Experimental Investigation of the Effect of Superplastic Deformation on the Specific Heat of a Zirconia-based Ceramic

ジルコニア系セラミックの比熱に対する超塑性変形の影響に関する実験的検討

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The effect of superplastic deformation on the specific heat of a zirconia-based ceramic, 3Y-TZP was investigated by using the differential scanning calorimetry (DSC) method in a wide temperature range from 473 K to 1273 K. The samples were prepared by superplastic deformations, as a function of initial strain rate, with the nominal strain of 70% at 1723K. Experimental results showed a general temperature dependence of the specific heat at elevated temperatures for the deformed samples. There was, however, no obvious effect caused by the deformations. It was also found that there was no correlation between the specific heat and the microstructural evolution due to the superplastic deformations. From these results, it is shown that the superplastic deformation has no influence on the specific heat of 3Y-TZP in this experiment.

[Keywords: specific heat, superplastic deformation, zirconia, 3Y-TZP, microstructure]

超塑性変形が 3Y-TZP の比熱に与える影響を、示差走査熱量測定法 (DSC) を用いて、473K から 1273K までの広い温度範囲で調べた。測定に供した試料は、初期ひずみ速度をパラメータとして、1723K で公称歪み 70%まで超塑性変形させたものである。実験の結果、超塑性変形後の試料の比熱について、高温では通常の温度依存性が観察されたが、超塑性変形に起因する明らかな影響は観察されなかった。また、超塑性変形後の試料の比熱と微視組織との相関も見られなかった。これらの結果により、今回の実験範囲においては、超塑性変形は 3Y-TZP の比熱に影響を与えないことを示した。

1. INTRODUCTION

Zirconia-based materials have long been recognized as

promising candidates for a wide variety of structural materials applications due to a toughening effect relying mainly on its martensitic transformation, high melting point and excellent chemical stability. However, because of their brittle nature, it has been difficult to manufacture ceramic parts directly by means of plastic working. Fortunately, Wakai et al. found high ductility at 1723 K in a zirconia-based ceramic in 1986 [1], which was named as 'ceramic superplasticity' later. Since then, the intensive and still ongoing theoretical and experimental works have been focused on this kind of promising ceramic materials. It is believed that superplastic phenomena may give a key to solve the problem [2-6]. In order to realize the industrial applications of plastic forming of ceramics by superplastic

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leformations, it is quite important to get as many undamental data as possible. Since this kind of materials is expected to endure severe circumstances at higher emperatures, understanding of the thermophysical roperties of the zirconia-based ceramics, especially for superplastically deformed ones, is of practical importance. Although there have been many studies on the thermal roperties as well as superplastic deformation behaviors of he ceramics, so far as we know, no investigation has been given concerning the thermophysical properties of superplastically deformed ones, which triggered our interest n the thermophysical investigations on this promising material.

Generally speaking, the mole isobaric specific heat of ceramic materials is thought to be insensitive to their microstructures. However, microstructural evolution of yttria stabilized tetragonal zirconia due to superplastic deformations is fairly uncommon among ceramics [2-4], and is primarily focused on the formation and growth of cavities, strain-induced dynamic grain growth, changes in grain boundary structures, grain aspect ratio and so on. In general, superplasticity arises in a fine-grained material. In this case the contribution of grain boundary, e.g., grain boundary area and its structure, to physical as well as mechanical properties may be higher than ordinary materials. Microstructural evolution resulted from superplastic deformations such as the segregation of ions and vacancies to grain boundaries will have influences on the grain boundary characteristics, which might change the specific heat of the material to some extent. Moreover, it was found that cavities formed in superplastically deformed samples are morphologically different from those crack-like pores in sprayed coating ceramics or cellular pores in refractory ceramics [7-8].

