Effect of Superplastic Deformation on Thermal Expansion Behavior of Tetragonal Zirconia Polycrystals

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Three mol% yttria stabilized tetragonal zirconia polycrystals (3Y-TZP) were superplastically deformed under various conditions and microstructural evolution was characterized. Thermal expansion properties of the 3Y-TZP specimens were then measured by a push-rod type dilatometer in a temperature range from 300 K to 1473 K. Experimental results showed that the mean coefficient of linear thermal expansion, \( \alpha \), decreased with an increase in the volume fraction of cavities. The cavity dependence of \( \alpha \) value was dependent on temperature and was weakened with an increase in temperature. Changes in the average grain size and grain aspect ratio due to the superplastic deformations were found to have little effect on the thermal expansion property within the present experimental range.

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1. Introduction

Superplastic behavior in yttria stabilized tetragonal zirconia polycrystals (Y-TZP) has been widely studied, and manufacturing of net-shaped or near-net shaped ceramic parts by utilizing the superplastic phenomena is drawing much attention lately.1–9) The in-service performance of such materials depends on their thermal properties. And so reliable information on thermal expansion properties is needed in order to estimate the influence of high temperature environment on the structural zirconia-based ceramics. However, to the authors’ knowledge, no experimental results of thermal expansion behaviors of superplastically deformed Y-TZP have been reported. Superplastic deformation-induced cavities have a significant influence not only on their room temperature mechanical properties2,3) but also on thermal shock behaviors.8) The change in thermal expansion coefficient of nuclear graphite has been found to be associated with the closing of cleavage microcracks.10–12) It is likely that the induced cavities have some effects on the thermal expansion behavior. It is, therefore, essential to study the thermal expansion behavior of superplastically deformed Y-TZP.

In the present paper, the thermal expansion behavior of 3 mol% Y\(_2\)O\(_3\) stabilized tetragonal zirconia polycrystals (3Y-TZP) was investigated by a push-rod type dilatometer from 300 K to 1473 K. The effects of superplastic deformation on the coefficient of linear thermal expansion were evaluated and discussed.

2. Experimental

The test pieces for superplastic deformation were produced by sintering powder of ZrO\(_2\) containing 3 mol% Y\(_2\)O\(_3\) in solid solution (3Y-TZP) at 1723 K under atmospheric pressure. The chemical composition has been reported in another paper.13) The test pieces were superplastically deformed to a nominal strain of 70% at 1723 K with different initial strain rates, \( \dot{\varepsilon}_0 \), of 4.2 \( \times 10^{-4} \) s\(^{-1}\), 1.4 \( \times 10^{-3} \) s\(^{-1}\) and 4.2 \( \times 10^{-3} \) s\(^{-1}\). Deformed specimens No. 01–No. 06 were cut from the gauge section of the specimens, whereas undeformed specimens No. 07 and No. 08 were cut from the grip section to ensure the same thermal history for both deformed and undeformed ones. The size of the specimens for the thermal expansion measurement is 3.2 \( \times 2.4 \) \( \times 15.0 \) mm\(^3\). The longitudinal axis of the specimens is the same with the tension axis.

Volume fractions of cavities, \( V_c \), evaluated from density measurement by the Archimedes method, average grain size and grain aspect ratio of the specimens are shown in Table 1. The microstructure and crystal structure of the specimens were examined by scanning electron microscopy (SEM) and X-ray diffraction analysis, respectively. Microstructural characterization has been reported in detail elsewhere.13,14)

A push-rod type dilatometer (Dilatometer 5000 made by MAC Science Co.) was used to determine linear thermal expansion. The measurement was carried out from 300 to 1473 K with a heating and cooling rate of 5 K/min. Argon gas was constantly passed through the measuring furnace with a flow-rate of 50 ml/min during the measurement. The temperature was controlled within \( \pm 1 \) K, and the accuracy of the measurement was within \( \pm 0.1 \) \( \mu \)m. During the measurement, the dimension change was measured at a rate of 20 times per minute. Considering practical application, the experimental data above 700 K were analyzed. The data shown in the following section are from the heating curves, since the cooling curves just traced the former ones.

