Doping Dependence of High Temperature Plastic Flow Behavior in TiO₂ and GeO₂-Doped Tetragonal ZrO₂ Polycrystals

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正方晶 ZrO₂ 多結晶体の高温変形における TiO₂ 及び GeO₂ 添加量依存性

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The doping dependence of high temperature plastic flow behavior in TiO₂-doped, GeO₂-doped and TiO₂ and GeO₂ co-doped tetragonal ZrO₂ polycrystal (TZP) was systematically examined at 1400°C in air under an initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$. The amount of dopant cations was in the range of 0.2–4 mol%. The flow stress in the TZP decreases with the increasing doping amount in TiO₂ and/or GeO₂-doped TZP, but levels off over a 3 mol% addition in the GeO₂-doped and TiO₂-GeO₂ co-doped TZP. The doping dependence of the flow stress in the TiO₂-GeO₂ co-doped TZP is close to that in the GeO₂-doped TZP rather than to that in the TiO₂-doped TZP; the flow stress in the GeO₂-doped and TiO₂-GeO₂ co-doped TZP is significantly lower than that in the TiO₂-doped TZP. The doped cations tend to segregate in the vicinity of the grain boundaries in TZP. The doping dependence of the flow stress is probably related to the amount of the grain boundary segregation of the dopant cations; the grain boundary segregation of the dopant cations is supposed to enhance the grain boundary atomic diffusion in the TZP, and hence the flow stress consequently decreases. On the other hand, elongation to failure in the TZP is highly improved by the TiO₂ and/or GeO₂ doping. The improved high temperature ductility of the TZP is attributed to the flow stress reduction due to the TiO₂ and/or GeO₂ doping.

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1. Introduction

Considerable interest has developed in recent decades about the high temperature plastic deformation of polycrystalline ceramics.^{1)–3)} In particular, since the superplastic deformation has been experimentally demonstrated,⁴⁾ the greater interest in the superplastic ceramics has occurred because a remarkable tensile ductility can be achieved even in the brittle materials. A significant number of studies on superplastic ceramics have been made, and a large tensile elongation to failure has been found in various ceramics and ceramic composites.^{5)–7)} Of the superplastic ceramics, the tetragonal ZrO₂ polycrystal (TZP) has been extensively studied because of its high temperature tensile ductility of more than 100% and its excellent mechanical properties.^{8)–11)} One of the reasons for its high tensile ductility is attributed to its grain size stability during high temperature deformation.¹⁰⁾

The mechanism of the superplastic flow has been discussed using a constitutive equation describing strain rate ($\dot{\epsilon}$)-flow stress (σ) relationship. It was originally demonstrated that a linear relationship in the $\log \dot{\epsilon}$ versus $\log \sigma$ plot has a single slope of about 2–3 in the TZP.^{8),9)} A more detailed examination revealed that the $\log$ - $\log$ plot of $\dot{\epsilon}$ vs. σ is not always given by a straight line even in a single material, but has a well-defined transition.^{7),12)} Various arguments have already been made to explain such a transition behavior in the $\log \dot{\epsilon}$ - $\log \sigma$ plot in TZP, and Jiménez-Melendo et al. reported that such a transition depends on the residual impurities with a critical level of 0.10 wt%.⁷⁾ However, no description has been given in previous papers as what types of impurities are responsible for the transient behavior and what the critical impurity level of 0.10 wt% means.

Our group has previously examined the doping effect on the superplastic flow in TZP.^{13),14)} Based on these results, the flow stress in the TZP strongly depended on type of doping cations. Among the various dopant cations, TiO₂ and/or GeO₂-doping is particularly effective to reduce the high temperature flow stress and to improve the tensile ductility.^{13)–15)} On the other hand, the doping dependence of the superplastic flow behavior has been recently investigated in the GeO₂-doped TZP.¹⁶⁾ The flow stress is drastically reduced by the 0.2–2 mol% GeO₂-doping, but is only slightly changed by more than a 3 mol% GeO₂-doping. These results indicate that the high temperature plastic flow behavior strongly depends not only on the type of dopant cations, but also on the doping amount. Therefore, it is necessary to investigate the doping dependence of the high temperature plastic flow behavior in various kinds of cation-doped TZPs. The present study aims to examine the GeO₂ and/or TiO₂ doping dependence of the high temperature plastic flow behavior in the TZP. The doping dependence was systematically investigated in the TiO₂ or GeO₂ singly-doped TZP as well as the TiO₂ and GeO₂ co-doped TZP with the doping amount of 0.2–4 mol%.

