in air.
Local Bonding States and High Temperature Ductility in Ti and Ge-doped TZP

Figure 2: Stress-Strain curves obtained for 3Y-TZP, 3Y:2 mol%TiO₂, 3Y:2 mol%GeO₂, 3Y:1 mol%GeO₂-1 mol%TiO₂, 3Y:2 mol%GeO₂-2 mol%TiO₂ at a strain rate of $1.3 \times 10^{-4}$ s⁻¹ at 1400 °C in air.

The (Y₄Zr₁₈O₈₆)₈₈⁻ cluster used for a calculation of 3Y-TZP is shown in Fig. 3. This cluster is composed of 108 ions and includes up to the sixth nearest neighbor oxygen ions from the Zr ions at C1 and C2 sites indicated by arrows. Two Y³⁺ ions are substituted with Zr⁴⁺ ions at the nearest neighbor zirconium sites from Zr C1. It has been reported that an oxygen vacancy exists at second nearest neighbor oxygen site from yttrium ions. An oxygen vacancy for maintaining electric neutrality is introduced at the mutual second nearest neighbor oxygen site from the two Y³⁺ ions. Similarly, two Y³⁺ ions are located at the nearest neighbor sites from Zr C2 and an oxygen vacancy exists at the second nearest neighbor site from these two Y³⁺ ions. The (Ge₂Y₂Zr₁₀O₆₈)₈⁻ and (Ti₂Y₂Zr₁₀O₆₈)₈⁻ clusters are constructed for calculations of GeO₂-doped TZP and TiO₂-doped TZP. The (GeTiY₄Zr₁₀O₆₈)₈⁻ cluster is made as a model cluster of GeO₂ and TiO₂ co-doped 3Y-TZP. The structure of each cluster is demonstrated in Table 1. All of these clusters are put into a field of Madelung potential composed of about 6000 point charges.

3. Result and Discussion

3.1 Chemical bonding states in GeO₂ or TiO₂-doped TZP

In order to analyze chemical bonding states, partial density of states (PDOSs) for each cation at C1 or C2 site, oxygen ion around C1 or C2 site, and yttrium ion in YZ, Y-2G and Y-2T clusters are shown in Fig. 4. The PDOS profiles are obtained by broadening each atomic orbital population at discrete MOs by a Gaussian function of 0.5 eV full width at half maximum. For appropriate investigation, the PDOSs for atoms in central parts of clusters are adopted. A significant mixture of Zr 4d and O 2p is observed in Fig. 4(a). In all clusters, Y 4p is mainly hybridized with O 2s and O 2p. Ge 4p and Ti 3d mix with O 2p in Y-2G and Y-2T clusters, respectively.

The PDOS profiles of doped-TZP indicate covalent bonding states between cations and anions. As mentioned before, we can quantitatively evaluate covalency from a bond overlap population (BOP). Figure 5(a) indicates BOPs of Ge–O and Ti–O bonds in Y-2G and Y-2T, respectively. In this figure, BOP of Zr–O bond at C1 and C2 site in YZ is also shown as a reference. As indicated in Fig. 5(a), the BOPs of Ge–O and Ti–O bonds are larger than that of Zr–O bond in YZ cluster. The BOP of Ge–O has the highest value. This means that Ge⁴⁺ or Ti⁴⁺ ions substituted into TZP lattice have stronger covalent bonds with oxygen ions than Zr ones, and that the covalency of Ge–O bond is higher than Ti–O bond. Figure 5(b) show BOPs of Y–O bonds in YZ, Y-2G and Y-2T clusters. All the BOPs of Y–O bond are negative and have almost the same absolute values among YZ, Y-2T and Y-2G clusters. This means that the Y–O bonds are in similar anti-bonding states.

A change in BOP can be analyzed from overlap population diagram (OPD) in detail. An OPD indicates bonding and anti-bonding components in molecular orbitals between atoms. OPDs of dopant-O, Zr–O and Y–O bonds in YZ, Y-2T...
Table 1 The structure of each cluster model.

