Superplastic Behavior in GeO₂ Doped Y-TZP

Junpei Mimurada[†], Kazutaka Sasaki[†],
Yuichi Ikuhara and Taketo Sakuma

Department of Materials Science, Faculty of Engineering, The University of Tokyo,
7-3-1 Tokyo, Japan

The superplastic behavior in GeO₂ doped 2.5Y-TZP was examined, especially, in terms of flow stress and tensile ductility by using high temperature tensile tests, X-ray diffraction analysis and scanning electron spectroscopy. ZrO₂-2.5 mol%Y₂O₃-1.0 mol%GeO₂ (TZP-1Ge) exhibits lower flow stress and larger tensile elongation than ZrO₂-2.5 mol%Y₂O₃ (2.5Y-TZP) in a temperature range of 1200 and 1550°C at an initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$. The decrease in flow stress mainly results from enhanced diffusivity with a reduction in superplastic activation energy due to GeO₂ addition. The improvement in tensile ductility in TZP-1Ge can also be explained by the enhanced diffusivity. Furthermore, the previous model proposed by Kondo *et al.* was applied to explain the tensile ductility in TZP-1Ge, however, it could not explain the tensile ductility in TZP-1Ge. It would indicate that the further consideration for the equation is required when applied to the superplastic behavior of TZP-1Ge.

(Received February 22, 1999; In Final Form July 19, 1999)

Keywords: superplasticity, flow stress, tensile ductility, tetragonal zirconia polycrystals, germanium oxide

I. Introduction

Superplasticity is a phenomenon that exhibits extensive ductility under tensile conditions in materials. Superplasticity in fine-grained ceramics has been examined since 1986⁽¹⁾. TZP (Tetragonal Zirconia Polycrystals) has a fine-grained microstructure and commonly exhibits large tensile elongation at high temperature tests. An elongation of 800% is obtained in Y₂O₃ stabilized TZP (Y-TZP) at 1550°C under a strain rate of $8.3 \times 10^{-5} \text{ s}^{-1}$ ⁽²⁾, and 1038% in SiO₂-doped Y-TZP at 1400°C under a strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$ ⁽³⁾. The high tensile ductility in TZP is explained by grain size stability during high temperature deformation⁽⁴⁾. However, Kondo *et al.* proposed a new analysis of tensile ductility in TZP and TiO₂-doped TZP⁽⁵⁾. Their analysis revealed that tensile ductility in TZP and TiO₂-doped TZP is maximized at an optimum temperature and strain rate, depending on their diffusivity. Enhanced diffusivity results in larger elongation at lower temperature and higher strain rate which is the preferable property for superplasticity. In the present study, 2.5Y-TZP was doped with germanium oxide (GeO₂) to obtain improved superplasticity by enhanced diffusivity as well as TiO₂-doped TZP, and the effect of GeO₂ on the tensile ductility in Y-TZP was investigated by high-temperature tensile test, and microstructure analysis.

II. Experimental Procedures

The chemical composition of the materials prepared in this study was ZrO₂-2.5 mol%Y₂O₃-1.0 mol%GeO₂

(TZP-1Ge). ZrO₂ powders (Tosoh Co. Ltd., TZ-2.5Y) were mixed with 1 mol% adding GeO₂ powders (Rare Metallic, 6N) by ball-milling for 24 h and dried in Ar atmosphere. Subsequently, the powders were uniaxially pressed under a pressure of 33 MPa and then cold-isostatically pressed (CIP) at 100 MPa. The green bodies of TZP-1Ge were sintered for 2 h in air at 1200°C. Some of the sintered bodies were further annealed in a temperature range of 1400–1500°C for a period of 0 to 20 h to examine the grain growth behavior or to control the grain size. Tensile test specimens with a gauge length of 13 mm and a cross sectional area of 2 mm × 2 mm were cut and ground from the sintered or annealed bodies. High-temperature tensile tests were conducted for TZP-1Ge in air at temperatures in the range of 1200–1550°C at an initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$ with a tensile machine (SHIMAZU AG-5000C). Microstructure analysis was carried out with a scanning electron microscope (SEM, JEOL JSM-5200) for the as sintered and annealed samples that were polished and thermally etched. The average grain size was measured directly from SEM micrographs by the linear intercept method.

III. Results

1. Behavior of high-temperature deformation in TZP-1Ge

To examine the superplastic behavior, high-temperature tensile tests for TZP-1Ge were conducted. The results are shown in Fig. 1(a) together with the data in 2.5Y-TZP (b) reported previously⁽⁶⁾. In TZP-1Ge, large elongations exceeding 100% are attained for temperatures greater than 1300°C as well as in 2.5Y-TZP under the same strain rate. Both of the materials deformed

[†] Graduate student, Tokyo University.