2. Experimental procedure

The materials used in this study were tetragonal ZrO₂ polycrystals (TZP), TiO₂ or GeO₂-doped TZP, and an equal amount of TiO₂ and GeO₂ co-doped TZP. The starting powders were tetragonal ZrO₂ powders containing 3 mol% Y₂O₃ (TZ3Y; Tosoh, Japan), titanium oxide (high-purity grade TiO₂; Sumitomo Osaka Cement, Co., Ltd.) and germanium oxide (purity > 99.999%, Rare Metallic). The TZP powders were mixed with 0.2–4 mol% TiO₂ and/or GeO₂ powders by

Table 1. Chemical Composition and Average Grain Size in the Undoped TZP and TiO₂ and/or GeO₂ Doped TZP Used in this Study

Specimen	Composition / mol%			Grain size / μm
	TZP	GeO ₂	TiO ₂	
TZP	100	0	0	0.38
TZP+0.2mol%TiO ₂	99.8	0	0.2	0.39
+1mol%TiO ₂	99	0	1	0.53
+2mol%TiO ₂	98	0	2	0.52
+4mol%TiO ₂	96	0	4	0.50
+0.2mol%GeO ₂	99.8	0.2	0	0.40
+0.5mol%GeO ₂	99.5	0.5	0	0.40
+1mol%GeO ₂	99	1	0	0.37
+2mol%GeO ₂	98	2	0	0.51
+3mol%GeO ₂	97	3	0	0.46
+4mol%GeO ₂	96	4	0	0.46
+0.25mol%(TiO ₂ -GeO ₂)	99.5	0.25	0.25	0.38
+0.5mol%(TiO ₂ -GeO ₂)	99	0.5	0.5	0.39
+1mol%(TiO ₂ -GeO ₂)	98	1	1	0.54
+1.5mol%(TiO ₂ -GeO ₂)	97	1.5	1.5	0.51
+2mol%(TiO ₂ -GeO ₂)	96	2	2	0.58

ball-milling for 24 h. The chemical compositions of the present materials are listed in **Table 1**. The total amount of dopant cations in the TiO₂-GeO₂ co-doped TZP is determined to be the same as that in the TiO₂ or GeO₂ singly-doped TZP for comparison with the TiO₂ or GeO₂-doping effect. The green compacts of the mixed powders were sintered at 1400°C for 2 h in air.

High temperature uniaxial tensile tests were carried out in air at a constant cross-head speed using an Instron-type testing machine with a resistance-heated furnace. The initial strain rate and temperature examined were $1.3 \times 10^{-4} \text{ s}^{-1}$ and 1400°C, respectively. The microstructures of the present materials were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The average grain size in the present materials was estimated by the linear intercept method using SEM photographs. The TEM specimens were prepared using standard techniques involving mechanical grinding to a thickness of 0.1 mm, dimpling to a thickness of 20 μm and ion beam milling to an electron transparency at about 4 kV. For further analysis of the grain boundaries in the TZP, high-resolution transmission electron microscopy (HRTEM) observations were performed using Hitachi H-9000NAR and Topcon 002BF field emission microscopes. An energy-dispersive X-ray spectroscopy (EDS) analysis was carried out with the Noran Voyager system attached to the Topcon microscope with the probe size of about 1 nm.

