Dynamics of Grain Boundary Network in Ceramics Superplasticity

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A ceramic material can be elongated extensively in tension above approximately half the absolute melting point provided it has a fine (\(<1\,\mu\text{m}\) diameter) equiaxed grain size that is stable during deformation. The discovery of superplasticity in ZrO$_2$-based ceramics triggered numerous research activities on ceramics superplasticity, because of potential applications to superplastic forming. Micrograins move past one another by grain boundary sliding during deformation. The analysis of grain boundary dynamics provides insight on the role of grain boundary in superplasticity and grain growth. Here, we review the current knowledge on ceramics superplasticity with a focus on how the grain boundary affects deformation behavior.

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1. Introduction

Superplasticity is phenomenologically defined as the ability of a polycrystalline material to exhibit extraordinarily large elongation at elevated temperatures and at relatively low stresses. It is a property found in many metals, alloys, intermetallics and ceramics when the grain size is very small: less than ten micrometers for metals and less than one micrometer for ceramics.\(^1\)-\(^3\) Such property is of interest firstly because the ability to achieve large strains makes superplastic forming an attractive option for the manufacture of complex-shaped components in the metal industry. Ceramics, such as oxides, nitrides and carbides, are hard, strong and stiff materials. They are brittle, and lack the ductility of metals at ambient temperatures. The application of superplasticity makes it possible to fabricate ceramic components just like superplastic metals. Secondly, despite decades of investigation, there is only limited understanding of the contribution of various possible mechanisms underlying superplasticity. The exact mechanism behind ceramics superplasticity still remains controversial.

Since Garvie et al.\(^4\) proposed the concept of transformation toughening in zirconia, ZrO$_2$-based ceramics have been used as tough and wear-resistant components. The discoveries of ceramics superplasticity in Y$_2$O$_3$-stabilized tetragonal ZrO$_2$ polycrystals (Y-TZP)\(^5,6\) and its composite\(^7,8\) prompted widespread interest in the possibility of attaining high tensile ductilities in ceramics and thus in the potential industrial applications. Figure 1 shows the first demonstration of superplastic elongation of Y-TZP.\(^3\) Many efforts have been devoted to improve the superplasticity of ZrO$_2$-based ceramics in the last decade.\(^9\) For example, a remarkably high elongation of 2,510% has been achieved at a high-strain rate.\(^10,11\) The research on ceramics superplasticity has further expanded from ZrO$_2$-based ceramics to silicon nitride (Si$_3$N$_4$)\(^12,13\) and bioceramics.\(^14\) Probably, superplasticity is a common feature of fine-grained polycrystalline materials and also nanocrystalline materials at intermediate temperatures.

2. Motion and topological evolution of grains

Polycrystals deform under an applied load at elevated temperatures. The creep deformation mechanisms include the diffusional transport of atoms and the movement of lattice dislocations by glide and climb. The grains elongate along the stress axis during creep. On the other hand, fine grains retain approximately an equiaxed shape even after extremely large elongations (\(>1000\%\)) in superplasticity.

Micrograins apparently move past one another during the superplastic flow of Y-TZP and its composite.\(^8\) Any motion of a rigid grain consists of the combination of both translation and rotation. The relative motion of two adjoining grains has components parallel and vertical to their common grain boundary. The grain boundary sliding is the component parallel to the grain boundary. The contribution of grain boundary sliding to the total strain is determined by the relative motion of the neighboring grains, and, as well as in metals, it is approximately 70% of the total strain in superplasticity of fine-grained ceramics. The motion of two adjoining grains vertical to the grain boundary is equivalent to the “non-conservative” motion of grain boundary to the crystalline lattice. Non-conservative motion occurs when the interface motion is coupled to long-range diffusional fluxes of the components to/from the interface.\(^15\) The examples of non-conservative motion are diffusional creep and sintering, in which the grain boundary acts as a source/sink of vacancy. The lattice sites at the boundary are created or destroyed, which in turn cause the relative motion of crystalline grains. In the diffusional creep of the

Fig. 1. First demonstration of superplastic elongation of Y$_2$O$_3$-stabilized tetragonal ZrO$_2$ polycrystals (Y-TZP).\(^3\) Specimens before and after deformation are shown.
one-dimensional chain of grains, the distance between grains increases. In the sintering of two spherical particles, the center of particles approach one another, then densification occurs.\textsuperscript{16,17} Superplasticity, as well as sintering, takes place at temperatures higher than half the melting point, as the deformation processes are affected by diffusion.