Fig. 1 Stress-strain curves in TZP-1Ge (a) and 2.5Y-TZP⁽⁶⁾ (b) in a temperature range of 1200–1550°C at an initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$. d_0 is the initial grain size.

uniformly and failed without necking. These results are rearranged in Fig. 2 in terms of elongation to failure as a function of testing temperature. TZP-1Ge exhibits larger tensile elongation compared with 2.5Y-TZP at every testing temperature and the addition of GeO₂ in 2.5Y-TZP is effective to improve the superplastic ductility in the testing temperature range. Another improvement in superplasticity for TZP-1Ge is the decrease in flow stress. Figure 3 shows the 10% flow stress for TZP-1Ge and 2.5Y-TZP. As one can see in the figure, both materials show similar tendencies in decreasing flow stress with increasing temperature, however the flow stresses of the two materials differ considerably. It means that the addition of GeO₂ is effective in decreasing the flow stress. We will discuss this effect in detail in the latter part of this article.

Furthermore, a relationship between flow stress and strain rate in TZP-1Ge was examined. Generally, flow stress of superplastic deformation in ceramics is sensitive to the change in average grain size as well as the change in testing temperature or strain rate. It is necessary that the grain size be stable during the test. The faster grain growth of TZP-1Ge prevents the usage of the as-sintered specimens for the testing. The grain growth behavior will be mentioned later. Thus, we used thermally treated specimens which were annealed at 1500°C for 2 h so that the effect of the grain growth would not be so significant

Fig. 2 Temperature dependence of nominal elongation to failure in TZP-1Ge and 2.5Y-TZP⁽⁶⁾ in a temperature range of 1200–1550°C at an initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$.

Fig. 3 Temperature dependence of flow stress at 10% deformation in TZP-1Ge and 2.5Y-TZP⁽⁶⁾ in a temperature range of 1200–1550°C at a strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$.

during the test. Figure 4 shows the relationship between flow stress and strain rate in TZP-1Ge for the temperature range of 1300–1500°C by the strain rate-change method. The strain rate sensitivity, m , of the material is estimated to be approximately 0.6 within the range of testing temperature and strain rate. This equability in m value indicates that the dominant deformation mechanism is the same for the temperature range and strain rate examined in this study.

2. Microstructure analysis

(1) Solubility of GeO₂ in 2.5Y-TZP

To estimate the solubility of GeO₂ in 2.5Y-TZP, XRD analysis was performed. It is important to know the solubility because a secondary phase can form in TZP if the amount of GeO₂ exceeds the solubility. In this case,

Fig. 4 A log-log plot of strain rate and flow stress in TZP-1Ge in a temperature range of 1300–1500°C.

the formation of a secondary phase would influence and complicate the superplastic behavior. Since there is no $\text{GeO}_2\text{--Y}_2\text{O}_3\text{--ZrO}_2$ phase diagram available, except for a study on 2Y-TZP doped with GeO_2 ⁽⁷⁾, we decided to compare XRD spectra of three samples with different GeO_2 compositions: TZP-1Ge, $\text{ZrO}_2\text{--}2.5\text{ mol}\%\text{Y}_2\text{O}_3\text{--}5.0\text{ mol}\%\text{GeO}_2$ (TZP-5Ge) and $\text{ZrO}_2\text{--}2.5\text{ mol}\%\text{Y}_2\text{O}_3\text{--}10\text{ mol}\%\text{GeO}_2$ (TZP-10Ge).

In the XRD profile of TZP-1Ge, only ZrO_2 peaks were observed. In TZP-5Ge and TZP-10Ge, on the other hand, several peaks were found, which were identified as ZrGeO_4 ⁽⁸⁾. Assuming that the intensity of each peak represents a volume fraction of the secondary phase, we can estimate the solubility of GeO_2 in 2.5Y-TZP to be about 4 mol% as shown in Fig. 5.