3. Results

A relative density of more than 99% and an average grain size of about 0.4 μm were obtained in the sintered materials. The average grain sizes of the present materials in the as-sintered condition are listed in Table 1. **Figure 1** shows an example of SEM images in an as-sintered (a) TZP, (b) 2 mol% TiO₂-doped TZP, (c) 2 mol% GeO₂-doped TZP and (d) 1 mol% TiO₂ and 1 mol% GeO₂ co-doped TZP. Fairly uniform and equiaxed grain structures were obtained in the present materials, and no dispersion of second phase particles was observed at least in the SEM images of the TiO₂ and/or GeO₂-doped TZP.

As previously reported, dopant cations tend to segregate along the grain boundaries in small amounts of the cation-doped TZP.^{14),16)–18)} **Figure 2** shows an HRTEM image of a grain boundary in 1 mol% TiO₂-doped TZP. The grain bound-

Fig. 1. Scanning electron microscopy images of (a) TZP, (b) 2 mol% TiO₂-doped TZP, (c) 2 mol% GeO₂-doped TZP and (d) 1 mol% TiO₂ and 1 mol% GeO₂ co-doped TZP in as-sintered state. **Fig. 2.** A high-resolution transmission electron microscopy image of a grain boundary in 1 mol% TiO₂-doped TZP.

dary is viewed at almost an edge-on condition. Distinct lattice images can be seen in the grains, and there is no second phase particle or amorphous layer along the grain boundary. The chemical composition at the grain boundary was examined by HRTEM-EDS analysis using a focused probe size of about 1 nm. **Figures 3(a)** and **(b)** show the typical EDS profiles taken from the grain boundary and the grain interior region, respectively, in the 1 mol% TiO₂-doped TZP. The analyzed points are indicated by the circles in Fig. 2. The intensity of the Ti⁴⁺ spectrum at the grain boundary is much higher than that of the grain interior. This result indicates that the Ti⁴⁺ cations segregate along the grain boundaries. Similar results

Fig. 3. An energy-dispersive X-ray spectroscopy profile obtained from (a) grain boundary and (b) grain interior region in 1 mol% TiO_2 -doped TZP with focused beam size of about 1 nm.

Fig. 4. Stress-strain curves in the TZP and TiO_2 -doped TZP at 1400°C and the initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$.

are also obtained in the GeO_2 -doped and TiO_2 - GeO_2 co-doped TZPs.^{16),17)}

Figures 4 and 5 are examples of the stress-strain curves of the TiO_2 -doped and GeO_2 -doped TZPs, respectively, under the initial strain rate of $1.310^{-4} \text{ s}^{-1}$ at 1400°C . The doping of the TiO_2 and GeO_2 effectively reduces the flow stress in the TZP; the flow stress in the 1 mol% GeO_2 -doped TZP is about one-third that in the TZP. The flow stress in the TiO_2 or GeO_2 -doped TZP decreased with the increasing total amount of dopant cations. On the other hand, elongation to failure of the TZP is increased by the TiO_2 or GeO_2 -doping. For instance, the 3 mol% GeO_2 -doped TZP exhibits an elongation to failure of about 450% under nominal strain, which is more than three times higher than that in the undoped TZP. The high tempera-

Fig. 5. Stress-strain curves in the TZP and GeO_2 -doped TZP at 1400°C and the initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$.

Fig. 6. Stress-strain curves in the TZP and TiO_2 - GeO_2 co-doped TZP at 1400°C and the initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$.

ture tensile ductility is fairly related to the doping amount; the higher doping amount allows the higher elongation to failure. However, the doping effect on the tensile ductility seems to level off over a 2 mol% doping of the GeO_2 -doped TZP; the stress-strain curve in the 3 mol% GeO_2 -doped TZP only slightly changes in comparison with that in the 2 mol% GeO_2 -doped TZP.

Figure 6 shows the stress-strain curves in the TiO_2 - GeO_2 co-doped TZP at an initial strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$ and 1400°C . The flow stress in TZP decreases, and the elongation to failure increases with the increasing amount of TiO_2 and GeO_2 -doping; in particular, the 2 mol% TiO_2 - GeO_2 co-doped TZP exhibits the lowest flow stress and the largest elongation to failure of 988%. The flow stress in the 1.5 mol% and 2 mol% TiO_2 - GeO_2 co-doped TZP increases in the latter stage of the deformation. The strain hardening is probably attributed to dynamic grain growth during the plastic flow.

