High Temperature Grain Boundary Plasticity in Ceramics

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Superplasticity in fine-grained materials has been generally analyzed on the basis of their experimental strain rate-flow stress relationship. The phenomenological analysis based on a constitutive equation is effective for understanding the overall flow and fracture behavior and to speculate on the rate-controlling mechanism of superplastic flow. However, it has been recently pointed out that the high temperature superplastic flow and failure in ceramics is significantly influenced by the atomic structure and chemistry of grain boundary. Such phenomenon cannot be explained based on the classical phenomenological analysis. Our research group has therefore proposed to establish a new research field, grain boundary plasticity, to describe the superplastic deformation related to the grain boundary quantum structure. This paper aims to point out the importance of the quantum structure analysis of the grain boundary to understand the high temperature plasticity in ceramics.

Keywords: superplasticity, grain boundary, tetragonal zirconia polycrystal (TZP), alumina

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1. Introduction

Considerable interests have developed in recent decades regarding the high temperature plastic flow of polycrystalline ceramics.¹⁻³ In particular, special interests in superplastic ceramics have arisen since superplastic deformation in a tensile manner was experimentally discovered.⁴ Superplastic bulging,⁵ forging⁶⁻⁷ and joining⁸ have been demonstrated in zirconia- and alumina-base materials, and a large tensile elongation to failure has been achieved in various ceramics and ceramic composites.⁹⁻¹¹ For instance, an elongation of 800% was obtained in TZP at 1550°C at the strain rate of 8.3 × 10⁻⁵ s⁻¹,¹² and 1038% in SiO₂-doped TZP at 1400°C at the strain rate of 1.3 × 10⁻⁴ s⁻¹.¹³ More recently, the maximum elongation to failure of more than 2500% was achieved in a ZrO₂-Al₂O₃-spinel composite.¹⁴

Of the superplastic ceramics, fine-grained, yttria-stabilized tetragonal ZrO₂ polycrystals (Y-TZP) have been extensively studied because of their excellent mechanical properties.¹³⁻¹⁵⁻¹⁷ One of the reasons for the high tensile ductility of TZP is attributed to its grain size stability during high temperature deformation.¹⁸ The high temperature flow stress and strain rate relationship in Y-TZP ceramics has been experimentally examined and phenomenologically analyzed by many research groups. The required conditions for the microstructures and processing to attain superplasticity have also been discussed based on the phenomenological analysis.¹⁹⁻²²

More recently, it has been reported that the superplastic stress-strain rate behavior in TZP is sensitively affected by residual impurities.¹⁷⁻²⁰ As pointed out later, the effect of a small amount of impurities is closely related to the atomic structure and chemistry of grain boundary. In addition, the analysis of the superplastic flow caused by grain boundary sliding or diffusion has been remarkably advanced in recent years through an atomistic analysis or electronic structure analysis. Our research group has proposed a new research field, grain boundary plasticity, to describe the high temperature plastic flow and failure based on the grain boundary atomic structure and chemical bonding state, namely grain boundary quantum structure.²⁷ This is not a special case in the study of high temperature plastic flow or failure, but a very microscopic approach has currently been made to understand the various well-known phenomena caused by grain boundary segregation in metallic systems.²⁸

The present paper aims to briefly review previous phenomenological analyses of the superplastic flow behavior in TZP ceramics and to describe how an atomistic or electronic structure analysis can effectively extend the limitation of the classical phenomenological approach. This type of analysis from the viewpoint of the grain boundary plasticity will become more important in the various fields of materials science.

2. Phenomenological Analysis of Superplasticity

Superplastic behavior in ceramics is generally investigated using a phenomenological analysis, which has been originally developed for high temperature creep or superplasticity in metals and alloys. A semi-empirical relationship between the strain rate and steady-state flow stress, namely the constitutive equation, is given by the following constitutive equation.¹₂⁹

\[ \dot{\varepsilon} = A \sigma^n d^{-p} \exp(-Q/RT) \]  