(2) Grain growth behavior in TZP-1Ge

Static grain growth behavior in TZP-1Ge was studied by SEM observation. Figure 6 is the grain size of the thermally treated body annealed in a temperature range of 1400–1500°C for 0–20 h. The initial grain size of TZP-1Ge was $0.37\text{ }\mu\text{m}$, which is smaller than that of 2.5Y-TZP because TZP-1Ge was sintered at 1200°C in contrast to 1450°C of 2.5Y-TZP. A quantitative estimation of grain growth rate, K , is difficult because the mechanism of grain growth in TZP is not yet understood well. Therefore, we assumed that the grain growth of TZP-1Ge is described by the following equation

$$d^n - d_0^n = Kt. \quad (1)$$

Since TZP-1Ge is found to be in the single phase field, it would be proper to use $n=2$ in the above equation as normal grain growth. This equation gives the curves in Fig. 6 at each temperature with an appropriate K value respectively. From the result, one can make an estimation of the activation energy for the grain growth (Q_{gg}) and pre-exponential term (K_0) in TZP-1Ge as $Q_{\text{gg}}=412$

Fig. 5 Comparison of XRD peak intensities in TZP-1Ge, TZP-5Ge and TZP-10Ge.

Fig. 6 Static grain growth behavior in TZP-1Ge annealed at 1400, 1450 and 1500°C for 0 to 20 h.

kJ/mol and $K_0=1\times 10^{11}\text{ }\mu\text{m}^2\cdot\text{h}^{-1}=2.8\times 10^{-5}\text{ m}^2\cdot\text{s}^{-1}$. One study reported 455 kJ/mol as the value of Q_{gg} in 2.5Y-TZP⁽⁵⁾, which is higher than that of TZP-1Ge.

It is well known that grain growth is accelerated during superplastic deformation, and it is sometimes called a strain enhanced or dynamic grain growth. Figure 7 shows the dynamic grain growth and the static grain growth in TZP-1Ge at 1400°C at an initial strain rate of $1.3\times 10^{-4}\text{ s}^{-1}$. Compared with the sluggish static grain growth, the dynamic grain growth is faster. One of the notable points in this figure is that the difference in grain size between dynamic growth and static growth increases with increasing strain. The other notable point is the grain growth during the early stage of deformation. The grain size of TZP-1Ge drastically changes from $0.38\text{ }\mu\text{m}$ to $0.48\text{ }\mu\text{m}$ during the initial 10% deformation while static grain growth shows no notable change. The dynamic grain growth becomes more slower after this period of time.

On the other hand, thermally treated TZP-1Ge speci-

Fig. 7 Dynamic and static grain growth behavior in TZP-1Ge at 1400°C at an initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$.

Fig. 8 Stress-strain curves of as-sintered TZP-1Ge (solid line) and annealed sample (broken line) tested at 1500°C at an initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$.

mens with larger initial grain size of $0.8 \mu\text{m}$ did not show the rapid growth. **Figure 8** is a comparison of two stress-strain curves. One curve is the as-sintered TZP-1Ge and the other is TZP-1Ge annealed at 1500°C for 4 h. The initial grain size of each specimen is about $0.4 \mu\text{m}$ for the as-sintered TZP-1Ge and about $0.8 \mu\text{m}$ for the annealed TZP-1Ge. The flow stress of as-sintered TZP-1Ge is lower than that of the annealed TZP-1Ge according to the difference in initial grain size. Consequently, the flow stress of the as-sintered TZP-1Ge increases gradually up to fracture while the flow stress of annealed TZP-1Ge remains relatively stable, which means relatively sluggish grain growth when compared to the curve of as-sintered TZP-1Ge. In addition, the difference in elongation to failure between the two specimens is not so large. The result seems to indicate that there may be a suitable range in grain size for superplastic deformation depending on the material and

Fig. 9 A log-log plot of 10% flow stress of TZP-1Ge and 2.5Y-TZP as a function of grain size at 1400 and 1500°C at a strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$.

testing condition. Further work is required to comprehend this phenomenon in terms of the mechanism of superplastic deformation.

3. Flow stress in TZP-1Ge

High-temperature deformations of metal and ceramic materials are generally described by the following equation

$$\dot{\epsilon} = A \frac{\sigma^n}{d^p} \exp\left(-\frac{Q}{RT}\right), \quad (2)$$

where $\dot{\epsilon}$ is strain rate, A is a constant depending on each material, n is the stress exponent, p is the grain size exponent, Q is the activation energy for deformation, R and T have the usual meaning. This equation is considered to hold for superplastic deformation. When comparing the flow stress in two materials, the same strain rate, temperature and grain size are required. Any difference in stress would be due to the activation energy Q and/or the constant A , where A contains the diffusion coefficient D_0 . In other words, the difference in stress in this case would represent the difference in diffusivity which dominates superplastic deformation in two materials.