Linear thermal expansion is given by \( \Delta L/L_0 = (L - L_0)/L_0 \), where \( L \) and \( L_0 \) are the lengths of the specimen at the measuring temperature \( T \) and at room temperature \( T_0 \), respectively. For a temperature interval \( \Delta T = T - T_0 \), the

| Table 1 Microstructural variables of the 3Y-TZP specimens. |
|-----------------|-----|-----|-----|-----|-----|-----|
| Specimen number | 1   | 2   | 3   | 4   | 5   | 6   |
| Volume fraction of cavities, \( V_c, \% \) | 1.1 | 1.0 | 1.7 | 1.6 | 3.1 | 3.4 |
| Average grain size, \( \mu m \) | 0.48 | 0.48 | 0.47 | 0.47 | 0.41 |
| Grain aspect ratio | 1.07 | 1.13 | 1.08 | 1.08 | 0.94 |
mean coefficient of linear thermal expansion, $\alpha$, is determined by $\alpha = (\Delta L/L_0)/\Delta T$. The $\Delta T$ was 10 K in the present experiment. The $\alpha$ value was not converted to the instantaneous one, since the difference between them must be quite small.\textsuperscript{15}

A rod shape specimen of polycrystalline alumina with 3 mm in diameter and 20 mm in length, sintered using 99.9% purity powder, was also measured in the same temperature range in order to determine the reproducibility and accuracy of the measurement system. The $\alpha$ value of the polycrystalline alumina was $9.4 \times 10^{-6} \text{K}^{-1}$ at 1273 K, which was in good agreement with the recommended value.\textsuperscript{16}

3. Results and Discussion

Linear thermal expansions, $\Delta L/L_0$, are shown as a function of temperature in Fig. 1. The fitting equations are listed in Table 2. By setting $\Delta L/L_0 = 0$ at 300 K, these data were fitted to a second order polynomial function of temperature by the least-squares method from 700 to 1473 K. The difference between experimental results and fitting data is less than 0.3%.

![Fig. 1 Linear thermal expansion, $\Delta L/L_0$, of 3Y-TZP as a function of temperature.](image)

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Fitting equation, $\Delta L/L_0$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 01</td>
<td>$\Delta L/L_0 = -0.32 + 1.04 \times 10^{-3} T + 5.02 \times 10^{-8} T^2$</td>
</tr>
<tr>
<td>No. 02</td>
<td>$\Delta L/L_0 = -0.32 + 1.06 \times 10^{-3} T + 4.45 \times 10^{-8} T^2$</td>
</tr>
<tr>
<td>No. 03</td>
<td>$\Delta L/L_0 = -0.31 + 1.01 \times 10^{-3} T + 7.01 \times 10^{-8} T^2$</td>
</tr>
<tr>
<td>No. 04</td>
<td>$\Delta L/L_0 = -0.31 + 1.03 \times 10^{-3} T + 5.72 \times 10^{-8} T^2$</td>
</tr>
<tr>
<td>No. 05</td>
<td>$\Delta L/L_0 = -0.31 + 1.02 \times 10^{-3} T + 5.01 \times 10^{-8} T^2$</td>
</tr>
<tr>
<td>No. 06</td>
<td>$\Delta L/L_0 = -0.31 + 1.00 \times 10^{-3} T + 7.46 \times 10^{-8} T^2$</td>
</tr>
<tr>
<td>No. 07</td>
<td>$\Delta L/L_0 = -0.32 + 1.04 \times 10^{-3} T + 5.43 \times 10^{-8} T^2$</td>
</tr>
<tr>
<td>No. 08</td>
<td>$\Delta L/L_0 = -0.30 + 0.99 \times 10^{-3} T + 7.15 \times 10^{-8} T^2$</td>
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</table>

There are some factors which affect the thermal expansion behavior such as composition, phase-transformations and prestraining.\textsuperscript{16–18} There existed no abrupt changes in the dilatometric curves, which suggested that no phase transformation happened in this material within the experimental range. For 3Y-TZP analysis by X-ray diffraction has also shown no traces of phase transformation during superplastic deformation.\textsuperscript{14} For a single crystal, nonisometric crystal structure may result in different thermal expansion behavior along different crystallographic axes.\textsuperscript{19} For the present 3Y-TZP, a fine-grained polycrystal with a random grain-orientation was preserved even after superplastic deformation.\textsuperscript{20} Moreover, anisotropy in the thermal expansion along the crystallographic axes is small in 3Y-TZP. Therefore, we can say that the crystallographic anisotropy had almost no effect on the present experimental results.