(1)

where \( \dot{\varepsilon} \) is the strain rate, \( A \) is the material constant, \( \sigma \) is the steady-state flow stress, \( d \) is the grain size, \( Q \) is the activation energy for superplastic flow, \( RT \) is the gas constant times the absolute temperature, and \( n \) and \( p \) are the stress exponent (inverse strain rate sensitivity) and grain size exponent, respectively. On the basis of eq. (1), the deformation mechanism has been discussed on the basis of the three parameters, i.e., the stress exponent, grain size exponent and activation energy. In addition, analyses of the high temperature fracture and nucleation and growth of cavitation are based on the phenomenological analysis.¹₉,₃₀,₃¹ The phenomenological analysis is significant for understanding the overall flow stress-strain rate relationship and to speculate on the deformation mechanism from the viewpoint of application. A great deal of knowledge on the high temperature flow and fracture behavior from this relationship has been obtained.
Figure 1 shows a schematic plot of the logarithmic relationship between the strain rate and flow stress in Y-TZP specimens. This plot was developed by Domínguez-Rodríguez’s group. It has been pointed out by many research groups that the logarithmic plot of the strain rate-stress relationship exhibits different domains of values for $n$ and $Q$. At very low stresses, the superplastic flow takes place by a diffusional process with $n$ and $Q$ values of around 1 and 450 kJ/mol, respectively. The values of $n$ and $Q$ increase with the increasing flow stress; the value of $n$ between 3 and 5 and value of $Q$ of about 700 kJ/mol has been reported in the intermediate stress level. At higher stresses, the $n$ and $Q$ values become 2 and 450 kJ/mol, respectively.

Several interpretations have been previously proposed to explain the transition in the deformation parameters. For instance, according to the analysis by Domínguez-Rodríguez’s group, the superplastic flow is rate-controlled by grain boundary sliding accommodated by lattice diffusion; the increased stress exponent in the intermediate flow stresses results from threshold stress of the grain boundary sliding, and Nabarro-Herring diffusional creep occurs at very low stresses. On the other hand, other interpretations, such as the interface reaction-controlled diffusional process and dislocation activity-involved grain boundary sliding process, have been proposed by other research groups. The discrepancy in the interpretations is probably attributed to the fact that different physical models for superplastic deformation often predict the same deformation parameters. It should be noted that it is still difficult to experimentally determine the steady-state flow stress, because the microstructure e.g. an average grain size continuously changes during high temperature deformation. In addition, the constitutive equation cannot provide any description of the atomic process for superplastic flow, since physical meaning of the deformation parameters remains unclear. This must be one of the limitations of the classical phenomenological analysis.

Another important point is in the well-known fact that the strain rate-flow stress relationship in TZP is affected by impurities. Figure 2 shows a summary of the logarithmic plot of the strain rate-stress relationship of the high- and low-purity Y-TZP. In this plot, the previous data for the 2–3 mol% $\text{Y}_2\text{O}_3$-stabilized TZP with the grain size of 0.3–0.4 $\mu$m were compiled. The high-purity samples contained a total impurity content of less than 0.1 mass%, whereas the low-purity materials contained more than 0.1 mass% of SiO$_2$ as an impurity. The high-purity TZP exhibits a sigmoidal stress-strain rate relationship with the $n$ value in the range from 1 to 5, as schematically shown in Fig. 1. In contrast, the data in the low-purity TZPs exhibit a deviation from the sigmoidal relationship in the high-purity TZP; the sigmoidal behavior becomes less-pronounced, and the strain rate is higher than that of the high-purity TZPs in the intermediate and low flow stress levels. Such a deviation due to an impurity level greater than 0.1 mass% has been reported by other research groups. However, the origin of the impurity effect on the transient behavior and the means of the critical impurity level of 0.1 mass% have not yet been clarified. These problems cannot be solved by a phenomenological approach.

In contrast to the classical analysis, our group is trying to establish another approach for obtaining a physical description of the high temperature superplasticity in ceramics. The trial is stimulated by experimental results that the superplastic flow in oxide ceramics strongly depends on the type of doped cations and doping amounts.

3. New Approach–Doping Effect on Superplasticity in Ceramics

3.1 Doping effect on superplastic flow stress in TZP

Figure 3 shows the stress-strain curves for various kinds of cation-doped TZPs at 1400°C and an initial strain rate of $1.3 \times 10^{-4}$ s$^{-1}$. The doping amount is 0.2 mol% for each
sample. The flow stress and tensile ductility depend on the type of doped cation; for instance, the Al$^{3+}$ or Ge$^{4+}$ cation-doping is effective for decreasing the flow stress and increasing the elongation to failure, while Ba$^{2+}$-doping increases the flow stress and decreases the tensile ductility. High-resolution transmission electron microscopy (HRTEM) observations and a nano-probe energy-dispersive X-ray spectroscopy (EDS) analysis revealed that a small amount of doped cations tend to segregate along the grain boundary. The result in Fig. 3 suggests that the grain boundary chemistry significantly influences the grain boundary sliding and/or grain boundary diffusion in the TZP.

