High-strain-rate superplasticity in oxide ceramics

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Abstract

Factors limiting the strain rate of superplastic deformation in ceramic materials are discussed on the basis of existing models and experimental results concerning high-temperature plastic deformation, intergranular cavitation and dynamic grain growth. From the discussion, it is indicated that simultaneously fulfilling the following conditions is essential for attaining high-strain-rate superplasticity (HSRS) in ceramic materials: reduction in the initial grain size, enhanced diffusivity, suppressed dynamic grain growth, a homogeneous microstructure and a reduced number of residual defects. In the light of these conditions, explanations are given for HSRS attained in earlier studies on some oxide materials. It is also shown that HSRS can be intentionally attained in doped yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) and composites synthesized from ZrO2, Al2O3 and MgO; the tensile ductility of these composites reached 300–2500% at a strain rate of 0.01–1.0 s−1. The postdeformation microstructure indicates that some secondary phases may suppress cavitation damage and thereby enhance HSRS.

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Keywords: Superplasticity; High-strain rate; Grain growth; Diffusion; Stress relaxation; Cavitation

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1. Introduction

Superplasticity is the ability of a material to exhibit large tensile ductility, defined as \( e_f = \frac{100(l_f - l_0)}{l_0} \) for the initial \((l_0)\) and final \((l_f)\) lengths of the material, and provides an attractive route for net-shape forming (Fig. 1) and the joining of materials. In ceramic materials, superplasticity was discovered by Wakai et al. [1] and this discovery was followed by demonstrations of superplastic bulging [2], forging [3,4], deep drawing (Fig. 1) and joining [5] in zirconia- and alumina-base materials. Industrial applications, however, are still limited, in contrast to those of superplastic metallic materials [6–8]. One of the major reasons for this situation is the limited strain rate that is available for superplastic forming. In most ceramics, superplasticity occurs at strain rates of approximately \( 10^{-4} \text{s}^{-1} \) or lower even at high temperatures in the range of 1400–1650 \(^\circ\text{C}\). At a strain rate of \( 10^{-4} \text{s}^{-1} \), it takes about 3 h to elongate a material having an initial length of 10 mm to a final length of 20 mm. Such a long forming time is unattractive to industry. The forming time can be markedly reduced to 2 min or less when the material is formable at a strain rate higher than \( 10^{-2} \text{s}^{-1} \). In metallic materials, superplasticity at \( 10^{-2} \text{s}^{-1} \), namely high-strain-rate superplasticity (HSRS), is of fundamental importance in industrial net-shaping [8] and this is also the case for ceramic materials.

The purpose of this paper is to give an overview of HSRS in oxide ceramic materials, while placing major emphasis on the microstructural conditions essential for the occurrence of HSRS. First, factors limiting the strain rate of superplastic deformation are discussed on the basis of the existing knowledge of high-temperature deformation and related phenomena in polycrystalline materials. Second, in the light of this discussion, an explanation is given for HSRS observed at a strain rate of \( 10^{-2} \text{s}^{-1} \) in earlier studies on some oxide materials. Finally, HSRS at \( 10^{-2}–10^{-3} \text{s}^{-1} \) attained by the present authors is described, along with a discussion on the new features found in the microstructure after high-strain-rate deformation.

2. Limiting factors

2.1. Creep equation

In ceramic materials in which the grains are rigid, the combination of grain-boundary sliding, grain switching and grain rearrangement due to diffusion [9–11] can be regarded as the main mechanism of superplastic deformation. If this combination is ideally uniform and successive, then superplastic deformation is also uniform and successive without cavitation damage along grain boundaries or at multiple junctions. For such an ideal case, the stress–strain rate relationship is given by

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

where \( \dot{\varepsilon} \) is the strain rate, \( A \) is a material constant, \( Q \) is the apparent activation energy, \( R \) is the gas constant, \( T \) is the deformation temperature, \( \sigma \) is the applied stress, \( n \) is the stress exponent, \( d \) is the grain size and \( p \) is the grain-size exponent. For a fixed combination of stress and temperature, Eq. (1) implies that the strain rate can be increased by a reduction in the grain size. For example, a grain-size reduction to \( 0.32d^{0.46} \) for a typical \( p \) value of 2–3 increases the strain rate by a factor of 10. The equation also implies that an increase in the \( A \exp\left(\frac{-Q}{RT}\right) \) term, which means enhanced diffusion along grain boundaries and/or within grains, increases the strain rate. Enhanced diffusion is known to occur upon the doping of some aliovalent cations [12] and is related closely to grain growth [13] and to stress concentration and relaxation [14,15] during deformation.

