The thermal diffusivity and specific heat of superplastically deformed 3Y-TZP specimens were measured in a temperature range from 298 to 1273 K. From these data, the thermal conductivity has been evaluated and discussed. A weak temperature dependence of the thermal conductivity was observed. The thermal conductivity showed almost no dependence on the grain size and grain aspect ratio of the 3Y-TZP specimens. On the other hand, the thermal conductivity was considerably sensitive to the deformation-induced cavities. The influence of the cavities on the thermal conductivity is related with temperature. An expression was proposed for predicting the relationship between the effective thermal conductivity and deformation-induced cavities within the present experimental range.

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Keywords: superplasticity, thermal conductivity, thermal diffusivity, specific heat, cavitation and 3 mol% yttria stabilized tetragonal zirconia polycrystal

1. Introduction

There have been considerable studies relating to superplasticity in ceramics since superplastic phenomenon was reported firstly in a zirconia-based ceramic in 1986.1) Basic researches for practical applications of superplasticity in ceramics are drawing much attention lately.2–11) With the aim of nuclear application at high temperature engineering field, a neutron irradiation research on the superplastic ceramics has been proposed as an innovative basic project using the High Temperature Engineering Test Reactor (HTTR) in Japan. One of this project’s targets is to study the thermophysical properties of superplastic zirconia-based ceramics.

Heat is mainly carried by lattice vibrations in solid oxides. For polycrystalline materials, the thermal conductivity is generally observed to decrease with temperature in a temperature range of 298–1273 K. This is explained by great mutual scattering of the vibrational waves through Umklapp processes which shortens the mean free path of phonon above Debye temperature.12) Meanwhile, microstructural factors can have significant influences on thermal conductivity.13)

There have been many studies on how cavity-like flaws such as pores affect thermal conductivity of ceramics, which have focused primarily on sintered or plasma sprayed ceramic materials.14–17) Actually, cavities existing in superplastically deformed ceramics are morphologically different from those crack-like pores in sprayed coating ceramics, cellular pores in refractory ceramics or residual pores of sintered ceramics. Generally, deformation-induced cavities in superplastic ceramics, locating at grain boundary triple points, are very fine in size, large in number, uniform in distribution and sphere-like in shape. These cavities may have different effects on the scattering of phonon. Additional thermal resistance may be caused by the changes of grain boundaries induced by superplastic deformations. In fact, a significant increase in the room temperature thermal conductivity for ceramics with large grain sizes has been reported.18) This can be attributed to the reduction in the grain boundary area blocking the heat flow path. Thermal conductivity is also sensitive to the crystal structure. The monoclinic zirconia shows a lower thermal conductivity than tetragonal zirconia, while cubic phase is lower than the former two phases.19,20) It was reported that stress-induced transformation might occur in zirconia-based ceramics.21) There is a possibility that superplastic deformations induce the transformation and cause the change in thermal conductivity. Although many empirical or semiempirical correlations between thermal conductivity and porosity have been reported, they are based on some special assumptions and their ranges of applicability are limited to special situations.14,22,23) Up to now, as long as we know, there is no report on the relationship between superplastic deformation-induced cavities and thermal conductivity. It is of interest to investigate the thermal conductivity of superplastic ceramics.

This paper is aimed to study the effect of superplastic deformations on the thermal conductivity of a typical superplastic ceramic, 3 mol% yttria stabilized tetragonal zirconia polycrystal (3Y-TZP). The specific heat and the thermal diffusivity of superplastically elongated 3Y-TZP specimens were measured in a temperature range from 298 to 1273 K, and then the thermal conductivity was evaluated and discussed. An equation was proposed to predict the effective thermal conductivity with volume fraction of cavities.

2. Experimental

2.1 Material preparation and microstructural characterization

The starting material was prepared by sintering powders of ZrO$_2$ containing $Y_2$O$_3 = 5.15$ mass%, SiO$_2 < 0.02$ mass%, Fe$_2$O$_3 < 0.01$ mass%, Al$_2$O$_3 < 0.01$ mass% in solid solution at 1723 K in air. Tension tests at constant cross-head rates were carried out 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$^{-1}$, respectively. A nominal strain was 70% for every specimen.
Specimens for specific heat measurements and thermal diffusivity measurements were cut from the central part of the deformed 3Y-TZP specimens. Meanwhile, dense 3Y-TZP specimens with the same dimension were used as undeformed ones.