The sliding of rigid grains generates cavities and cracks inevitably. Thus, the essential mechanism underlying superplasticity is the accommodation process of grain boundary sliding so that the polycrystalline materials can be stretched extensively without fracture. Grain boundary sliding, grain rotation, diffusion, dislocation motion and grain boundary migration are the main processes associated with superplasticity.\textsuperscript{11}

The grain boundary migration, which causes grain growth,\textsuperscript{18} is an example of “conservative” motion of grain boundary. The conservative motion is defined as the motion of an interface which occurs in the absence of a diffusion flux of any component in the system to/from the interface.\textsuperscript{15} The positions of the two grains adjoining the interface remain fixed during the conservative motion. Both conservative and non-conservative motions change the topology of the grain boundary networks. Before we discuss the physical characteristics of superplasticity, we first summarize the topological aspects of the three-dimensional evolution of grain boundary networks in grain growth and superplasticity.

The grain boundary migrates toward minimizing its total energy, which is proportional to the total boundary area, and then the motion changes the size and shape of grains at elevated temperatures. The small grains shrink and disappear, and the mean size of the remaining grains increases.\textsuperscript{19} The topological state of a grain is classified according to its number of faces \( f \) or coordination number. The elimination and formation of grain boundaries can be observed during grain growth, in which one grain changes its \( f \) with time. The process of changing \( f \) is called grain switching, that is, grain switching creates or eliminates a face of the grain.\textsuperscript{20} Figure 2\textsuperscript{(1)} shows the disappearance of a four-sided face and formation of a new four-sided face that is observed in a three-dimensional simulation of grain growth.\textsuperscript{20} The four-sided face at \( f = 3 \) by face-formation switching changes to a new face at \( f = 4 \) by face-elimination switching. The new four-sided face is orthogonal to the original face. The original face becomes triangular and disappears by face-elimination switching at \( f = 4 \).

Ashby and Verral\textsuperscript{21} identified grain switching as a geometrical requirement to maintain the equiaxed shape of grains during superplasticity. In their two-dimensional model, grains exchange their neighbors. In three dimensions, face-formation switching and face-elimination switching occur independently during superplastic deformation as well as during grain growth. Figure 3 schematically illustrates the difference between creep and superplasticity in three dimensions.\textsuperscript{22} While grains are elongated in diffusional creep and dislocation creep without grain switching, the grains maintain approximately equiaxed shape during deformation due to grain switching. One grain is caged in a cluster of neighboring grains (Fig. 3(a)). As a result of face-formation switching, a red grain emerges from inside the cluster of grains (Fig. 3(c)). Giffins\textsuperscript{23} proposed grain emergence as a model of rearrangement of grains in three dimensions. His grain emergence is equivalent to the cage breakup of the cluster.

The rate of grain growth during superplastic deformation is often higher than that caused by annealing alone (static grain growth). The enhancement of grain growth is termed strain-enhanced grain growth, or dynamic grain growth. The mechanistic origin of dynamic grain growth is probably associated with grain boundary migration,\textsuperscript{24} which is enhanced by grain boundary sliding, grain switching, or grain boundary diffusion. The grain switching during grain growth also contributes to the maintenance of the equiaxed shape of grains, if the grain boundary mobility and the grain boundary energy are isotropic.

3. Physical characteristics of ceramics superplasticity

The grain compatibility during grain boundary sliding is maintained by a concurrent accommodation process which involves diffusion, dislocation motion, and grain boundary migration. Most of the physical models proposed for superplasticity consider that the accommodation mechanism is the rate-controlling process. The importance of each accommodation process varies with materials, temperature and stress.

The strain rate in superplasticity of many metals and ceramics is often expressed by the following semiempirical equation,

\[
\dot{\varepsilon} = \frac{AGb}{kT} \left( \frac{b}{d} \right)^{\frac{1}{2}} \left( \frac{\sigma - \sigma_0}{G} \right)^n D
\]