In actual ceramic materials, however, the combination of grain–boundary sliding, grain switching and grain rearrangement and accommodation is not ideal. Also note that Eq. (1) does not consider any microstructural changes during deformation. Experimental studies have shown that superplastic deformation is inherently accompanied by accelerated grain growth (dynamic grain growth) [12,16–18] and intergranular cavitation [12,16–27]. The former increases the level of flow stress for a given strain rate and enhances...
the latter. Since cavitation damage leads to premature failure [12,16–19,24–27] or degrades the postdeformation strength [28], consideration of these dynamic phenomena is indispensable for attaining HSRS and for industrial applications.

### 2.2. Cavity nucleation

Theoretical models for intergranular cavitation [14,15,29] indicate that cavity nucleation occurs owing to stress concentrations arising from the inhomogeneity of microstructures and chemical compositions. Even in a monolithic material, there are distributions of grain size, grain shape and chemical composition. For this reason, stress distribution, chemical potential, and hence the combination of grain–boundary sliding and grain switching coupled with diffusion, also become inhomogeneous at the microscopic scale. There is, consequently, a finite probability of the breakdown of the accommodation process, particularly in some local regions where the geometry and chemical composition rapidly change. This means that, in such regions, stress concentrations caused by grain–boundary sliding cannot always be relaxed sufficiently by diffusion. Typical examples of such regions are multiple grain junctions and phase boundaries, where cavity nuclei have frequently been observed after superplastic deformation (Figs. 2(a) and (b)).

Although detailed relationships among diffusion, stress concentrations, stress relaxation and cavity nucleation have not yet been established in superplastic ceramics, it is possible to estimate [30] the relaxation length, $A$ [15], over which grain–boundary diffusion can relax the stress concentrations caused by deformation. The relaxation length is given as

$$\frac{A}{d} = \left(\frac{L}{d}\right)^{1/[1-st(n-1)/3]}$$

(2)
where \( L \) is the characteristic diffusion length given by Eq. (3) and \( s \) is the extent of the stress singularity at the triple junction in the absence of diffusion:

\[
L = \left( \frac{\delta D_b \sigma \Omega}{k_B T c} \right)^{1/3}.
\]  

Eq. (3)

Here, \( \delta D_b \propto \exp(-Q/RT) \) is the grain-boundary diffusion coefficient, \( Q \) is the atomic volume and \( k_B \) is the Boltzmann constant.

When we assume an aggregate in the shape of a tetrakaidecahedron having a facet length of \( e = d/3 \) (Fig. 3), there are three cases to consider for the relationship between the relaxation distance and the grain facet length, \( e \); (a) \( A > e \), (b) \( A = e \) and (c) \( A < e \). For (a), stress relaxation is sufficient, and consequently cavity nucleation should be suppressed. Cavity nucleation is expected to occur for (c), where relaxation is insufficient. In an extreme case of \( A < e \), instantaneous de-bonding may occur along grain boundaries or interfaces. Using the diffusion data for Ce-doped tetragonal \( \text{ZrO}_2 \) [31] and an average dihedral angle of 120\(^\circ\), for which \( s \) is 0.45, and assuming that \( n = 3 \) and \( \sigma = 30 \text{ MPa} \), we can calculate the critical case (b), for which \( d_c = 3e = 3A \). The results of this calculation are shown in Fig. 4 for \( T = 1400–1500 \text{ } ^\circ\text{C} \) with and without enhanced diffusion.