The density, $\rho$, and volume fraction of cavities, $V_c$, of all specimens were measured by the Archimedes method. The specimens polished to a flat mirror face were thermally etched and then were used for scanning electron microscopy (SEM) investigation. The SEM images were used to evaluate the average grain size, $d_{av}$, and grain aspect ratio, $A_s$, of the 3Y-TZP specimens. Ten visual fields were chosen randomly for the measurements of the $d_{av}$ and $A_s$. Crystal structure of the 3Y-TZP specimens was characterized by X-ray diffraction analysis (XRD, 20 was between 36 and 160°).

### 2.2 Determination of thermal properties

Differential scanning calorimetry (DSC) method was used to measure specific heat with DSC 8270, which is a kind of heat-flux DSC and was provided by Rigaku Corporation Japan. The measurements were carried out upon heating in the temperature range from 473 to 1273 K. A purge gas of helium was constantly passed through the heating block and over pans with a flow-rate of 100 ml/min. The heating rate was 5 K/min, and pre-determined temperature region was 50 K. The $\alpha$ alumina powder commercially available was used as the standard sample in this study.

Thermal diffusivity was measured by the laser flash method with a Shinkuriko type TC-700. In the present study, a ND laser was used as a heat source. Thermal diffusivity measurements were carried out in a vacuum ($<2 \times 10^{-3}$ Pa) at temperatures from 298 to 1273 K during heating in 200 K intervals. Prior to the thermal diffusivity measurements, the specimens were coated with a thin layer of graphite to ensure uniform and complete absorption of the laser pulse and identical surface radiative characteristics for all specimens. The thermal diffusivities of Ta and IG-110, as the reference samples in this work, were determined at 298 K, 773 K, 1273 K and 1673 K for calibration of the measurement system. The effect of thermal expansion on the bulk density can be neglected because thermal expansion within the present temperature range is extremely small. Thermal conductivity was evaluated from these measurement results.

### 3. Results and Discussion

#### 3.1 Microstructural characterization

The SEM images show homogeneous distribution of the grains for all the 3Y-TZP specimens. Strain-induced concurrent grain growth and change in grain aspect ratio were found in the deformed specimens. Fine cavities were uniformly distributed in the deformed specimens, while it is difficult to find those extremely fine deformation-induced cavities, probably locating at grain boundary triple points and being much smaller than 100 nm, because the resolution of SEM was limited. The $V_c$ value was calculated from the results of the density measurements, which were within the error of ±3%. The results of microstructural characterization and deformation conditions are listed in Table 1. The crystal structure of the 3Y-TZP specimens was characterized using the XRD technique and the diffraction patterns are shown in Fig. 1. There is almost no difference among them, and most of the phases in the deformed 3Y-TZP specimens were found to be tetragonal one. It can be concluded that different initial strain rates cause no change in the crystal structure of the 3Y-TZP specimens within the experimental range.\(^{24}\)

#### 3.2 Specific heat

Experimental results of specific heat measurements are shown in Fig. 2. The specific heat is about 0.55 J·g\(^{-1}\)·K\(^{-1}\) at 473 K, then it gradually increases with increasing temperature and becomes to be about 0.63 J·g\(^{-1}\)·K\(^{-1}\) at 1273 K. The slope of curves decreases with increasing temperatures, that is, increase rate of the specific heat slows down with temperatures. The specific heat values of yttria stabilized zirconia were reported at temperatures from 298 to 873 K by Hasselman et al.\(^{20}\) Raghavan et al.\(^{24}\) also reported specific heat capacities of commercially available 3Y-TZP, which were measured in the temperature range of 373–1273 K by the DSC method. Comparison of those results with the data obtained in this study are plotted in Fig. 3. The average specific heat values in the present study show a good agreement with the reported values. Swain et al. studied specific heat values of porous partially stabilized zirconia with 3.3 mass%MgO.\(^{21}\) Although