4. Discussion

The mechanism of the superplastic flow in crystalline materials has been phenomenologically analyzed by the steady-state stress-strain behavior based on the constitutive equation,

Fig. 7. Flow stress versus total amount of TiO₂ and GeO₂ addition in the TiO₂ and/or GeO₂-doped TZP. The flow stress is normalized to the value for a grain size of 0.38 μm .

$$\dot{\epsilon} = A \sigma^n d^{-p} \exp(-Q/RT)$$

where $\dot{\epsilon}$ is the strain rate, σ is the flow stress, d is the grain size, n and p are the stress and grain size exponents, respectively, Q is the activation energy for plastic flow and RT is the gas constant times the absolute temperature.¹⁾ Since the flow stress depends on the grain size for a constant strain rate and temperature, the flow stress is usually defined as the value at the nominal strain of 10% in order to neglect the effect of the microstructural change such as the dynamic grain growth. Moreover, in order to compare the flow stress in the present materials, the flow stress should be converted to the value for a certain grain size. **Figure 7** shows a plot of the converted 10% flow stress versus the total amount of TiO₂ and GeO₂ in the present materials; the flow stress in the present materials is normalized to the value for a grain size of 0.38 μm using $p/n = 1$.¹³⁾ The flow stress in the TiO₂-doped TZP decreases with the increasing amount of the TiO₂ addition. The flow stresses in the GeO₂-doped and TiO₂-GeO₂ co-doped TZPs also decrease with the increasing amount of the dopant addition up to 2 mol%, but almost levels off over a 3 mol% addition. The doping dependence of the flow stress in the TiO₂-GeO₂ co-doped TZP is closer to that in the GeO₂-doped TZP compared to that in the hTiO₂-doped TZP; the flow stresses in the GeO₂-doped and TiO₂-GeO₂ co-doped TZPs are significantly lower than that in the TiO₂-doped TZP. This fact suggests that the flow stress in the TiO₂-GeO₂ co-doped TZP is influenced mainly by the GeO₂-doping. The sluggish change in the flow stress in the TiO₂-doped TZP is probably related to the solid solubility of TiO₂ in the TZP which will be discussed later.

The doping effect on the flow stress must be attributed to the grain boundary segregation of the dopant cations. In our recent study, the Ge⁴⁺ cation content at the grain boundaries and the grain interior regions has been investigated in the 0.2–3 mol% GeO₂-doped TZP by HRTEM-EDS analysis using a focused beam size of about 1 nm.¹⁶⁾ Based on the results, the Ge⁴⁺ content at the grain boundaries increases with the increasing amount of GeO₂ addition, but levels off over a 2 mol% GeO₂ addition. The doping dependence of the Ge⁴⁺ content at the grain boundaries is similar to that of the flow stress in the GeO₂-doped TZP. **Figure 8** shows the reduc-

Fig. 8. Flow stress reduction in TZP versus atomic content of Ge⁴⁺ cation at grain boundaries in the 0.2–3 mol% GeO₂-doped TZP. The Ge⁴⁺ content is an average of the estimated values at eight grain boundaries in each material.¹⁶⁾

tion in the flow stress versus the atomic content of the Ge⁴⁺ cation at the grain boundaries in the 0.2–3 mol% GeO₂-doped TZP. The flow stress in Fig. 8 is the converted value for the grain size of 0.38 μm , and the flow stress reduction is defined as the flow stress in the TZP minus that in the GeO₂-doped TZP. The atomic content of Ge⁴⁺ is an average of the estimated values at eight grain boundaries in each material. The flow stress reduction in the GeO₂-doped TZP is linearly related to the Ge⁴⁺ content at the grain boundaries. Therefore, one can conclude that the flow stress in the TZP is dominated mainly by the chemical composition at the grain boundaries. On the other hand, the rate-controlling mechanism for the superplastic flow in the TZP is not well understood; the accommodation process for the superplastic flow is usually explained from either the grain boundary diffusion¹⁹⁾ or the lattice diffusion.^{7),12)} However, the present results indicate that the grain boundary's chemical composition significantly affects the plastic flow behavior in the TZP. TiO₂ or GeO₂-doping is supposed to enhance the grain boundary atomic diffusion as an easy accommodation process for the superplastic flow, and consequently, to decrease the flow stress in the TZP.