Besides the microstructural evolution, it is likely that superplastic deformation has an unexpected effect on the zirconia-based ceramics. For instance, stress-induced martensitic transformation and domain switching process may occur during superplastic deformations [9-10]. Furthermore, it was reported that the variation in specific heat of some materials could be the results of some phase transformations and order-disorder transformations occurring during the thermophysical examinations [11-12]. Moreover, Y^{3+} ions segregate to grain boundaries [13]. Therefore, it is probable that these characteristic phenomena have some unexpected effects on thermophysical properties of this kind of materials.

To study whether the microstructural evolution due to the superplastic deformations has influence on other thermal

properties, e.g., thermal conductivity and thermal expansion coefficient, is our next target. Therefore, accurate measurement on specific heat value as a function of superplastic deformation will also be necessary to evaluate the thermal conductivity and thermal expansion coefficient of superplastically deformed ceramics.

As stated above, it is quite significant to investigate and verify whether the microstructural evolution, phase transformations and so forth will give birth to the change in specific heat of this kind of ceramic.

In the present study, a typical superplastic ceramic, 3 mol.% yttria stabilized tetragonal zirconia polycrystal (3Y-TZP), which has become one of the most promising candidates for industrial applications and is with characteristic fine-grained microstructure, was superplastically deformed under different conditions, and then specific heat measurements were conducted on the deformed samples. The experimental results were evaluated and discussed with the results of microstructure investigations.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation and Characteristics of Samples

The 3Y-TZP samples for superplastic deformations were provided by a commercial source and were produced by sintering powders of ZrO_2 containing 3 mol.% Y_2O_3 in solid solution at 1723 K in air. They are all from a single batch, which ensures each sample with the identical composition and properties. The chemical composition of the 3Y-TZP is shown in Table 1. Superplastic deformations were carried out at 1723 K. Specimens of No.1 to 2, No.3 to 4 and No.5 to 6 were superplastically elongated to the nominal strain of 70% with initial strain rates, $\dot{\epsilon}_0$, of $4.2 \times 10^{-4} s^{-1}$, $1.4 \times 10^{-3} s^{-1}$ and $4.2 \times 10^{-3} s^{-1}$, respectively, while No.7 to 8 are undeformed samples.

Table 1 Chemical composition of 3Y-TZP (in wt%)

Y_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	ZrO_2
5.15	0.01	0.02	0.01	0.04	bal.

The samples for the specific heat measurements were cut from the deformed ones with a diamond cutter. These pieces of samples are about 1 mm in thickness, and are with the mass around 40 mg. Meanwhile, two commercially available 3Y-TZP dense discs, 4 mm in diameter and 0.5 mm in thickness, were used as undeformed samples to compare with deformed ones. All

samples are with fine surfaces, which assure the good heat contact and transfer between the sample and a pan during the measurement.

The bulk density measurement was performed by the Archimedes method. Measuring procedure was based on the JIS Z 8807. The accuracy of mass measurement was within $\pm 0.01\text{mg}$. A special vessel was designed for the density measurement and liquid methanol was used. The effect of infiltration of methanol into the surface of a sample was ignored because deformation-induced cavities were quantitatively quite small and were not being interlinked within the present experiment. Volume fraction of cavities, V_c , was calculated from the change in the densities of the samples.

Samples for microstructure investigations were prepared by thermal etching and were examined by the scanning electron microscopy (SEM). Average grain size, d_{av} , and grain aspect ratio, A_s , were evaluated from SEM images. The X-ray diffraction (XRD) technique was employed to evaluate the crystal structures of deformed samples at room temperature. Diffraction angle, 2θ , is from 36 to 160° .

2.2 Specific Heat Measurement

Specific heat, C_p , was determined by the differential scanning calorimetry (DSC) method. The technique has been widely utilized for specific heat measurements because of its many advantages such as high accuracy, convenience and economy over other methods. The features of this technique are stated in published literatures [14-15].