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Initial strain rate, $\dot{\varepsilon}$, s(^{-1})</th>
<th>Bulk density, $\rho$, g mm(^{-3})</th>
<th>Volume fractions of cavities, $V_c$, %</th>
<th>Grain aspect ratio, $A_s$</th>
<th>Average grain size, $d_{av}$, $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1, 2</td>
<td>$4.2 \times 10^{-4}$</td>
<td>5.99, 6.00</td>
<td>1.1, 1.0</td>
<td>1.07</td>
<td>0.48</td>
</tr>
<tr>
<td>No. 3, 4</td>
<td>$1.4 \times 10^{-3}$</td>
<td>5.87, 5.86</td>
<td>1.7, 1.6</td>
<td>1.13</td>
<td>0.48</td>
</tr>
<tr>
<td>No. 5, 6</td>
<td>$4.2 \times 10^{-3}$</td>
<td>5.96, 5.96</td>
<td>3.1, 3.4</td>
<td>1.08</td>
<td>0.47</td>
</tr>
<tr>
<td>No. 7, 8</td>
<td>6.05</td>
<td>0</td>
<td>0.94</td>
<td>0.41</td>
<td></td>
</tr>
</tbody>
</table>
there were different ratios of the tetragonal-to-monoclinic phase content among the specimens with various porosities, little difference in the specific heat was found. In this study, the factor of crystal structure can be neglected because the crystal structure of the 3Y-TZP showed no change within the present experimental range. The inaccuracy of the measurements is not more than 5% by comparison with the standard data. The experimental results showed that there was no relationship between specific heat and microstructural evolution caused by the superplastic deformations.25)

3.3 Thermal diffusivity

The thermal diffusivity of the 3Y-TZP specimens are shown in Fig. 4 with other reported data. The error of the thermal diffusivity measurements is within ±5%. All the specimens show similar temperature dependence of the thermal diffusivity over the whole temperature range. The thermal diffusivity value at room temperature is around 1.15 × 10⁻⁶ m²·s⁻¹ and decreases to about 0.60–0.70 × 10⁻⁶ m²·s⁻¹ at 1273 K. There is an obvious temperature dependence at the beginning stage, and then the dependence becomes smaller with increasing temperatures. The thermal diffusivity values at higher temperatures reported by Hasselman et al. are slightly less than our results.20) On the other hand, an increase in the thermal diffusivity with temperature above 1000 K was reported by Owada et al.20)

3.4 Thermal conductivity

Thermal conductivity (λ) is determined from thermal diffusivity (α), density (ρ) and specific heat (C_p) through the formula:

\[ \lambda = \alpha \cdot \rho \cdot C_p. \]  

(1)

The results of the calculation are shown in Fig. 5. The decreased thermal diffusivity with increasing temperature was compensated by the increased specific heat, which gives rise to slight temperature dependence of thermal conductivity. The thermal conductivity is about 3.2 W·m⁻¹·K⁻¹ at 298 K, then slowly decreases with increasing temperature, and then becomes nearly constant, 2.6–2.8 W·m⁻¹·K⁻¹, above 873 K. This temperature dependence is very similar to that of ZrO₂ containing different amounts of Y₂O₃ and sintered nanocrystalline YTZ.20, 24) The weak temperature dependence frequently observed at higher temperatures may be attributed to a radiative component. Around 1273–1473 K the lattice and radiative components are usually comparable with each other.27) The tendency of the increase in the thermal conductivity with temperature is occasionally reported. For example, Raghavan et al. reported that 63% dense nanocrystalline TZP specimen showed a slight increase in the thermal conductivity at temperature above 873 K resulted from strong radiation contributions because of the high porosity.24)

The low thermal conductivity of the zirconia-based ceramics stems primarily from the scattering of phonons by point defects.27) The influence of lattice imperfection on phonon conduction can be from cavities, grain boundaries, cracks and so on.