It has been confirmed that the grain boundary segregation of cations is not a special phenomenon in the TiO₂ and/or GeO₂-doped TZP, but also occurs in other kinds of cation-doped TZPs.^{16)–18),20)} McLean has proposed the equilibrium grain boundary solute segregation isotherm in metals:

$$C_{\text{gb}} = C_0 \exp(\Delta G_{\text{seg}}/RT) / \{1 + C_0 \exp(\Delta G_{\text{seg}}/RT)\}$$

where C_{gb} is the solute concentration at the grain boundary in equilibrium with the bulk solute concentration, C_0 , and ΔG_{seg} is the change in the internal energy on the segregation or the segregation energy.²¹⁾ This relationship indicates that the grain boundary segregation is proportional to the bulk solute content at a constant temperature. The doping dependence of the grain boundary segregation amount in the cation-doped TZP has only been experimentally investigated in the GeO₂-doped TZP.¹⁵⁾ However, the grain boundary segregation amount is probably related to their solid solubility limit in the TZP; the amount of the dopant cation segregation must increase with the increasing dopant cation addition, but levels off near the solubility limit in the matrix. The solid solubility limit of the TiO₂ and/or GeO₂ in 3 mol% Y₂O₃-stabilized TZP has not yet been examined, but the solubility limit of TiO₂ in pure ZrO₂

Fig. 9. A logarithmic plot of elongation to failure versus flow stress in TZP and the TiO_2 and/or GeO_2 -doped TZP.

was about 16 mol% at 1400°C ,²²⁾ and that of GeO_2 in the 2 mol% Y_2O_3 -stabilized TZP was reported to be about 4 mol% at 1350°C .²³⁾ The solubility of TiO_2 or GeO_2 in the 3 mol% Y_2O_3 -stabilized TZP will not be very different from the reported values. Based on the assumption that the flow stress reduction in the TZP is attributed to the cation grain boundary segregation, the flow stress reduction in the TiO_2 and/or GeO_2 -doped TZP is consistent with the above speculation about the doping dependence of the grain boundary segregation. The sluggish change of the flow stress in TiO_2 can be explained by the relatively high solid solubility limit of TiO_2 in ZrO_2 ; the TiO_2 -doping effect on the flow stress will be saturated at a doping level greater than 4 mol%.

It has been pointed out that the superplastic elongation to failure ϵ_f in ceramics is well described by the Zener-Hollomon (ZH) parameter of $\dot{\epsilon} \exp(Q/RT)$.²⁴⁾ Since the ZH parameter is proportional to the flow stress for a constant grain size, the above description indicates that a lower flow stress provides a greater elongation to failure. This elongation-stress rule is satisfied over fairly wide temperature and strain rate ranges.²⁴⁾ Figure 9 shows a logarithmic plot of the elongation to failure versus the converted flow stress in the present materials; the flow stress in the present materials is converted to the value for a grain size of $0.38 \mu\text{m}$. In Fig. 9, the data in the TZP obtained at 1300°C and 1500°C are also plotted for comparison.²⁰⁾ The slope of the line in Fig. 9 has the theoretical value of -0.66 .²⁴⁾ The elongation to failure roughly tends to increase with the decreasing flow stress, though the data are slightly scattered. The improved high temperature ductility of the TZP is attributed to the flow stress reduction due to the TiO_2 and/or GeO_2 doping.