It is convenient to express the thermal expansion behavior with coefficient of linear thermal expansion, $\alpha$, instead of linear thermal expansion, because the thermal expansion versus temperature is not sensitive enough to detect a small change in expansion or a small anomaly.\textsuperscript{21} Fig. 2 shows the relation between the $\alpha$ value and volume fractions of cavities at different temperatures. Note that the $\alpha$ values have a tendency to decrease slightly with increasing $V_c$ at each temperature. Although cavities may be expanded or shrunken by the stresses such as thermal stresses,\textsuperscript{23} the compressive stress that was loaded on the specimens during the measurements was $2.5 \times 10^{-2} \text{MPa}$, which was so small that it had almost no effect on the cavities. The $\alpha$ values versus $V_c$ values were fitted using the least-squares method and the fitting equations are shown in Table 3. The slope of fitting curve is $-2.52 \times 10^{-6}$ at 713 K while it is $-0.24 \times 10^{-6}$ at 1473 K. It is found that the slopes of the fitting curves decrease with increasing temperature. The $\alpha$ values, obtained

![Fig. 2 The coefficient of linear thermal expansion of 3Y-TZP as a function of volume fraction of cavities at different temperatures. Data are obtained from fitting equations shown in Table 2.](image)
from the fitting equations in Table 3, are shown in Fig. 3. It is evident that the cavity dependence of $\alpha$ is weakened with increasing temperature and becomes quite indistinct around 1473 K.

The results shown in Fig. 3 can be explained as follows: Crack-like flat cavities, which were probably caused by superplastic deformation under high strain-rate or low-temperature conditions, were found in 3Y-TZP by means of SANS, in addition to normal (conventional) cavities. These flat cavities were formed along the grain boundaries and they had saucer shapes lying roughly normal to the tension axis. The initial strain-rates and temperature used to deform the specimens are similar to those under which the flat cavities were found to occur. It can be inferred, therefore, that the flat cavities should be contained in the present specimens. In this case, the flat cavities may absorb the thermal expansion caused by temperature increase. That is, when the flat cavities are crushed along the tension axis, the thermal expansion should be decreased along the longitudinal axis of the specimen.

The phenomenon stated above is very similar to the results obtained in the thermal expansion behavior of graphite. That is, transcrystalline cleavage microcracks were formed along the basal plane (0001) in plenty of graphite crystal grains upon cooling after graphitization. The coefficient of linear thermal expansion, $\alpha_{gr}$, of polycrystalline graphite can be expressed by $\alpha_{gr} = R\alpha_a + (1 - R)\gamma\alpha_c$, where $\alpha_c$ is the coefficient of linear thermal expansion perpendicular to the basal plane and $\alpha_a$ is the coefficient parallel to the basal plane of graphite single crystal, $R$ is a preferred orientation parameter and $\gamma$ is the accommodation coefficient smaller than unity. When there exist such microcracks, an apparent $\alpha_a$ value is reduced owing to the closing of the microcracks, which appears in a decrease in the $\gamma$ value, resulting in a decrease in the $\alpha_a$ value. This kind of process has been named as “accommodation”.

An effect of the flat cavities in the present study may be similar to that of the accommodation of the cleavage microcracks found in graphite. That is, it is probable that the thermal expansion along the tension axis was reduced by the crushing and/or closing of the flat cavities, resulting in the apparent decrease in the $\alpha$ value. Because the measurement was carried out during heating, the flat cavities would be gradually crushed and the space, which could absorb the thermal expansion, would decrease i.e., the cavity dependence of $\alpha$ weakened with increasing temperature. Moreover, it seemed that the spaces of the flat cavities would be almost lost at around 1473 K and accordingly the cavity dependence of $\alpha$ disappeared at 1473 K.