Grain boundaries play a very important role in superplastic deformations since grain boundary sliding is a main deformation mechanism for zirconia-based ceramics. Superplastic deformations result in the concurrent grain growth in the deformed specimens, which brings about change in grain boundary area per unit volume. Theoretically, it is inferred that the thermal conductivity of yttria stabilized zirconias with very small grain sizes be lower than that of those coarse zirconias,24) since grain boundary can inhibit heat conduction additionally. In this experiment, the grain boundary area per unit volume of the deformed specimens is about 10% less than that of the undeformed specimen at least. However, at each temperature, the thermal conductivity value was almost independent of the average grain size within the range of 0.9–1.2 µm, which might not be small enough to affect the thermal conductivity. Consequently the grain size dependence of the thermal conductivity was not well pronounced. On the other hand, other characteristics of grain boundary can affect thermal conduction. Strong segregation of Y³⁺ to the grain boundaries of zirconia-based ceramics, which was thought to be favorable for superplastic deformation, has been reported.23) Cations can be assumed to go into the zirconia lattice which results in greater scattering of the lattice vibrations. In fact, the decrease in the thermal conductivity of Y-TZP with increasing Y₂O₃ content has been found. The amount of Y³⁺ segregation can increase with the deformation. It is inevitable that this kind of numerous cations can cause additional scattering of phonon. An alternative explanation can be put forward for such effect.28) Although yttria cations may be practically soluble in lattice of zirconia, the segregated cations lo-
cate at the periphery of the grains, i.e., in a segregated layer. Because the vibration of these enriched cations at the grain boundary area can be strengthened with raising temperature, there is a possibility that the characteristic microstructure at grain boundaries of 3Y-TZP may affect the phonon mean free path. However, grain boundary scattering of lattice vibrations should have less influence on the thermal conductivity as the phonon mean free path shortens at higher temperatures.

The results of different thermal conductivity measurements made on zirconia-based ceramics have been scattered within a certain region, which may be attributed to different composition as well as experimental procedures. The effective thermal conductivity $\lambda_\text{e}$ values obtained in the present study are slightly smaller than other reported data.\textsuperscript{21,24} It can be explained by the thermal resistance caused by the deformation-induced cavities. As well known, various lattice imperfections give rise to anharmonicities and result in phonon scattering. Strengthened phonon-phonon scattering with increasing temperature can lead to decreasing in the phonon mean free path and further affect the thermal conductivity.\textsuperscript{29} Pores or cavities are one of the most effective factors to affect the phonon scattering. Therefore, the thermal conductivity values obtained are plotted in Fig. 6 as a function of $V_\text{c}$. As shown in the figure, it seems that the cavity dependence of
3Y-TZP is not much pronounced at room temperature, however, the thermal conductivity at higher temperatures is fairly dependent on the cavities although the experimental data are somewhat scattered at higher temperatures.

Several theories on the evaluation of thermal conductivity have been published and used to explain experimental data for thermal conductivity of porous materials. The following relation,

\[ \lambda_e = \lambda_0 \left(1 - V_c \right) \left(1 - 0.5V_c \right) \] (2)

is an expression known as Maxwell-Eucken’s equation, where \( \lambda_e \) (W m\(^{-1}\) K\(^{-1}\)) is the effective thermal conductivity, and \( \lambda_0 \) is the thermal conductivity for the completely dense matrix material. It is assumed that pores are far apart so that mutual interaction between pores can be neglected. Some other expressions showed good agreement with the Maxwell-Eucken’s equation when such factors as shape and orientation of pores were simplified and the contribution of convection and a radiative component to the thermal conduction were neglected. For example, Schulz proposed a simple model by assuming closed spherical pores.\(^{23}\) For a low porosity condition \( (V_c \leq 10\%) \), the effect of porosity on the thermal conductivity of solid composites can be described as follows:

\[ \lambda_e = \lambda_0 \left(1 - V_c \right)^{1.5} \] (3)

Schulz’s equation shows quite similar correlation with eq. (2) within a certain porosity range. After analyzing some published theories on the thermal conductivity of two-phase materials, Kawashima et al. came up with a modified effective-medium theory for the thermal conductivity of porous Ni/YSZ particulate composites and provided a relationship between the thermal conductivity and porosity:\(^{14}\)

\[ \lambda_e = \frac{1}{2}\lambda_0 \left(1 - V_c \right) \left(2 - 3V_c \right), \left(0 \leq V_c < 67\% \right) \] (4)

This correlation predicted the experimental data well in their study. Because the thermal radiation and convection within pores are extremely weak, the thermal conductivity of the pores themselves is often very small compared with that of the matrix material. Thus, the effect of temperature is usually neglected in many empirical equations.

A modified Loeb’s formula, which put temperature as a variable, was proposed based on the measurements on unirradiated UO\(_2\) fuel:\(^{22}\)

\[ \lambda_e = \lambda_0 \left(1 - \eta V_c \right) \] (5)
where \( \eta \) is an empirical parameter and is expressed as a function of temperature, where \( \eta = 2.6 - 0.5 \times 10^{-5}T \), and \( T \) is temperature in °C.