<table>
<thead>
<tr>
<th></th>
<th>(Y$<em>4$Zr$</em>{16}$O$_{86}$)$^{88-}$</th>
<th>(Ge$<em>2$Y$<em>4$Zr$</em>{16}$O$</em>{86}$)$^{88-}$</th>
<th>(Ti$<em>2$Y$<em>4$Zr$</em>{16}$O$</em>{85}$)$^{88-}$</th>
<th>(SiTiY$<em>4$Zr$</em>{16}$O$_{85}$)$^{88-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Zr</td>
<td>Ge</td>
<td>Ti</td>
<td>Ge</td>
</tr>
<tr>
<td>C2</td>
<td>Zr</td>
<td>Ge</td>
<td>Ti</td>
<td>Ti</td>
</tr>
<tr>
<td>Name</td>
<td>YZ</td>
<td>Y-2G</td>
<td>Y-2T</td>
<td>Y-1G1T</td>
</tr>
</tbody>
</table>

and Y-2G clusters are shown in Fig. 6. The Zr–O, Y–O, Ti–O and Ge–O bonds are mainly composed of Zr 4d–O 2p, Y 4p–O 2p, Ti 3d–O 2p, and Ge 4p–O 2p, respectively. From this figure, it can be seen that the Ge–O and Ti–O bonds have larger bonding component than the Zr–O bond, and that they have no anti-bonding component in contrast to the Zr–O bond. It is shown in Fig. 5 that the BOP of the Ge–O and Ti–O bonds is larger than the Zr–O bond. This is due to the increment in bonding component and the diminution in anti-bonding component of the Ge–O and Ti–O bonds. Shapes of OPDs for the Y–O bonds are almost the same among these clusters. This must be the reason why the values of BOPs in the Y–O bonds among all clusters are almost constant. Covalent bonding state of a Y–O bond is scarcely affected by an addition of dopant.

3.2 Effect of covalent bonding state on tensile ductility

Figure 7 shows a relationship between a total BOP, which corresponds to a sum of all BOP between cation and anion in a cluster, and elongation to failure in doped and undoped TZP shown in Fig. 2. All of the clusters containing dopant have larger total BOP than YZ cluster. Y-2G cluster has the highest value of total BOP among clusters with a single dopant. This means that doping of TiO$_2$ or GeO$_2$ results in enhancement of covalency in TZP, and that an addition of GeO$_2$ is more effective to increase total covalency than that of TiO$_2$. The total BOP of Y-2G2T takes the highest value among all clusters. As shown in Fig. 7, the elongation to failure of TZP increases when the total BOP becomes larger. This figure suggests that there is a relationship between covalency and elongation to failure in TZP. Imamura
et al. also reported that covalency would affect on tensile ductility in glass-doped TZP. Our calculation reveals that substitution of Ge$^{4+}$ or Ti$^{4+}$ ions reinforces covalent bonding strength in a bulk of TZP. In cation-doped TZP, the segregation of dopant cations at grain boundary is observed through TEM-EDS analysis. Assuming that Ge$^{4+}$ or Ti$^{4+}$ ions at grain boundaries have the same effect on a chemical bonding state as in grain interior, segregation of these ions strengthens covalent bonds nearby grain boundaries. Tensile fracture in TZP is likely to be dominated by crack propagation in perpendicular direction to applied stress. Wu et al. analyzed effects of impurities on the cohesive energy of iron grain boundary using FLAPW total energy calculation. Their conclusion is that phosphorus with embrittlement character has non-hybridized interaction with surrounding iron atoms. On the other hand, boron and carbon, which enhance cohesion of grain boundary in iron, forms strong covalent bonding normal to grain boundaries. We suppose that segregation of Ge$^{4+}$ or Ti$^{4+}$ ions enhances grain boundary cohesion in TZP because these ions increase covalency of TZP. This must be the reason tensile ductility of TZP increases with increasing of covalency.