Fig. 4 provides the following insights into the stress relaxation. First, the critical grain size for a given temperature decreases rapidly with an increase in the strain rate. The estimation indicates that the critical grain size at \( T = 1400 \text{ } ^\circ\text{C} \) is 0.26\( \mu \text{m} \) for ordinary superplasticity at a strain rate of \( 10^{-4} \text{s}^{-1} \), whereas it is reduced to 0.06\( \mu \text{m} \) for HSRS at \( 10^{-2} \text{s}^{-1} \). Second, for a fixed grain size, the critical temperature, \( T_c \), above which stress relaxation becomes sufficient, increases with increasing strain rate. For \( d_c = 0.2 \mu \text{m} \), \( T_c \) increases from 1400 to 1600 \( ^\circ\text{C} \) as the strain rate increases from about \( 2 \times 10^{-4} \) to \( 10^{-2} \text{s}^{-1} \). Finally, enhanced diffusion increases the critical grain size for a given strain rate. From Fig. 4, it is predicted that, when the grain boundary diffusivity increases by a factor of 50 at 1400 \( ^\circ\text{C} \), the critical size increases from 0.06 to 0.2\( \mu \text{m} \) at \( 10^{-2} \text{s}^{-1} \). The estimation also shows that enhanced diffusion by factors of 10 and 50 correspond to increases in the critical temperature by about 100 and 200 \( ^\circ\text{C} \), respectively. For 50\( \delta D_b \), stress relaxation at \( 10^{-2} \text{s}^{-1} \) is expected to become sufficient for \( d = 0.2 \mu \text{m} \), even at 1400 \( ^\circ\text{C} \). Grain-size reduction, suppressed grain growth and enhanced diffusion are thus essential for achieving sufficient stress relaxation and suppressed cavity nucleation during high-strain-rate deformation.

The existing models [14,15,29] also predict the following relationship between cavity nucleation and material parameters. The probability of cavity nucleation depends on the grain–boundary diffusivity, surface energy, \( \gamma_s \), grain–boundary energy, \( \gamma_b \), and geometrical factors such as the dihedral angle between the grain facets. For a fixed grain size, for example, the probability of cavity nucleation decreases with increasing \( \delta D_b \) and \( \gamma_s \) and with decreasing \( \gamma_b \). In spite of such knowledge of cavity nucleation, information is still limited on the relationships among these parameters, chemical compositions and minor additives. Recent studies on fixed-grain-size Y-TZP doped with aliovalent cations [32–35] suggest, however, that a first-principles molecular-orbital calculation may highlight a new aspect of this issue. A close relationship was found between the tensile ductility and the total bond-overlap population (BOP), which represents the strength of covalent bonding among the constitutive ions; ductility increases with increasing BOP. This result suggests a close relationship between BOP and \( \gamma_b \) and/or \( \gamma_s \), since tensile ductility should strongly be controlled by the rate of cavity nucleation for a fixed combination of the major chemical constituents, initial grain size and loading conditions [30]. The final point regarding cavity nucleation is the level of flow stress. Since the rate of nucleation depends on \( \exp(-1/\sigma^2) \) [14,15,29], achieving a reduction in the flow stress is of particular importance.

2.3. Cavity growth and cracking

During superplastic deformation, nanometer-sized cavity nuclei and defects remaining after sintering grow into micrometer-sized voids (Fig. 2(e)). It has been found in zirconia-base [22,23] and alumina-base [26,36] materials that the growth of micrometer-sized voids follows \( dD/dc = \eta D \), where \( D \) is the cavity diameter and \( \eta \) is a constant taking a value of about unity. This equation means that the voids are grown by the plastic flow of the material [37]. Such a plastic-growth mechanism is not contradictory to the fact that the grains are rigid, since the aggregate of the rigid grains surrounding the micrometer-sized voids behaves as a plastic body in superplastic ceramics. In the plastic-growth mechanism, the increase in void volume during deformation is determined by the increase in plastic strain. Accordingly, the void growth cannot be easily controlled by modifications in the chemical composition and microstructure. The growing voids interlink with each other, resulting in cracking perpendicular to the stress axis [16–19,24–27]. A strong resemblance has been found between this process and that of ductile failure in metallic materials containing microvoids or hard inclusions [27]. The cavity growth and cracking processes indicate that a reduction in the number of residual defects after sintering and the suppression of cavity nucleation during deformation are essential for reducing the accumulation of damage due to void growth.

2.4. Dynamic grain growth

Suppressed dynamic grain growth is necessary for maintaining a lower level of flow stress (Eq. (1)) and a shorter length of grain facet to be relaxed by diffusion (Eq. (2)), both of which are indispensable for the suppression of cavity nucleation. Out of the models for dynamic
grain growth [38–43], a model derived from a diffusion mechanism [43] may provide a useful insight into this issue, owing to the simplicity of its expression and its agreement with experimental data. The model gives the differential of grain size during deformation as the sum of the dynamic and static components, which are expressed by the first and second terms of the right-hand-side of Eq. (4), respectively: 

\[ \frac{d \omega}{d \varepsilon} = \frac{k}{m} d^{1-m} \rho d t, \]  

where \( \omega \) is a constant depending on the grain shape and grain size distribution, and \( m \) and \( k \) are the grain growth exponent and kinetic constant, respectively, of the static grain-growth law, \( d^m - d^m_0 = kt \), where \( t \) is the heating time. Under an initial condition of \( d = d_0 \) at \( \varepsilon = 0 \), Eq. (4) yields the following equation for constant displacement-rate loading [26]:

\[ d = \left[ d_0^m \exp(\omega m) + \frac{k(\exp(\omega) - \exp(\omega m))}{\omega(1 - \omega)} \right]^{1/m}. \]  