The curves calculated from eqs. (2) to (4) are shown in Fig. 6. It is interesting to note that the curves calculated from the above three eqs. (2) to (4) do not fit well with the experimental data in the present study. Why can’t the well-employed expressions explain well the measured results? One of the reasons may be that these equations are applicable only for a limited range of materials. That is, it is difficult for one expression to predict accurately the thermal conduction behavior of different porous materials. Another reason may be that pores or cavities with different properties probably have different effects on thermal conductivity. Schulz23) took such parameters as the shape, orientation, structure type, distribution of the pore, and porosity into consideration when he studied the thermal conductivity of porous composites. However, these factors can be neglected or simplified for the present 3Y-TZP specimens, since the deformation-induced cavities are sphere-like, very fine and distributed quite uniformly in the deformed specimens. What should be emphasized is the size of the cavities. Residual pores of sintered ceramics are often very large in size, and cellular pores in refractory materials are often more than 1 mm in diameter. On the contrary, the deformation-induced cavities in the present 3Y-TZP are much smaller than these pores. The presence of nanocavities at the grain boundary triple points in the superplastically deformed materials has been confirmed. It means that there is larger total cavity surface area in superplastically deformed 3Y-TZP than ordinary sintered or refractory ceramics for the same porosity or \( V_c \) value. Obviously, additional thermal resistance may be caused by those small cavities locating at the grain boundary triple points. Thus, phonon scattering can be affected more strongly in the deformed 3Y-TZP than general porous ceramics. Therefore, the above empirical eqs. (2) to (4) can’t explain the experimental data well in this study.

In the present study, the measured data were found to agree well with the modified Loeb’s eq. (5), in which the empirical parameter, \( \eta \), indicating the contribution of cavity scattering to the thermal conductivity, was expressed as a function of absolute temperature. The \( \lambda_0 \) value was obtained according to the fitting curve of thermal diffusivity of the undeformed specimen. It is assumed that all the cavities in the deformed 3Y-TZP specimens are spherical and \( V_c \) is independent of shape and size of cavities. Fitting equations of the relationship between the volume fraction of cavities and the effective thermal conductivity of the 3Y-TZP specimens at different temperatures are listed in Table 2. The cavity dependence of the thermal conductivity is comparatively weaker at room temperature than at other temperatures. The relationship between \( \eta \) and temperature is shown in Fig. 7. The \( \eta \) can be expressed as follows: \( \eta = -0.1 + 6.9 \times 10^{-3}T - 3.7 \times 10^{-5}T^2 \) (298 K < \( T \) < 1273 K, \( 0 \leq V_c \leq 4 \% \)). On the whole, the above expression (5) can show the contribution of the cavity scattering to the thermal conductivity. Although the \( \eta \) values at 523 K and 1073 K are somewhat deviated the fitting curve, no explanation can be given here. Generally, The cavity dependence of the thermal conductivity is not very high at room temperature, and then the effect of the cavities on the thermal conductivity increases with temperature, because the vibration of these enriched cations at the grain boundary area can be strengthened with raising temperature. Meanwhile, a radiative component, usually neglected at low or middle temperatures, becomes significant at higher temperatures. When the effect of other factors on heat transfer doesn’t change, with increasing temperatures, the photon conductivity fraction of the total thermal conductivity of the ceramic substances gradually becomes large. Thus, \( \eta \) may tend to decrease slightly above approximately 1000 K. The larger \( V_c \) of the 3Y-TZP from further superplastic deformations will be helpful to verify the cavity dependence.

### 4. Conclusions

The thermophysical investigations were performed on superplastically deformed 3Y-TZP specimens within a temperature range from 298 to 1273 K. A weak temperature dependence of the thermal conductivity was observed within the present experimental range. The effect of the grain size and grain aspect ratio of the deformed 3Y-TZP specimens on the thermal conductivity is not pronounced. Experimental results revealed that the thermal conductivity values are dependent on the deformation-induced cavities and decrease with increasing the volume fractions of cavities. The effect of the cavities is dependent on temperature. The effective thermal conductivity measured in the present study can be expressed with a modified Leob’s equation as a function of \( V_c \) and temperature, which is as follows: \( \lambda_c = \lambda_0 (1 - \eta V_c) \), \( \eta = -0.1 + 6.9 \times 10^{-3}T - 3.7 \times 10^{-5}T^2 \).

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REFERENCES