The DSC 8270 with an analysis software was used in this study, which is a kind of heat-flux DSC and was provided by Rigaku Corporation. The measurements were carried out according to some principles [15-16]. The specific heat value was determined by 'the scanning method'. The two platinum pans were equilibrated within a precision of ± 0.1 mg. The α alumina powder commercially available was used as the standard sample in this study. The measurements were carried out upon heating in the temperature range from 473 K to 1273 K. The heating rate was 5 K/min, and pre-determined temperature region was 50 K. In order to assure the accuracy of measurement, five target temperature regions were assigned to two operation programs, one being from 473K to 873K, and another from 873K to 1273K. A purge gas of helium was constantly passed through the heating block and over pans with a flow-rate of 90 ml/min. Random errors were minimized to as low as possible. In addition, the accuracy and the reproducibility of the measurements were checked with the α alumina powder as the standard sample in this study.

3. RESULTS AND DISCUSSION

3.1 Characterization of 3Y-TZP Samples

Some SEM images of the samples are shown in Fig. 1. Homogeneous distribution of grains and a fine grain size being maintained after superplastic deformations are found. The average grain size of the undeformed sample is smaller than those of deformed ones, indicating the occurrence of deformation induced concurrent grain growth. Grain aspect ratio varied slightly, suggesting that the grain was elongated a little along the tensile direction. These variables are plotted in Fig. 2.

(a) Undeformed sample

(b) $\dot{\epsilon}_0 = 4.2 \times 10^{-3} \text{ s}^{-1}$

←Tensile direction→

Fig. 1 Scanning electron micrographs of superplastically deformed 3Y-TZP samples. Nominal strain is 70%, and deformation temperature is 1723 K.

The X-ray diffraction patterns of the 3Y-TZP samples are shown in Fig. 3. According to the analysis on the peak values, there is little difference between deformed samples and undeformed one. And almost all of the phases in the deformed 3Y-TZP samples are tetragonal one, which may be attributed to the characteristic of stabilized zirconia and fine grain size. Different initial strain rates did not cause difference in the crystal structure of 3Y-TZP within the present experimental range.

Some small cavities were uniformly distributed in

deformed samples, while lots of extremely small strain-induced cavities may be invisible because of limited resolution of the SEM. Large-scale cavities and cavity linkage were not found, while few residual pores were found in the undeformed sample, as is shown in Fig.1 (a). The V_c of undeformed samples is assumed to be zero, and the V_c of deformed samples is shown in Table 2. Although the largest V_c is not more than 4%, it is about three times larger than the lowest one. This difference is sufficient to cause different effects on properties of the samples.

Fig. 2 Variations in the average grain size and grain aspect ratio of the 3Y-TZP samples with initial strain rates.

From a viewpoint of engineering applications, if the V_c induced by superplastic deformations is less than a few percent, the degradation of mechanical properties is permissible for zirconia-based ceramics. It is, therefore, meaningful to evaluate the cavity dependence of thermal properties of 3Y-TZP with V_c of around 3% at most.

Table 2 Volume fractions of cavities of superplastically deformed 3Y-TZP samples

Sample 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

3.2 Specific Heat

3.2.1 Reproducibility and accuracy of measurements

It is extremely important to assure the accuracy and reproducibility of measurements by DSC [15-16], because experimental data can be affected by many factors. In this study, much attention was paid on each point of experimental procedures to evaluate the experimental results. The accuracy and the reproducibility of the measurement were checked with α alumina powder as the standard sample. Obtained data are shown in Fig. 4. The

inaccuracy in the measurements is not more than 5% by comparison with the standard data [17]. Moreover, the reproducibility of the measurement was within $\pm 3\%$. These results showed good agreement with the conclusion in a technical report provided by Rigaku Corporation [18].

Fig. 3. X-ray diffraction patterns for superplastically deformed 3Y-TZP with various initial strain rates at 1723 K.

Fig. 4 Accuracy of specific heat measurements on the α alumina powder as the standard sample.