Eq. (4) implies that the grain size for a given strain becomes smaller with a reduction in the initial size and with an increase in the deformation rate. In addition, experimental data indicate that the value of \( \omega \) for superplastic deformation is insensitive to chemical compositions; \( \omega \) is about 0.5–0.6 for various oxide materials (ZrO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} [26,43], ZrO\textsubscript{2}–spinel–Al\textsubscript{2}O\textsubscript{3} [44], ZrO\textsubscript{2}(3Y) [45] and superplastic metals (Zn–Al) [40]). Such data used with Eq. (5) suggest that the mechanism of dynamic grain growth can be estimated from the values of \( k \) and \( m \). It is consequently essential to suppress static grain growth by grain-boundary pinning and/or dragging. Highly limited grain growth can be expected in a microstructure consisting of three or more phases where the amount of each phase is similar. Such a multiphase structure decreases the frequency of the grain boundaries between the same phases and increases the separation distance between the phases. This situation is beneficial for achieving suppressed grain growth, since grain growth occurs by the migration of such grain boundaries and/or by the growth of grains through interphase boundary diffusion.

2.5. Processing dependence

For a given combination of chemical composition, grain size and relative density, superplastic properties may vary with differences in the homogeneity of the microstructure or the number of fine residual defects, which have negligibly small volume and hence have little effect on the relative density. A typical example is shown in Fig. 5 for 10 vol% ZrO\textsubscript{2} (3Y)-dispersed Al\textsubscript{2}O\textsubscript{3} [26]. For a grain size
size of 0.45 μm and a relative density of 99.5%, the tensile ductility of a material prepared by conventional dry processing (designated as D in the figure) was about half that of a material prepared by colloidal processing (designated as C). Such a difference is due to the enhanced cavity damage that accumulates owing to the higher numerical density of fine residual defects and from accelerated grain growth. The accelerated growth is due to the lower efficiency of grain-boundary pinning by ZrO₂ [26]. The lower pinning efficiency and higher numerical density of fine residual defects arise from the agglomeration of ZrO₂ and Al₂O₃ particles in the green bodies, where the extent of the agglomeration is strongly process dependent [46].

3. Prerequisites for the occurrence of HSRS

From the discussion in the previous section, factors necessary or desirable for attaining HSRS are shown in the first column of Table 1. The second column summarizes the relationship between these factors and superplastic deformation or cavitation. The third column indicates the dependence of these factors on the process (P), chemical constituents (C) and phases (Ph). For a given combination of chemical constituents and phases, factors (a), (b), (d) and (e) are strongly process dependent, particularly in composites.

In Table 1, note that some factors appear to conflict with each other. For example, second-phase pinning is effective in suppressing dynamic grain growth, but it may act as a site of stress concentrations resulting in cavity nucleation. A solution to this problem is the grain-size refinement of the second phase or both the second and matrix phases—namely, decreasing the distance that must be relaxed by diffusion (Figs. 3 and 4). A minor additive that enhances diffusion may also bring about conflicting effects; the additive should simultaneously enhance stress relaxation and dynamic grain growth. Our discussion of Eq. (5) indicates, however, that this problem is diminished as the strain rate is increased, and grain-size refinement combined with second-phase pinning may provide a solution. Factors (a)–(c) and (g) listed in Table 1 have been noted in studies on conventional superplasticity, whereas there have been a very limited number of studies that consider factors (a)–(h) simultaneously. The present discussion indicates that simultaneously controlling these factors is essential for attaining HSRS.