where \( \dot{\varepsilon} \) is the strain rate, \( b \) is Burgers vector, \( G \) is the shear modulus, \( \sigma \) is the stress, \( \sigma_0 \) is the threshold stress, \( n \) is the stress exponent, \( D \) is the diffusion coefficient \( \left( = D_0 \exp \left( -Q/kT \right) \right) \), where \( D_0 \) is a frequency factor, \( Q \) is the activation energy and \( k \) is Boltzmann’s constant, \( d \) is the grain size, and \( p \) is the grain-size exponent. The value of \( p \) is 2 when the rate-
controlling process is lattice diffusion, and 3 when it is grain boundary diffusion. The threshold stress \( \sigma_b \) is 0 in many cases. The threshold stress depends on the nature of the grain boundaries.\(^9\)
The crystalline grains in Y-TZP, as well as those in metals, are directly bonded atomically at grain boundaries. To understand the intrinsic mechanism of superplasticity, the deformation of Y-TZP with a minimum amount of impurities has been extensively analyzed. The deformation of high-purity Y-TZP is characterized by a stress exponent of \( n \approx 2 \) at comparatively high stresses, whereas the deformation at low stresses is associated with \( n \geq 3 \).\(^9,20\) The values differ from that of grain boundary sliding accommodated by diffusion, which nearly predicts a Newtonian flow \((n = 1)\).\(^21\) Some hypotheses of interface-controlled diffusional creep\(^20,28\) were proposed to explain this discrepancy. Although the mechanical data can be consistent with the interface-controlled Coble creep,\(^21\) the retention of an equiaxed grain shape after superplasticity is apparently in conflict with the expectation of grain elongation accompanying diffusional creep. This conflict is partly resolved if significant grain growth occurs during deformation,\(^29\) because grain switching also accompanies grain growth. Alternatively, the grain boundary sliding with threshold stress \((n = 2, p = 2 \text{ in Eq. (1)})\) can predict the characteristics of Y-TZP.\(^9,30\) Originally, the grain boundary sliding model with \( n = 2 \) was developed for superplastic alloys, in which intragranular dislocation plays an important role in the accommodation process. While the phenomenological constitutive equation agrees with the experimental results of Y-TZP, the role of intragranular dislocation\(^31\) in grain boundary sliding has not yet been clearly elucidated, because flow stress in superplasticity is much lower than the stress required for the dislocation activity.\(^32\)

4. Grain refinement and suppression of grain growth
The semi-empirical equation, Eq. (1), provides strategies for achieving superplasticity at high strain rates and at low temperatures, that is, grain refinement and diffusion enhancement.

The essential requirement for superplasticity is fine grain size. The strain rate increases by decreasing the grain size. While various thermomechanical processes are used to develop the fine microstructure of metals, fine-grained ceramics are usually produced by sintering ultrafine powder. To avoid grain growth during sintering, a low sintering temperature is used in stress-assisted sintering, for example, hot-isostatic pressing,\(^7,14\) hot pressing,\(^12\) and sinter forging.\(^12\)

Thermal stability of the fine microstructure at elevated temperatures is required for the achievement of superplasticity. The grain boundary mobility depends strongly on the presence of solute or impurity segregation at grain boundaries. The rate at which the solute and impurity atoms can diffuse along with the boundary is slower than that at which the boundary can otherwise move.\(^15\) The sluggish grain growth in Y-TZP is controlled primarily by the solute-drag effect of \( Y^{3+} \) ions segregating along grain boundaries.\(^33\)

The motion of grain boundaries is also impeded by second-phase particles which are dispersed throughout the material. In two-phase composites, grain growth through grain boundary migration is coupled with Ostwald ripening via long-range diffusion, if there are limited mutual solubilities among the phases.\(^34\) This coupling results in inhibited grain growth for both phases. Many fine-grained two-phase and multiphase composites, for example, ZrO\(_2\)-Al\(_2\)O\(_3\),\(^7,15\) and ZrO\(_2\)-Al\(_2\)O\(_3\)-spinel,\(^16,17\) exhibit superplasticity.

The addition of the second phase affects superplasticity and the creep of composites in two ways. First, it modifies the continuum deformation mechanics. The effect of volume fraction of the second phase on strain rate can be predicted using a rheology model\(^7\) or a composite theory.\(^35\) Second, the constituent atoms of the second phase affect interface-related deformation characteristics, for example, grain boundary diffusion, and will be discussed in detail in the following section.

5. Diffusion enhancement
The additions of impurity atoms and solute atoms have various effects on the grain boundary diffusivities and the lattice diffusivities of both solvent and solute species including the combinations of enhancing or retarding effects. The solute atoms can change the vacancy concentration and the jump probability. From the atomistic view of point defects, differences in the ionic radii and in the valence contribute to the differences in diffusion coefficient. The doping of a small amount of impurities significantly affects sintering and diffusional creep.\(^36\)

The superplasticity of Y-TZP is affected by the addition of a small amount of impurities, particularly Al and Si atoms.\(^9,25,37,38\) These impurities segregate at grain boundaries, and increase the strain rate of Y-TZP at low stresses. The deformation behavior of impurity-doped Y-TZP is characterized by \( n = 2 \) and \( p = 2 \) over a wide stress range. The transition of the stress exponent in high-purity Y-TZP disappears upon the doping of impurities, or the apparent threshold stress becomes zero.\(^9,30\) The threshold stress becomes apparently negligible by cosegregation of impurity atoms, such as Al\(^{3+}\) or Si\(^{4+}\), with Y\(^{3+}\), but its physical mechanism has not yet been fully elucidated.

