Development of High-Strain-Rate Superplastic Oxide Ceramics

Keijiro HIRAGA
National Institute for Material Science, 1–2–1, Sengen, Tsukuba-shi, Ibaraki 305–0047

Examinations of factors limiting the strain rate available to superplastic deformation lead to the following guide: simultaneously controlling the initial grain size, diffusivity, dynamic grain growth, homogeneity of microstructure and the number of residual defects is essential to heighten the strain rate available to superplastic deformation in oxide ceramics. Along this guide, high-strain-rate superplasticity (HSRS) is attained in materials consisting of tetragonal zirconia, α-alumina and a spinel phase: tensile ductility reached 300–2500 % at a strain rate of 0.01–1.0 s⁻¹. Post-deformation microstructure indicates that some secondary phases may suppress cavitation damage and thereby enhance HSRS. The guide is also effective in lowering the limit of deformation temperature for a given strain rate. In monolithic tetragonal zirconia, size refinement combined with doping of aliovalent cations such as Mg²⁺, Ti⁴⁺ and Al³⁺ led to HSRS at 1350°C.

Key-words: High-strain-rate, Superplasticity, Grain-boundary sliding, Accommodation, Stress relaxation, Intergranular cavitation, Dynamic grain growth

1. Introduction

SUPERPLASTICITY, defined as the ability of a material to sustain large tensile elongation, provides an attractive route for net-shape forming or joining of materials. In ceramic materials, this ability was first discovered by Wakai et al. and this discovery was followed by the demonstrations of superplastic bulging, forging and joining in zirconia- and alumina-base materials. Industrial applications, however, have still been limited, in contrast to superplastic metallic materials. One of the major causes of this situation is the limited strain rate available to superplastic forming: superplasticity in most ceramics appears at a strain rate around 10⁻³–10⁻⁴ s⁻¹ even at high temperatures around 1400–1650°C. Estimation given in Table 1 indicates that, at a strain rate of 10⁻⁴ 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 long forming time is unattractive in industry. The deformation time can drastically be reduced to 2 minutes or less, when the material is formable at a strain rate higher than 10⁻² s⁻¹. In metallic materials, superplasticity at 10⁻² s⁻¹, namely high-strain-rate superplasticity (HSRS) has been a key to commercial net-shaping and is also the case in ceramic materials. The present paper describes the necessary conditions in microstructures and processing for attaining HSRS in ceramic materials and reviews the recent attainment of HSRS in oxide ceramics.

2. Necessary conditions for attaining HSRS

2.1 Conventional creep equation

According to widely accepted recognition, ceramic grains are rigid, and accordingly the combination of grain-boundary sliding and grain switching accommodated by diffusion (Fig. 1) 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 the intergranular cavitation damage that will later be described. For such an ideal case, deformation can be described by the following conventional creep equation.

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

where \(\dot{\varepsilon}\) is the strain rate, \(A\) is a material constant, \(Q\) is the 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) tells that the strain rate can be heightened by a reduction in the grain size. For example, a grain size reduction to 0.32–0.46 mm for a typical value of 2–3 increases the strain rate by a factor of 10. The equation also indicates that an increase in the \(A \exp (-Q/RT)\) term, which means enhanced diffusion along grain-boundaries and/or within grains, heightens the strain rate. Enhanced diffusion is empirically known to arise from doping of some aliovalent cations and relates closely to grain growth and stress relaxation during deformation.

In actual ceramic materials, the combination of grain-boundary sliding, grain switching and accommodation processes does not take place ideally. We should also note that Eq. (1) does not give any information on microstructural change during deformation. Superplastic deformation is inherently accompanied by accelerated grain growth (dynamic grain growth) and intergranular cavitation. The former increases the level of flow stress for a given strain...
rate and enhances the latter. Since cavitation damage leads to premature failure and degradation in post-deformation strengths,\textsuperscript{29} consideration to these dynamic phenomena is essential for attaining HSRS and industrial applications.