Figure 4 shows the doping dependence of GeO$_2$ on the superplastic flow behavior in Y-TZP at 1400°C and the initial strain rate of $1.3 \times 10^{-4}$ s$^{-1}$. The doping amount was in the range from 0.2 to 3 mol%. The flow stress and elongation to failure are sensitively affected by the small amount of GeO$_2$-doping; the flow stress decreases, and the elongation to failure increases with the increasing doping amount. The 2 mol% GeO$_2$-doped TZP exhibits one-third of the flow stress in the TZP and the elongation to failure of more than 400%. However, the 3 mol% GeO$_2$-doping slightly changes the superplastic behavior in comparison to the 2 mol%-doping.

Figure 5 shows the atomic composition of Ge cations at the grain boundary and grain interior as a function of the total amount of Ge$^{4+}$ addition in the TZP. The chemical composition was measured by a nano-probe EDS technique. The Ge composition at the grain boundary is higher than that in the grain interior for the examined additive amount. This fact indicates that the Ge cations segregate along the grain boundary in the TZP. The Ge composition at the grain boundary levels off beyond the total additive amount of 2 mol%, while the Ge composition in the grain interior linearly increases with the increasing total additive amount. The leveling-off behavior of the segregation is similar to that of the doping dependence of the flow behavior in the Ge-doped TZP. Figure 6 shows a plot of the reduction in the flow stress versus the Ge$^{4+}$ cation content at the grain boundary in the Ge-doped TZP. The change in the flow stress correlates well with the Ge$^{4+}$ composition at the grain boundary in the TZP. This fact indicates that the chemical composition at the grain boundary is closely related to the superplastic flow in the TZP.

Our group has recently examined the change in the chemical bonding state due to cation doping by a first-
principle molecular orbital calculation through a discrete-variational (DV)-Xα method. Based on the molecular orbital calculations, the bond overlap population (BOP) between atoms and net charge (NC) for each atom are obtained; the values of BOP and NC correspond to the covalency between atoms and effective ionic charge for each atom, respectively. It has been found that the doping effect on the flow stress shows a good correlation with the net charge value. Figure 7 shows the flow stress at the nominal strain of 10% in the 0.2 mol% cation-doped TZP versus the net charge value of oxygen anion. The model cluster of TZP, [Zr$_{18}$Y$_4$O$_{86}$]$_{C_{08}}$, which was used for the molecular orbital calculation, is inserted in this figure. The flow stress decreases with the increasing net charge value of the oxygen anion. In other words, the higher ionicity around the oxygen anion produces a higher flow stress. Because the Coulomb attractive force between the anion and cation is proportional to the effective ionic charge of the ions, the increased ionicity must suppress the atomic diffusion and accordingly increase the flow stress. The result in Fig. 7 also indicates that the chemical bonding state in the vicinity of the grain boundary segregated with the doped cations plays a key role in the superplastic flow in TZP.

3.2 Doping effect on high temperature tensile ductility in SiO$_2$-doped TZP

The addition of the SiO$_2$ glass phase to the TZP decreases the flow stress, and increases the elongation to failure in TZP ceramics. Figure 8 shows five kinds of SiO$_2$-doped TZPs that failed at 1400°C and the initial strain rate of 1.3 × 10$^{-4}$ s$^{-1}$. The amount of doped cations in the SiO$_2$ phase is 2 mass%, that is, the composition of the doped cation is only 1000 ppm for the TZP material, but the tensile ductility depends on the type of doped cations. For instance, the elongation to failure reaches 1100% for the nominal strain in the TZP-undoped SiO$_2$, while the elongation is only 38% in the TZP-(SiO$_2$-2 mass%Li$_2$O).

An HRTEM-nano probe EDS analysis confirmed that the doped cations tend to segregate along the grain boundary. Figure 9 shows a plot of the chemical composition ratio (Y/Zr, Si/Zr or Al/Zr) in TZP-5 mass%SiO$_2$ and TZP-5 mass%(SiO$_2$-2 mass%Al$_2$O$_3$) as a function of the distance from the grain boundary.