4. Earlier studies on HSRS

Substantial HSRS, namely, tensile elongation exceeding 200% [47] at a strain rate of $\geq 10^{-2}$ s⁻¹, was reported by Chokshi et al. [19] for commercial 20-mass%-Al₂O₃-dispersed ZrO₂(3Y), by Kajihara et al. [48] for 5-mass%-SiO₂-doped ZrO₂(2.5Y) and by Oka et al. [49] for ZrO₂(3Y) codoped with 2 mol% TiO₂ and 2 mol% CaO. These materials have grain sizes of about 0.3 μm and matrices consisting of Y-TZP. The latter is particularly advantageous for HSRS, since grain growth in Y-TZP is inherently slow compared with that in other materials such as Ce-TZP, cubic zirconia and alumina [12].

In the light of Table 1, the above materials, which have additional advantages for attaining HSRS, are noted in Table 2. In Al₂O₃-dispersed ZrO₂, the Al₂O₃ particles may contribute not only to suppressing grain growth by second-phase pinning, but also to enhancing diffusion by supplying Al³⁺ to the ZrO₂ matrix. The latter effect is consistent with studies [50–52] on Y-TZP doped with a small amount of Al³⁺.

The doping of SiO₂ introduces the segregation of Si⁴⁺ along grain boundaries and a glass phase at multiple junctions [53]. A study [54] on tensile creep in 3Y-TZP doped with small amounts of SiO₂, for which the glass phase is absent, shows that the segregation increases the strain rate for a given stress. A molecular-orbital calculation [55] indicates that the Si segregation strengthens the grain–boundary bonding in Y-TZP and thereby enhances superplastic tensile ductility. In the cavitation mechanisms, this may correspond to an increase in $\gamma_b$ and/or a decrease in $\gamma_p$, both of which should lead to suppressed cavity nucleation. In addition, the viscous flow of the glass phase may suppress the formation of stress concentrations and

| Material | Prerequisites | $\dot{\epsilon}$ (s⁻¹) | $\varepsilon_f$ (%) | $T$ (°C) | Ref. |
|----------|---------------|-----------------|-----------------|---------|-----|
| 20Al₂O₃–ZrO₂(3Y)b | (b), (c) | 0.04 | 300 | 1650 | [19] |
| 5SiO₂–ZrO₂(2.5Y)b | (b), (c)–(g) | 0.01 | 360 | 1400 | [48] |
| 2CaO–2TiO₂–ZrO₂(3Y)c | (b), (c) | 0.01 | 400 | 1400 | [49] |
| 0.2Al₂O₃–ZrO₂(3Y)b | (a), (c)–(e) | 0.03 | 370 | 1450 | [50] |
| 3(Y₂O₃,MgO)–97(Zr₀.₉₅Ti₀.₀₅)O₂b | (a), (c)–(e) | 0.01, 0.01 | 220, 300 | 1350, 1450 | [57] |
| 0.2MnO₂–0.3Al₂O₃–ZrO₂(3Y)b | (a), (c)–(e) | 0.01 | 600 | 1450 | [58] |
| 40ZrO₂(3Y)–30spinel-Al₂O₃c | (a), (d) | 0.01, 0.08, 1.0 | 500, 2500, 390 | 1500, 1650, 1650 | [59–61] |
| 30MgAl₂O₄–ZrO₂(3Y)b | (a)–(d), (b)d | 0.02, 0.7 | 660, 250 | 1450, 1550 | [62–65] |

*aMass%.

*bMol%.

*cVol%.

*dSee Table 1.
hence cavity nucleation around the multiple junctions. It should also be noted that the dispersion of the glass phase suppresses grain growth [48,56].

The codoping of CaO and TiO$_2$ is probably the first example of the design of a chemical composition with the aim of attaining HSRS in a ceramic material. The following merits were expected upon codoping [49]: suppressed grain growth due to dragging from the doping of Ca$^{2+}$ and enhanced diffusion from Ti$^{4+}$. The codoping resulted in a dual-phase structure consisting of 22 vol% cubic phase and 78 vol% tetragonal phase and the attainment of HSRS. It is not clear whether the dispersed cubic phase has a positive or negative effect on HSRS. Inspection of the earlier data indicates that, out of the factors listed in Table 1, four or more factors should be simultaneously satisfied to attain HSRS.

5. Recent studies on HSRS and aspects on newly found features

Paying special attention to factors (a)–(e) of Table 1, we aimed to attain HSRS in monolithic [50,57,58] and composite [44,59–65] materials, without forming a glassy phase. We also noted that factors (a), (b), (d) and (e) are process-dependent. This is particularly the case when fine powders are used. Fine powders tend to agglomerate spontaneously owing to van der Waals forces [46]. The agglomeration results in the formation of large pores in green bodies, and sintering at a lower temperature cannot eliminate the pores. To prevent agglomeration, we applied colloidal processing [66] to fine oxide powders.