Regarding the effect of thermal history on the flat cavities, although the accommodation due to closing of the flat cavities would be almost lost at around 1473 K, the flat cavities seems to close incompletely. This is because the data for the second trial agreed well with those of the initial measurement. The following figures support the above idea: (1) The flat cavities survived in the specimens despite the fact that the specimens were pulled to 70% elongation at 1723 K and were then cooled with furnace cooling to room temperature. (2) The highest temperature for the thermal expansion measurement was 1473 K and the specimens were held at 1473 K for only 600 s. To find out a proper annealing condition to close the flat cavities completely should be a future task.

Let consider the average thickness of the gaps of flat cavities. It can be estimated roughly from the difference in the $\alpha$ values for specimens with $V_c = 0$% and 3.0%. For example, the difference at 713 K is approximately $1 \times 10^{-7}$ K$^{-1}$ from Fig. 3. Since the thermal linear expansion at 300 K was set to be zero and the initial specimen length was 15 mm, the difference in the expanded lengths at 1473 K should be about 1.76 μm, if the difference in the $\alpha$ values at 713 K is used. Since the average interval of flat cavities along the tensile direction has been estimated to be about 4 μm by SANS, the number of flat cavities along the specimen length is roughly 3700 pieces, if the flat cavities are assumed to be forming a line along the tensile direction. Then the average gap thickness of the flat cavities is estimated to be about 0.48 nm. This value is quite small in comparison with the gap, approximately 3 nm, of crack-like cavities observed by TEM. However, the actual average gap thickness of the flat cavities may be larger than 0.48 nm, perhaps, in the order of magnitude in comparison with the gap, approximately 3 nm, of crack-like cavities observed by SEM.

If there existed sufficient number of the flat cavities, it is reasonable that when $V_c$ becomes large, so does the number
of the flat cavities. It seems that the conventional cavities would have almost no effect on the thermal expansion, which agrees with the result that gross open pores play no noticeable role in the accommodation of thermal expansion in graphite.10–12)

Thermal barrier coatings of yttria stabilized zirconia containing 100% tetragonal phase have shown \( \alpha \) values similar to the present ones which are about 11.0–12.0 \( \times 10^{-6} \) K\(^{-1} \) at 500–1250 K.\(^{24,25} \) In the thermal expansion of nanocrystalline Ni–P alloys having different grain sizes, \( \alpha \) was shown to decrease with an increase in the average grain size from 7.5 to 127 nm.\(^{25} \) In the present study, the average grain size was in the range from 0.41 to 0.48 \( \mu \)m, which was dependent on the amount of deformation, temperature and strain rate. Since the difference in the grain boundary area of the present specimens is much less than that of Ni–P alloys, the grain size dependence of \( \alpha \) in the 3Y-TZP must be not obvious. In addition, the \( \alpha \) value showed little dependence on the grain aspect ratio, which was 0.94 before deformation and increased to 1.07–1.13 after deformation, within the present experiment.

4. Conclusions

The thermal expansion behavior of superplastically deformed 3Y-TZP specimens was investigated in a temperature range from 300 to 1473 K. The mean coefficient of linear thermal expansion, \( \alpha \), showed an approximately linear increase with increasing temperature within the present experimental range. The effects of the average grain size and grain aspect ratio of the deformed 3Y-TZP specimens on the thermal expansion property were not pronounced. However, the \( \alpha \) value was found to be sensitive to deformation-induced cavities and decreased with increasing volume fractions of cavities. It is inferred that crack-like flat cavities can accommodate the thermal expansion and consequently result in a low \( \alpha \) value. The effect of cavities on the \( \alpha \) value was also dependent on temperature, and the gradual closing of the flat cavities with temperature seemed to be responsible for the diminishing of the cavity dependence of the \( \alpha \) value.

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REFERENCES