Concerning the mechanism of the doping effect on the grain boundary atomic diffusion, it must be reasonable to assume that a change in the chemical bonding state due to the dopant cation segregation affects the grain boundary diffusion in the TZP; it has been recently reported that the grain boundary diffusion coefficient in the 0.1 mol% cation-doped polycrystalline Al_2O_3 well correlated with its ionicity.²⁵⁾ In order to examine the change in the chemical bonding state in the TiO_2 and/or GeO_2 -doped TZP, a first-principle molecular orbital calculation was recently performed¹⁵⁾ by self-consistently solving the Hartree-Fock-Slater equations using a discrete-vari-

Fig. 10. Normalized flow stress in the 2 mol% TiO_2 or GeO_2 -doped TZP and the 1 mol% TiO_2 - GeO_2 co-doped TZP versus an average value of products of net charges in neighboring cations and oxygen anions obtained by molecular orbital calculations. The model cluster of the TZP used for the calculations is inserted in this figure.

tional (DV)- $X\alpha$ method developed by Adachi et al.²⁶⁾ The detailed calculation procedures are described elsewhere.¹⁵⁾ The model cluster for the Y_2O_3 -stabilized TZP used in the molecular orbital calculations was $[\text{Zr}_{18}\text{Y}_4\text{O}_{86}]^{-88}$, and one Ti^{4+} cation and/or one Ge^{4+} cation are substituted at the Zr^{4+} cation sites as a first approximation; it is still difficult to precisely define the configuration of the dopant cations and vacancies in the various types of grain boundaries. From the Mulliken population analysis, we can obtain information about the chemical bonding state such as the net charge for each atom, which corresponds to the effective ionic charge for each atom.²⁶⁾ Figure 10 shows the normalized flow stress for the grain size of $0.38 \mu\text{m}$ in the 2 mol% TiO_2 or GeO_2 -doped TZP and the 1 mol% TiO_2 - GeO_2 co-doped TZP versus the average value of products of the net charges in the neighboring cations and oxygen anions. The flow stress decreases with the increasing net charge products. Since the products of the net charges are supposed to correspond with Coulomb's attractive force between the cations and anions, the calculations suggest that the grain boundary segregation of the Ti^{4+} and Ge^{4+} cations reduces the ionic bonding strength in the vicinity of the grain boundaries. The grain boundary atomic diffusion in the TZP must be enhanced by a reduction in the ionic bond strength, and the flow stress consequently decreases in the TiO_2 and/or GeO_2 doped TZP.

The present results indicate that the TiO_2 and/or GeO_2 doping effect of the high temperature plastic flow behavior in the TZP is attributed to the grain boundary segregation of the dopant cations, and the reduced flow stress is probably related to the ionic bonding state in the cation-doped TZP. However, the present study is still a preliminary step toward the grain boundary atomistic structure analysis. Further quantitative investigations on the segregation behavior and chemical bonding state are necessary to elucidate the doping effect on the high temperature plastic flow behavior in the superplastic TZP.

5. Conclusions

The TiO_2 and/or GeO_2 doping dependence of the high temperature plastic flow behavior in the TZP was systematically investigated at 1400°C with the doping amount in the range of 0.2–4 mol%. The flow stress in the TZP decreases with the increasing doping amount, but the flow stress reduction levels off over a 3 mol% GeO_2 -doping or TiO_2 - GeO_2 co-doping. The TiO_2 - GeO_2 co-doping dependence of the flow stress seems to be affected by the GeO_2 -doping effect; the flow stress in the GeO_2 -doped and TiO_2 - GeO_2 co-doped TZP is significantly lower than that in the TiO_2 -doped TZP. The doping dependence of the flow stress is attributed to the grain boundary segregation of the dopant cations. On the other hand, the elongation to failure in the TZP is highly improved by the TiO_2 and/or GeO_2 doping, and the improved high temperature ductility in the TZP is roughly related to the flow stress reduction due to TiO_2 and/or GeO_2 doping. The first-principle molecular orbital calculations suggest that the ionic bonding state affects the atomic diffusion in the TZP; the reduction in the ionicity due to the grain boundary segregation is supposed to enhance the grain boundary atomic diffusion in the TZP, and the flow stress consequently decreases.

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