5.1. Monolithic tetragonal zirconia

For Y-TZP, since grain growth is inherently slow, factors (a), (c), (d), (e) and (f) are essential for attaining HSRS. Out of these factors, we tried to control (a) and (c)–(e). With the aiming of enhancing diffusion, we doped or codoped aliovalent cations using commercially available high-purity powders of $\alpha$-Al$_2$O$_3$ [50], Mn$_3$O$_4$ [57] and MgO [58]. We also used TiO$_2$ [57], since earlier data [67] on grain growth and superplastic properties indicate that diffusion in Y-TZP is enhanced by TiO$_2$ addition. Along with the addition of TiO$_2$, we codoped MgO to stabilize the tetragonal phase. Upon colloidal processing followed by sintering at 1300°C for 2 h, almost fully dense materials were obtained in Al$_2$O$_3$-doped 3Y-TZP and Y-TZP codoped with TiO$_2$ and MgO or with Mn$_3$O$_4$ and Al$_2$O$_3$ (Table 2). The sintered materials consisted of a single tetragonal phase with an average grain size of 0.23 μm, where the grain size was defined as 1.56 times [68] the average intercept length of the grains. The examination of sintering behavior and the rate of static grain growth confirmed the occurrence of enhanced diffusion in these materials. As listed in Table 2, the synthesized materials exhibited HSRS at approximately 1400°C and at a strain rate of the order of $10^{-2}$ s$^{-1}$. By the codoping of TiO$_2$ and MgO, the deformation temperature can be lowered to 1350°C. This is the lowest temperature that has been reported for HSRS, and this temperature is below the lower limit for conventional superplasticity in Y-TZP.

5.2. Dual- and triphase composites

In composite materials, strongly suppressed grain growth and improved fracture strength can be expected [69]. When Y-TZP is dispersed in composite materials, toughening can be expected below the transformation temperature. In spite of these merits, grain–boundary pinning may simultaneously impede grain–boundary sliding. For this reason, enhanced diffusion in the matrix and grain-size refinement are indispensable. For the latter, the elimination of agglomeration in the raw materials is particularly important, since it enables us to sinter the materials at a lower temperature. Of the factors listed in Table 1, we attempted to control (a), (c), (d) and (e). We examined second-phase dispersion and a tri-phase structure in which the volume fraction of each phase was similar. In such structures, strongly suppressed grain growth can be expected, as described before. For a large amount of second-phase dispersion, during which clustering of the phases is unavoidable, we used a secondary phase that itself exhibits superplastic or superplastic-like deformation. From these considerations, we synthesized materials consisting of tetragonal ZrO$_2$, $\alpha$-Al$_2$O$_3$ and MgO $\cdot$ Al$_2$O$_3$-spinel, where MgO $\cdot$ Al$_2$O$_3$-spinel is expected to supply Al$^{3+}$ and Mg$^{2+}$ to the ZrO$_2$ phase and Mg$^{2+}$ to the Al$_2$O$_3$ phase.

Fig. 6. Tensile elongation as a function of the initial strain rate and temperature in the developed monolithic Y-TZP (■) and composite materials (□). Earlier data are also plotted for monolithic materials (∇), composite materials (□) and SiO$_2$-doped Y-TZP for comparison.
The synthesized materials were 30 vol% MgAl_2O_4–ZrO_2(3Y) [62–65] and 40 vol% ZrO_2(3Y)–30 vol% (MgO·1.1Al_2O_3)–Al_2O_3 [59–61]. To synthesize the former, colloidal processing was applied to MgAl_2O_4 and ZrO_2(3Y) powders. For the latter, conventional processing was applied to ZrO_2(3Y), MgO and Al_2O_3 powders. Sintering at 1400°C for 1–2 h resulted in densified bodies with grain sizes of 0.29 μm (ZrO_2) and 0.42 μm (MgAl_2O_4) for the dual-phase composite material and 0.28 μm (ZrO_2 and spinel) and 0.45 μm (α-Al_2O_3) for the triphase composite material. In the triphase material, the spinel phase was formed by a chemical reaction between the MgO and Al_2O_3 powders. The grain size of each phase became smaller than that obtained by sintering each phase alone, particularly for the Al_2O_3 and spinel phases. The composite materials sustained high strain rates (10^{-1}–10^0 s^{-1}) and large tensile elongation (390–2500%) [59–62,64]. As plotted in Fig. 6, the developed monolithic and composite materials attained superplasticity at higher strain rates than the conventional and HSRS materials reported in earlier studies [1,12,16–20,23–27,47–49].