Fig. 7 Flow stress at the nominal strain of 10% in the 0.2 mol% cation-doped TZP versus net charge value of oxygen anion obtained by molecular orbital calculations. The model cluster of the TZP used for the calculations is inserted in this figure.

Fig. 8 Five kinds of SiO$_2$-doped TZPs that failed at 1400°C and the initial strain rate of 1.3 × 10$^{-4}$ s$^{-1}$.

Fig. 9 A plot of the chemical composition ratio (Y/Zr, Si/Zr or Al/Zr) in TZP-5 mass%SiO$_2$ and TZP-5 mass%(SiO$_2$-2 mass%Al$_2$O$_3$) as a function of the distance from the grain boundary.
cations, such as Al\(^{3+}\), should form oxygen anions in order to maintain electric neutrality in the TZP. Since high temperature fracture in the superplastic TZP takes place by intergranular failure, the elongation to failure must be closely related to the change in the chemical bonding state in the vicinity of the grain boundary.

It should be noted that the tensile ductility decreases with the decreasing atomic valence of the doped cations; Si and Zr are quadra-valent cations, while Li, Mg and Al take +1, +2 and +3 valences, respectively. The order of the elongation to failure is in the same order of the cations’ valence. This result suggests that the tensile ductility is related to the dangling-bond state in the vicinity of the grain boundary. It has been found that the tensile ductility correlates well with the BOP value.\(^{51-53}\) Figure 10 shows a plot of the elongation to failure in several kinds of cation-doped TZP and TZP-SiO\(_2\) systems versus the total value of bond overlap populations in the TZP model clusters.\(^{51}\) The elongation to failure increases with the increasing BOP value. For instance, the Si\(^{4+}\) or Ge\(^{4+}\) cation increases covalency between the cation and oxygen anion, and the increased covalent bonds should improve the resistance against intergranular failure. On the other hand, Mg\(^{2+}\) decreases the BOP value, and the tensile ductility decreases accordingly.

The results on the doping effect indicate that the superplastic flow and failure in ceramics is significantly influenced by the atomic structure and chemistry of the grain boundary. Our group has accordingly proposed the new research concept.\(^{27}\) In contrast to the classical phenomenological analysis, our new approach for the grain boundary plasticity aims to analyze the superplasticity in ceramics based on the grain boundary quantum structure. HRTEM observation and atomistic analysis techniques such as EDS, electron energy-loss spectroscopy (EELS)\(^{49}\) and X-ray absorption fine structure (XAFS)\(^{54}\) are powerful methods for microstructural investigation on grain boundary. In addition to the experimental study, theoretical approach such as an \textit{ab initio} molecular orbital calculation must be necessary in elucidation of superplasticity through the grain boundary plasticity. The present analysis regarding the doping effect on the superplasticity is still a preliminary step toward the grain boundary plasticity, but demonstrates the effectiveness of the new research concept.

4. Toward Designing of Grain Boundary Quantum Structure in Ceramics

The grain boundary plasticity includes not only the superplastic flow and failure, but also general high temperature plasticity of the polycrystalline ceramics. In fact, the doping effect is not a special case in superplasticity, but also observed in high temperature creep deformation in ceramics. For instance, high temperature creep resistance in Al\(_2\)O\(_3\) is highly improved by grain boundary segregation of certain kinds of cations. Figure 11 shows the creep curves in undoped and cation-doped polycrystalline Al\(_2\)O\(_3\) at 1250°C and an applied stress of 50 MPa.\(^{52}\) The doping amount was 0.1 mol%, but the creep deformation is highly suppressed by Zr\(^{4+}\) and Lu\(^{3+}\) doping, while the creep rate is slightly accelerated by Ti\(^{4+}\)-doping. Such a significant doping effect also results from the grain boundary segregation of the doped cations.\(^{55,56}\) In addition, it has been found that the doping effect on the creep rate shows a high correlation with the NC values in Al\(_2\)O\(_3\).\(^{55,56}\) Since the high temperature creep in polycrystalline Al\(_2\)O\(_3\) is rate-controlled by the grain boundary diffusion process,\(^{57}\) the correlation between the creep rate and ionicity corresponds to the result in Fig. 7.