Figure 9 is the plot of flow stress and grain size at 10% deformation obtained at 1400°C and 1500°C at a strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$. It is obvious that the flow stress of TZP-1Ge is much lower than that of 2.5Y-TZP at each temperature. Therefore, we conclude that the stress reduction in TZP-1Ge is not only from the decrease in initial grain size of TZP-1Ge, which leads to an apparent reduction in flow stress, but also enhanced diffusion due to the doping of GeO₂. Meanwhile, Fig. 9 gives 1.2 as the inclination of the line of TZP-1Ge, which is the value of the product m and p . Assuming that the m value of

TZP-1Ge is hardly affected by the grain size, one obtains a grain size exponent p of 2 for m equal to 0.6 from Fig. 4. This value of 2 is within the range of those reported in TZP⁽⁹⁾.

IV. Discussion

1. Enhancement of diffusivity in TZP-1Ge

It is well known that the major process of superplastic deformation in TZP is grain boundary sliding. As mentioned above, the addition of 1%Ge into TZP affects the activation energy for deformation, Q . The value of Q reported in TZP varies within a range of about 450–600 kJ/mol⁽¹⁰⁾⁽¹¹⁾. The dispersion in Q may result from the amount of impurities or testing method and condition⁽¹²⁾. We will use the value of 530 kJ/mol for Q in 2.5Y-TZP obtained in our previous study⁽¹³⁾ because the impurity level and the other factors are essentially the same in this study.

Figure 4 gives the activation energy of $Q=454$ kJ/mol at a flow stress of 10 MPa in TZP-1Ge, which is lower than the reported value of 530 kJ/mol for 2.5Y-TZP. The decrease in Q of TZP-1Ge supports the idea that an enhancement in diffusivity controlling superplastic deformation is the reason for the stress reduction in TZP-1Ge.

2. Analysis of tensile ductility in TZP-1Ge

The improvement in tensile ductility is due to the addition of GeO₂ into TZP shown in Fig. 2. To investigate the cause of this enhancement, the grain size at failure in TZP-1Ge was measured and compared with that in 2.5Y-TZP. **Figure 10** gives this comparison. Although the initial grain size of TZP-1Ge is smaller than that of 2.5Y-TZP, the grain size at failure in TZP-1Ge is larger than that in 2.5Y-TZP. It shows that the improved ductility in TZP-1Ge is related to the larger grain size. This result must be caused by the decrease in flow stress of TZP-1Ge.

Kondo *et al.* proposed an equation to describe the tensile ductility as a function of deformation temperature at certain conditions and parameters⁽⁵⁾⁽¹⁴⁾. The equation consists of two parts on the grain size. One part is the description of grain size at failure as follows

$$d_f = \frac{C}{\dot{\varepsilon}^{1/4}} \exp\left(\frac{Q_{\text{sup}}}{4RT}\right), \quad (3)$$

where d_f is the grain size at fracture, C is a material dependent constant, Q_{sup} is the activation energy for superplastic flow⁽¹⁴⁾. The second part is the description of grain growth during deformation given by

$$d = \left\{ d_0^2 + K_0 \exp\left(-\frac{Q_{\text{gg}}}{RT}\right) \frac{\varepsilon}{\dot{\varepsilon}} \right\}^{1/2} \exp(\alpha\varepsilon), \quad (4)$$

where d_0 is the initial grain size, K_0 is a constant, Q_{gg} is the activation energy for grain growth, ε is the true strain and α is a proportional constant⁽¹⁴⁾. The value of α for each material is estimated by the following equation,

Fig. 10 Comparison of grain size at fracture between TZP-1Ge and 2.5Y-TZP⁽⁶⁾ in a temperature range of 1400–1550°C at an initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$.

$$\ln \frac{d_D}{d_s} = \alpha \varepsilon \quad (5)$$

where d_D is the grain size for dynamic grain growth and d_s is that for static grain growth at a time, t .

At the time of failure, d should be replaced by d_f and ε by ε_f in eq. (4) where ε_f is the true strain at the time of failure. Therefore, it is possible to estimate the elongation to failure as a function of strain rate as well as temperature⁽¹⁴⁾, which is written as

$$\begin{aligned} & \frac{C}{\dot{\varepsilon}^{1/4}} \exp\left(-\frac{Q_{\text{sup}}}{4RT}\right) \\ &= \left\{ d_0^2 + K_0 \exp\left(-\frac{Q_{\text{gg}}}{RT}\right) \frac{\varepsilon_f}{\dot{\varepsilon}} \right\}^{1/2} \exp(\alpha\varepsilon_f). \end{aligned} \quad (6)$$