![Fig. 7. Dislocation substructures observed in (a) ZrO_2 and (b) spinel grains of ZrO_2–spinel–Al_2O_3 superplastically deformed at 1500°C and at ~0.2 s^{-1}.

![Fig. 8. Comparison of grain shape in MgAl_2O_4-dispersed ZrO_2 (a) before and (b) after superplastic deformation. While the white zirconia grains are equiaxial after deformation, the dark spinel grains are noticeably elongated by deformation. The tensile axis is horizontal.

![Fig. 9. Comparison of cavitation damage between (a) 40ZrO_2–30spinel–Al_2O_3 deformed to 2500% at 1650°C and at 10^{-1} s^{-1} and (b) ZrO_2–10Al_2O_3 deformed to 550% at 1500°C and at 10^{-5} s^{-1}.]
5.3. New features in the oxide materials

In the tensile data given in Fig. 6, a different tendency appears for the monolithic materials and the composite materials. The former materials are located in a region of lower superplasticity temperature, strain rate and tensile ductility, while the latter materials are located in a region of higher superplasticity temperature, strain rate and ductility. The difference may relate to the balance between the resistance and grain growth and diffusivity, and that between the resistance and grain-boundary sliding. Further grain-size refinement in the composites may shift these balances toward a low-temperature region.

Inspection of the deformed microstructure revealed some noticeable features in the ZrO2 and spinel [63–65] grains: dense intragranular dislocations and dislocation-related substructures such as sub-boundaries (Fig. 7). Such dislocation substructures and grain elongation were not found in undeformed materials. Elongation along the stress axis was also found in the spinel grains in the MgAl2O4-dispersed ZrO2(3Y) (Fig. 8) [62–65]. Thus, these observed features indicate that the phases of these phases may not be perfectly rigid—that is, the grains may deform to some extent by dislocation mechanisms during high-strain-rate loading.

Another notable feature was found in the cavitation behavior [59,61,62]. As shown in Fig. 9(a), some cavities were extremely elongated along the stress axis and micrometer-sized cavities were sparse in the remaining matrix. Such a microstructure should appear when a small number of residual defects grow with plastic flow when cavity nucleation is strongly suppressed. If cavity nucleation is active, as observed in conventional materials [17–18,26], a large number of micrometer-sized voids (Fig. 2(c)) grow from cavity nuclei during superplastic deformation. The void growth is followed by coalescence and microcracking [17–19,23,24,26,27] normal to the stress axis (Fig. 9(b)).

The dislocation substructures and cavitation behavior indicate that the grains of ZrO2 and MgAl2O4 in the composites should contribute to the suppression of stress concentrations around the multiple junctions and/or phase boundaries. Although further studies are desirable regarding this issue, the results indicate that the dispersion of some secondary phases may provide a potential route for enhancing HSRS. This is an additional positive factor for attaining HSRS and is noted as factor (h) in Table 1.

6. Summary

HSRS can be intentionally attained in doped Y-TZP and composites synthesized from ZrO2(Y-TZP), Al2O3, MgO2 and TiO2. To achieve this, the knowledge of superplastic deformation, cavitation and dynamic grain growth underlines the importance of simultaneously controlling the following factors: initial grain size, the number of residual defects, diffusivity, dynamic grain growth and the homogeneity of the microstructure. Recent studies indicate that the grains of ZrO2 and spinel phases may contribute to stress relaxation around multiple grain junctions, resulting in the suppression of cavity nucleation during high-strain-rate deformation. For industrial application, further studies are desirable with the aim of attaining HSRS at lower temperatures and developing high-strain-rate-forming technology suitable for ceramic materials.