Another remarkable phenomenon related to the grain boundary plasticity is the co-doping effect. Figure 12 shows the creep rate under 50 MPa at 1250°C in polycrystalline Al\(_2\)O\(_3\) doped with two kinds of cations, namely the co-doped Al\(_2\)O\(_3\).\(^{58}\) The doping amount was 0.1 mol% for each dopant cation. The co-doping effect in several samples is non-additive; for instance, the Zr\(^{4+}\) and Y\(^{3+}\) co-doped Al\(_2\)O\(_3\) exhibits a lower creep rate than the Zr\(^{4+}\) or Y\(^{3+}\) cation singly-doped Al\(_2\)O\(_3\), whereas the Mg\(^{2+}\) and Sr\(^{2+}\) co-doped Al\(_2\)O\(_3\)
shows an intermediate creep rate between the Mg\(^{2+}\)-doped and Sr\(^{2+}\)-doped Al\(_2\)O\(_3\). This result suggests that the origin of the co-doping effect on the high temperature creep is closely related to the interaction between the co-doped cations. In other words, it is possible that the co-doping effect will provide surprising characteristics, which cannot be explained solely by single cation-doping.

The origin of the significant co-doping effect has not yet been clarified, but the new atomistic approach can probably contribute to the understanding of the origin of the co-doping effect. Our group has examined the chemical bonding state in cation-doped or cations co-doped Al\(_2\)O\(_3\) based on the Al\(_2\)O\(_3\) model cluster. Figure 13 shows a plot of the creep rate in the cation-doped and cations co-doped Al\(_2\)O\(_3\) versus the net charge value of the oxygen anion.\(^{58}\) The model cluster of Al\(_2\)O\(_3\) ([Al\(_{14}\)O\(_{45}\)]\(^{48}\) \(^{-}\)doped Al\(_2\)O\(_3\)) is inserted in this figure. The creep rate correlates well with the NC value of the oxygen anion. This result indicates that the creep rate is closely related to the ionicity.

The co-doping effect is a typical example of the dominant influence of the grain boundary quantum structure on the high temperature plasticity in ceramics. The result in Figs. 12 and 13 also indicate that the controlling of the grain boundary quantum structure through the cation-doping will be an effective method for development of high-performance ceramics for high temperature use. It should be noted that the controlling of the grain boundary quantum structure is essentially different from the common grain boundary engineering of ceramics. The common grain boundary engineering in ceramics usually refers to chemical composition-controlling and/or crystallization of grain boundary amorphous phase. On the other hand, the controlling of the grain boundary quantum structure means the designing of atomic structure and interatomic interaction of grain boundary. The designing of grain boundary quantum structure will be of importance for fabricating high-performance ceramics in the near future, because the grain boundary structure often influences not only the superplasticity but also other matter transport phenomena such as sintering and ionic conduction.\(^{59}\) In fact, the research and development of nanometer or sub-nanometer structure-controlled ceramics have been internationally started in recent years, and the importance of the grain boundary quantum structure is rapidly growing. For instance, the specific area research project of the Ministry of Education, Culture, Sports, Science and Technology, Japan, “Nano Materials Science for Atomic-scale Modification” was started in 2007. This project aims to develop new functional materials by controlling the atomic and electronic structures in a localized, nanometer-scale area such as the grain boundary and surface of a material. This kind of approach is still challenging, almost unprecedented worldwide, but recent advancements in observation instruments and theoretical calculations will allow the atomic-scale approach. We hope the grain boundary plasticity concept will provide a potential breakthrough to structural and functional ceramics in the near future.

5. Concluding Remarks

The common phenomenological analysis based on the constitutive equation is significant to know the overall superplastic flow and fracture behavior, but often meets difficulties to understand the atomistic process. The doping effect on the superplasticity in TZP ceramics is one of the typical examples of requirement of a new atomistic approach. The HRTEM-nano probe EDS analyses and molecular orbital calculations indicate that the high temperature plasticity in ceramics is dominantly influenced by the chemical bonding state in the grain boundaries. In contrast to the classical analysis, we have proposed the grain boundary plasticity as a new research field based on the grain boundary quantum structure. Based on the grain boundary plasticity, we have also proposed the designing of the grain boundary quantum structure for fabricating high-performance ceramics. The grain boundary plasticity concept is essentially different from the phenomenological approach and common meaning of the grain boundary engineering in ceramics. The grain boundary plasticity concept will provide a potential breakthrough to research and development of ceramics in the near future.
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