The solid curves in **Fig. 11** show the calculated lines of ductilities in 2.5Y-TZP and TZP-1Ge. Although the solid curve for 2.5Y-TZP in Fig. 11 describes the ductility of 2.5Y-TZP well, the solid curve for TZP-1Ge cannot describe the ductility of TZP-1Ge. All constants for 2.5Y-TZP used are those from Kondo *et al.*⁽⁵⁾ The values of Q_{sup} and K_0 for TZP-1Ge are $Q_{\text{sup}}=454$ kJ/mol and $K_0=2.8 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ obtained in this study. The value of α for TZP-1Ge is estimated to be 0.4 from the grain growth behavior in Fig. 7 by using eq. (5). Because it was reported about the constant C that the value of $1.1 \times 10^{-3} \text{ m} \cdot \text{s}^{-1/4}$ is the same for 2.5Y-TZP and TZP-5 wt%TiO₂⁽⁵⁾, the value was also applied to the calculation for the ductility of TZP-1Ge. However, the experimentally obtained ductility in TZP-1Ge is not expressed by the expected ductility calculated from the equation. This discrepancy is connected with the fact that the calculated d_f cannot express the experimentally obtained d_f for TZP-1Ge. It would indicate that the further consideration for the equation is required when applied to the superplastic behavior of TZP-1Ge. One of possibilities which may explain the difference is a change in C by the

Fig. 11 Estimation of elongation to failure for TZP-1Ge and 2.5Y-TZP⁽⁵⁾⁽⁶⁾.

GeO₂ addition. The other one is the change in grain boundary strength when the doped cations segregate at boundaries that is not taken into consideration in the equation. Further work is necessary to clarify these problems.

V. Conclusion

The superplastic behavior of GeO₂-doped TZP was studied by high-temperature tensile tests, X-ray diffraction analysis and scanning electron spectroscopy. The following conclusions were obtained.

- (1) The GeO₂ addition within the solid solubility of ZrO₂ reduces high temperature flow stress. This reduction is considered to be due to enhanced diffusivity in *t*-ZrO₂ caused by the GeO₂ addition.
- (2) Tensile ductility is improved at temperatures between 1300 and 1550°C by the addition of 1 mol%GeO₂

in 2.5Y-TZP. The improvement is related to the flow stress reduction due to GeO₂ addition.

(3) The previous model proposed by Kondo *et al.* could not be applied to explain the tensile ductility in TZP-1Ge. It would indicate that the further consideration for the equation is required when applied to the superplastic behavior of TZP-1Ge.

Acknowledgement

The authors would like to express their gratitude for the financial support of the Grant-in-Aid for Scientific Research on Priority Area "Innovation in Superplasticity" 08242102 and for Scientific Research B 09555208 from the Ministry of Education, Science and Culture, Japan.

REFERENCES

- (1) F. Wakai, S. Sakaguchi and Y. Matsuno: *Adv. Ceram. Mater.*, **1** (1986), 259-263.
- (2) T. G. Nieh and J. Wadsworth: *Acta Metall. Mater.*, **38** (1990), 1121-1133.
- (3) K. Kajihara, Y. Yoshizawa and T. Sakuma: *Scr. Metall. Mater.*, **28** (1993), 559-562.
- (4) Y. Yoshizawa and T. Sakuma: *Acta Metall. Mater.*, **11** (1992), 2943-2950.
- (5) T. Kondo, Y. Takigawa and T. Sakuma: *Mater. Sci. Eng.*, **A231** (1997), 163-169.
- (6) K. Tsurui and T. Sakuma: *Scr. Mater.*, **34** (1996), 443-447.
- (7) D. J. Kim, J. W. Jang, H. J. Jung, J. W. Huh and I. S. Yang: *J. Mater. Sci. Letters.*, **14** (1995), 1007-1009.
- (8) K. L. McCarthy: *JCPDS Grant-in-Aid Report*, (1982).
- (9) F. Wakai: *Tetsu-to-Hagane*, **75** (1989), 389-395.
- (10) T. G. Langdon, T. R. McNelly and H. C. Heikkinen (eds.): *Superplasticity in Aerospace II*, TMS, Warrendale, P A, (1990), p. 3.
- (11) A. H. Chokshi: *Mater. Sci. Eng.*, **A166** (1993), 119-133.
- (12) T. G. Nieh, C. M. McNelly and J. Wadsworth: *Scr. Metall.*, **22** (1988), 1297-1300.
- (13) K. Kajihara, Y. Yoshizawa and T. Sakuma: *Acta Metall. Mater.*, **43** (1995), 1235-1242.
- (14) T. Kondo, Y. Takigawa, Y. Ikuhara and T. Sakuma: *Mater. Trans., JIM*, **39** (1998), 1108-1114.