### 3.3 Effect of dopant on grain boundary fracture energy

Our calculation suggests that the improvement of ductility in GeO$_2$ and/or TiO$_2$-doped TZP is originated from enhancement of grain boundary cohesion. Kim et al. tried to apply fracture mechanics approach to explain the tensile ductility of fine-grained ceramics. If the cavity growth is governed by plastic flow, the growth rate will be described as

$$\frac{da}{d\varepsilon} = q\varepsilon$$

where $a$ is the cavity size, $\varepsilon$ is the true strain and $q$ is the cavity growth rate parameter. By solving the differential equation, cavity size at failure is expressed as

$$a_f = a_0 \exp(q\varepsilon_f)$$

where $a_0$ and $a_f$ is the initial cavity size (normally related to initial grain size) and the cavity size at failure, respectively. $\varepsilon_f$ means the true strain at failure. Assuming that intergranular failure in TZP occurs when energy release rate ($G$) overcomes crack resistance force ($R$), $G$ and $R$ are described as follows,

$$G = \frac{K_l^2}{2E'} = \frac{\sigma^2\pi a}{2E'}$$

$$R = 2\gamma_s - \gamma_{gb} = \Delta\gamma$$

where $\gamma_s$ is the surface energy and $\gamma_{gb}$ is the grain boundary energy. $E'$ is the function of Young's modulus ($E$) and Poisson's ratio ($\nu$) described as $E' = E$ under a plane stress state or $E' = E(1 - \nu^2)$ under a plain strain condition. At the time of failure, the follow equation will be satisfied,

$$\frac{\sigma_f^2\pi a_f}{2E'} = \Delta\gamma.$$  \hspace{1cm} (5)

Substituting eqs. (2) into (5), one obtains

$$\frac{\sigma_f^2\pi a_0 \exp(q\varepsilon_f)}{2E'} = \Delta\gamma.$$  \hspace{1cm} (6)

Equation (6) gives that the elongation to failure is determined from fracture stress, fracture energy and cavity growth rate. It is reasonable to assume that the change of bonding strength should affect mainly the fracture energy term, $\Delta\gamma$, in eq. (6). We estimate the values of $\Delta\gamma$ in GeO$_2$ or TiO$_2$-doped TZP from substituting Young’s modulus of 200 GPa,\textsuperscript{19} initial cavity size of 0.5 $\mu$m,\textsuperscript{6} cavity growth rate of 4\textsuperscript{1} and maximum flow stress into eq. (6). Figure 8 shows a relationship between calculated $\Delta\gamma$ and total BOPs. The $\Delta\gamma$ of 3Y-2Ge2Ti has an incredible value, almost equal to 10 J/m$^2$. This overestimation must result from that inappropriate value of cavity growth rate for 3Y-2Ge2Ti. In this analysis, we evaluate $\Delta\gamma$ on the
assumption that cavity growth rate is unchangeable among doped specimens. There is a possibility that doping changes a cavity growth rate. Since \( q \) is one of the exponential terms, the value of cavity growth rate so much affects fracture energy. Therefore, more precise estimation needs an investigation of cavitation behavior in TZP. However, as shown in Fig. 8, the total BOP basically has a good relationship with \( \Delta \gamma \). Fracture energy term of \( \Delta \gamma \) increases with the increment of total BOP. Our calculations demonstrate that intensification of covalency caused by segregation improves the grain boundary cohesion of TZP. We can conclude that reinforcement of bond strength at grain boundary probably suppresses intergranular fracture during tensile deformation. We conclude that covalency is one of the major parameters to decide the tensile ductility of TZP.

4. Conclusion

The chemical bonding state of GeO\(_2\) and/or TiO\(_2\) doped TZP was evaluated using first principle molecular orbital calculation, DV-X\(_\alpha\) method. From the calculation, doping of these oxides increases covalent bonding strength in TZP. The increment of covalency has a good relationship with enhancement of tensile ductility in doped TZP. Dopant cations segregate at grain boundary in doped TZP. Segregation of Ge\(^{3+}\) or Ti\(^{4+}\) ions increases covalent bonding strength nearby grain boundary and enhances grain boundary cohesion. Reinforcement of bond strength at grain boundary probably suppresses intergranular fracture during tensile deformation. We conclude that covalency is one of the major parameters to decide the tensile ductility of TZP.

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14) The cluster model including two Ge\(^{4+}\) ions and two Ti\(^{4+}\) ones cannot be constructed because of lack of equivalent substitution sites with C1 and C2 sites. Total BOP of 3Y-2G2Ti, therefore, is inferred by the equation,
\[
\text{BOP}_{\text{3Y-2G2Ti}} = \text{BOP}_{\text{3Y}} + 2(\text{BOP}_{\text{G1T}} - \text{BOP}_{\text{3Y}}).
\]