The diffusion coefficients of ceramics depend on chemical composition (stoichiometric or nonstoichiometric) and its crystal structure. Hydroxyapatite (\( Ca_10(PO_4)_6(OH)_2 \)) can be superplastically deformed at a relatively low temperature of 1000°C due to its rapid diffusivity.\(^34\) Hydroxyapatite is biocompatible with bone, and can be used in orthopedic and dental implants.

The addition of liquid phase can enhance the deformation of polycrystalline solids significantly. The distribution of liquid phase amongst the crystalline grains depends on the amount of liquid phase and the ratio of \( \gamma_2/\gamma_3 \), where \( \gamma_2 \) and \( \gamma_3 \) are the grain boundary energy and the interface energy between solid and the liquid phase, respectively. When \( \gamma_2/\gamma_3 \geq 2 \), the liquid phase covers the faces of all grains. In creep and superplasticity of some advanced ceramics, the intergranular liquid phase acts as a lubricant for grain boundary sliding, and also as a path for material transport by solution-precipitation process.\(^39,40\) Silicon nitride (Si\(_3\)N\(_4\)) is a promising material for engine components. The glass phase pocket and thin glass film\(^41\) with the thickness of about 1 mm often remain at grain boundaries of liquid-phase sintered Si\(_3\)N\(_4\). The glass behaves as a liquid at elevated temperatures. The superplasticity and creep of Si\(_3\)N\(_4\) are affected by the viscosity of the intergranular liquid and the solubility of the solid to the liquid, and have been reviewed recently.\(^42\) The mechanism of superplasticity of glass-containing Si\(_3\)N\(_4\) is different from the intrinsic superplasticity of metals and ceramics that do not contain glass film. The “classical” microstructural requirement for superplasticity is a material consisting of equiaxed fine grains. The liquid phase promotes the grain boundary sliding, so that even the materials which contain rod-shaped \( \beta\)-Si\(_3\)N\(_4\) can be superplastically deformed. In this type of non-
classical superplasticity, the anisotropic grains tend to align with the strain, producing a fiber-strengthening effect. This phenomenon leads to the strengthening and toughening of $\text{Si}_3\text{N}_4$ by compressive deformation.\(^{43}\)

6. Superplastic forming

The process of superplastic forming (SPF) of ceramics can be an advanced manufacturing method for producing complex thin-sheet components.\(^{44}\) The superplastic forming concurrent with diffusion bonding (SPF/DB) process, which is used in the production of titanium alloys for the aerospace industry, is also applicable to ceramics. The superplastic ceramic sheet is used for diffusion bonding of dissimilar materials.\(^{45}\) In the ceramic industry, complex-shaped components with accurate dimensions have been usually fabricated by sintering the shaped powder compact. Therefore, in comparison to the sintering, two factors are important for the practical application of superplastic forming: reliability, and efficiency.

First, it is necessary to assure the reliability of the products. The source of variability in strength relates to flaws, particularly for ceramics, due to its inherent brittleness. Many voids or cavities are formed in the extremely elongated specimens in tension. The cavity growth is regarded as an inverse process of sintering. The suppression of cavitation is of utmost importance to superplastic forming of ceramics. A fast grain boundary diffusion, a small grain size, and a small ratio of grain boundary energy to surface energy are necessary for preventing the nucleation of cavities.\(^{46}\) The cavitation can be suppressed by selecting appropriate forming conditions, so that $\text{ZrO}_2$-toughened ceramics can maintain excellent strength even after elongation of more than 100\%.\(^{17}\)

High-strain-rate superplasticity of ceramics rendered the superplastic forming an attractive technology for shaping components efficiently. However, the microstructural optimization of superplasticity is not necessarily a demand of the market. For practical applications, superplasticity should be compatible with other properties, such as hardness, toughness, wear-resistance, and strength. The high-strain-rate superplasticity of useful materials, such as $\text{Si}_3\text{N}_4$, having excellent properties, will be a target for future development.

7. Concluding remark

In this brief review on ceramics superplasticity, we have summarized mainly our work, and many other important contributions to this field have not been included. The grain boundary dynamics is a key to understanding and controlling the microstructural evolution in materials science. The structure of the grain boundary network evolves dynamically in superplasticity, as well as in grain growth and sintering. The research on ceramics superplasticity has elucidated some of the basic principles in topological transformation of grains, and the role of grain boundary chemistry in deformation. Although significant advances have been made in developing and improving the superplasticity of various ceramics, our understanding of the deformation mechanism at the atomic level is yet limited. In the coming decades, new experimental techniques and computer simulations will provide new insights on grain boundary dynamics. The fundamental knowledge obtained on ceramics superplasticity will be useful for many research fields in materials science.

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References

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