3.2.2 Results of specific heat measurements

Experimental results of the specific heat measurements are shown in Fig. 5. The relationship between the specific heat and temperature seems to be linear above 800 K. Similarly, a linear relationship with positive coefficient was found on a thermophysical investigation of zirconia cermet in a temperature range from 1073K to 1273K [19]. Temperature dependence of the specific heat of 3Y-TZP is in good agreement with the general rule [11].

Fig. 5 Variation of specific heat measurements with temperature on superplastically deformed 3Y-TZP.

Development of defects and some special processes such as phase transformation can contribute to the change in specific heat at higher temperatures, i. e., the variation in specific heat of some materials could be the results of some phase transformations and order-disorder transformations occurring during the thermophysical examinations [11]. Combined with the microstructural evolution due to superplastic deformations, the experimental data are discussed as follows.

Strain-induced cavities in ceramics are almost unavoidable. The V_c Value, as one of the parameters characterizing microstructures, was utilized to investigate whether some changes in the specific heat of this material is related to superplastic deformation. The specific heat is shown in Fig.6 as a function of V_c . It is found that very few data deviated from the average. There is not any observable tendency to increase or decrease with varying V_c at a given temperature, e.g., all data are around $6.20 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 1073 K. We can say, therefore, that the specific heat of 3Y-TZP may be insensitive to the deformation-induced cavities.

Experimental data shows little dependence of the specific heat on V_c . However, it may be insufficient to conclude that the specific heat is insensitive to the

Fig. 6 Relationship between specific heat and volume fraction of cavities of the superplastically deformed 3Y-TZP samples at various temperatures.

microstructural evolution, because grain boundary sliding is a main deformation mode of superplastic deformation of 3Y-TZP. The changes in grain boundary structures and the volume fraction of grain boundaries associated closely with the grain boundary sliding could have occurred, which might induce change in the specific heat. Therefore, it is necessary to consider the effects of grain boundaries.

As shown in Fig.2, there are differences in the grain aspect ratio and the average grain size among the samples. So the effect of grain aspect ratio and average grain size on the specific heat was examined by plotting the C_p vs. d_{av} and C_p vs. A_s relationships. However, it was found that there is

little difference among the measured specific heat values of 3Y-TZP samples at each temperature, which implies that grain boundary structure and volume fraction of the grain boundaries have no effect on the specific heat within the present experimental range.

Additionally, a change in the specific heat of zirconia-based ceramics may be caused by phase transformation, because the transformation is often accompanied by absorbing or releasing energy. An investigation has been performed on several kinds of plasma sprayed zirconia coatings with different amounts of Y_2O_3 [7]. A quite different temperature dependence of the specific heat in 20-YSZ was found, which suggests that phase transformation might contribute it.

The stress-induced tetragonal to monoclinic ($t \rightarrow m$) martensitic transformation in zirconia-based ceramics has been reported [9]. Therefore, the behavior of martensitic transformation can be a potential factor to affect specific heat. In this study, abnormal and sharp changes were not found in the DSC chart record traces. If the martensitic transformation occurred, there would be monoclinic phase in samples. According to the results of X-ray diffraction analysis, no monoclinic phase was found in both the deformed and undeformed 3Y-TZP samples.

Considering all these results, we can say that the microstructural evolution due to the superplastic deformations has little influence on the isobaric specific heat of 3Y-TZP within the error of the present measurement.

4. CONCLUSIONS

Specific heat measurements were performed on the superplastically deformed 3Y-TZP in a wide temperature range from 473 K to 1273 K. The specific heat was discussed with the microstructural evolution. Superplastic deformation-induced cavities and other characteristics had no observable effect on the specific heat of 3Y-TZP. Except for the general temperature dependence of the specific heat at elevated temperatures, anything anomalous was not found. Therefore, it is most probable that superplastic deformation has no influence on the specific heat of 3Y-TZP within the present experimental range.

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