References

[1] F. Wakai, S. Sakaguchi, Y. Matsuno, Adv. Ceram. Mater. 1 (1986) 259.
[2] X. Wu, I.-W. Chen, J. Am. Ceram. Soc. 73 (1990) 746.
[3] I.A. Akmoulin, M. Djhazi, N.D. Buravova, J.J. Jonas, Mater. Sci. Technol. 9 (1993) 26.
[4] J. Wittenauer, Mater. Sci. Forum 243–245 (1997) 653.
[5] A. Dominguez-Rodriguez, F. Guiberteau, M. Jimenez-Melendo, J. Mater. Res. 13 (1998) 1631.
[6] A.J. Barnes, Mater. Sci. Forum 357–359 (2001) 3.
[7] T.G. Langdon, Mater. Sci. Forum 304–306 (1999) 13.
[8] K. Hiraga, Mater. Sci. Forum 357–359 (2001) 345.
[9] M.F. Ashby, A. Verral, Acta Metall. 21 (1973) 149.
[10] R.C. Gifkins, Mater. Sci. 13 (1978) 1926.
[11] F. Wakai, Y. Shinoda, S. Ishihara, A. Dominguez-Rodriguez, Acta Mater. 50 (2002) 1177.
[12] I.-W. Chen, L.-A. Xue, J. Am. Ceram. Soc. 73 (1990) 2585.
[13] S.-L. Hwang, I.-W. Chen, J. Am. Ceram. Soc. 73 (1990) 3269.
[14] A.G. Evans, J.R. Rice, J.P. Hirth, J. Am. Ceram. Soc. 63 (1980) 368.
[15] H. Riedel, Fracture at High Temperatures, Springer, Berlin, 1987.
[16] D.J. Schissler, A.H. Chokshi, T.G. Nieh, J. Wadsworth, Acta Metall. Mater. 39 (1991) 3227.
[17] Y. Yoshizawa, T. Sakuma, Mater. Sci. Eng. A 149 (1991) 59.
[18] Y. Yoshizawa, T. Sakuma, Acta Metall. Mater. 40 (1992) 2943.
[19] A.H. Chokshi, T.G. Nieh, J. Wadsworth, J. Am. Ceram. Soc. 74 (1991) 869.
[20] Y. Ma, T.G. Langdon, Acta Metall. Mater. 42 (1994) 2753.
[21] D.M. Owen, A.H. Chokshi, S.R. Nutt, J. Am. Ceram. Soc. 80 (1997) 2433.
[22] K. Hiraga, K. Nakano, Mater. Sci. Forum 243–245 (1997) 387–392.
[23] S. Takeli, T.J. Davies, Scr. Mater. 39 (1998) 119.
[24] K. Hiraga, K. Nakano, T.S. Suzuki, Y. Sakka, Scr. Mater. 39 (1998) 1273.
[25] Z.C. Wang, N. Ridley, T.J. Davies, J. Mater. Sci. 34 (1999) 2695.
[26] K. Hiraga, K. Nakano, T.S. Suzuki, Y. Sakka, J. Am. Ceram. Soc. 85 (2002) 2763.
[27] K. Hiraga, K. Nakano, Z. Metallkd. 95 (2004) 559.
[28] F. Wakai, H. Kato, Adv. Ceram. Mater. 3 (1998) 71.
[29] K.S. Chan, R.A. Page, J. Am. Ceram. Soc. 76 (1993) 803.
[30] K. Hiraga, B.-N. Kim, K. Morita, T.S. Suzuki, Y. Sakka, J. Ceram. Soc. Jpn. 113 (2005) 191.
[31] Y. Sakka, Y. Oishi, K. Ando, S. Morita, J. Am. Ceram. Soc. 74 (1991) 2610.
[32] T. Sakuma, Adv. Quantum Chem. 42 (2003) 23.
[33] A. Kuwabara, M. Nakano, H. Yoshida, Y. Ikuhara, T. Sakuma, Acta Mater. 52 (2004) 5563.
[34] A. Kuwabara, S. Yokota, Y. Ikuhara, T. Sakuma, Mater. Trans. 45 (2004) 2144.
[35] H. Yoshida, J. Ceram. Soc. Jpn. 114 (2005) 155.
[36] K. Hiraga, K. Nakano, T.S. Suzuki, Y. Sakka, Mater. Sci. Forum 304–306 (1999) 431.
[37] W. Hancock, Met. Sci. 10 (1976) 319.
[38] M.A. Clark, T.H. Alden, Acta Metall. 21 (1973) 1195.
[39] D.S. Wilkinson, C.H. Caceres, Acta Metall. 32 (1984) 1335.
[40] O.N. Senkov, M.M. Myshlaev, Acta Metall. 34 (1986) 97.
[41] E. Sato, K. Kuribayashi, R. Horiuchi, J. Jpn. Inst. Met. 52 (1988) 1043.