2.2 Intergranular cavitation

Knowledge of intergranular cavitation has particular importance to the present issue. Existing theories\textsuperscript{36-38} indicate that cavities nucleate 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 compositions. For this reason, stress distribution and chemical potential, and hence grain-boundary sliding and grain switching coupled with diffusion flux are also inhomogeneous in a microscopic scale. There is consequently a finite probability of the breakdown of the accommodation processes, particularly in some localized portions where the geometry and the chemical composition are steeply changed. This means equivalently that in such portions, stress concentrations caused by grain-boundary sliding cannot always be relaxed sufficiently by diffusion. Typical examples of such portions are multiple grain junctions and phase boundaries, where cavity nuclei have frequently been observed after superplastic deformation (Figs. 2(a) and 2(b)).

Although the detailed relationship among diffusion, stress concentrations, stress relaxation, cavity nucleation has not been established yet in superplastic ceramics, estimation\textsuperscript{39} is possible of the relaxation length, $L$, over which grain-boundary diffusion relieves the stress concentrations caused by deformation obeying Eq. (1). As shown in Fig. 3, there are three representatives in 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 a model\textsuperscript{20} for stress relaxation by grain boundary diffusion and assuming an aggregate of a tetrakaidecahedron having a facet length of $e = d / 3$, we can calculate the critical situation of Fig. 3(b), for which $d_c = 3e = A$.\textsuperscript{29} Taking the diffusion data for a Ce-doped tetragonal $\text{ZrO}_2$\textsuperscript{30} and assuming $n = 3$ and $\sigma = 30$ MPa, we obtain Fig. 4.

Figure 4 gives the following prediction for attaining sufficient stress relaxation. First, the critical grain size for a given temperature decreases steeply with an increase in the strain rate. The estimation indicates that the critical grain size at $T = 1400^\circ$C is 0.26 $\mu$m at $10^{-4}$ s$^{-1}$ for ordinary superplasticity, whereas the size is reduced to 0.06 $\mu$m at $10^{-2}$ s$^{-1}$ for HSRS. Second, for a fixed critical grain size, the critical temperature, $T_c$, above which stress relaxation becomes sufficient, increases with increasing strain rate. For $d_c = 0.2 \mu$m, for example, $T_c$ increases from 1400 to 1600$^\circ$C as the strain rate increases from about $2 \times 10^{-4}$ to $10^{-2}$ s$^{-1}$. Finally, enhanced diffusion increases the critical grain size for a given strain rate. Figure 4 predicts that when the grain boundary diffusivity, $\delta D_b \propto \exp (-Q/RT)$, increases by a factor of 50 at 1400$^\circ$C, the critical size increases from 0.06 $\mu$m to 0.2 $\mu$m at $10^{-2}$ s$^{-1}$. The estimation also shows that the enhanced diffusion by a factor of 10 and 50 corresponds to an increase in the temperature by about 100$^\circ$C and 200$^\circ$C, respectively. For 50 $\delta D_b$, stress relaxation at $10^{-2}$ s$^{-1}$ is expected to become sufficient for $d = 0.2 \mu$m even at 1400$^\circ$C. Thus, the estimation of the critical grain size gives the following guide for attaining HSRS. Grain-size reduction and suppressed grain growth are essential for sufficient stress relaxation and hence suppressed cavity nucleation during high-strain-rate deformation. For attaining HSRS at a lower temperature, enhanced diffusion is indispensable.

The existing models\textsuperscript{26-28} also predict the following relationship between cavity nucleation and material parameters. The probability of cavity nucleation depends on the grain-boundary diffusivity, the surface energy, $\gamma_s$, the 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 $\delta D_g$ and $\gamma$, and with decreasing $\gamma_c$. Despite such knowledge about cavity nucleation, information has still been limited or empirical on the relationship among these parameters, chemical compositions and minor additives. As noted elsewhere, a recent approach developed on the basis of a first-principle molecular-orbital calculation is expected to give a new aspect to this issue. The final point of cavity nucleation is the level of flow stress. Since the rate of nucleation depends on $\exp(-1/\sigma^2)$, reduction in the flow stress level is of particular importance.

During superplastic deformation, nanometer-sized cavity nuclei and defects remaining after sintering grow into micrometer-sized voids (Fig. 2(c)). In zirconia-base and alumina-base materials, it has been found that the growth of the micrometer-sized voids obeys $dD/dz = \eta D$, 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, that is, the increment of the void size is determined by the increment of plastic strain. Accordingly, the void growth can hardly be controlled by the modifications of chemical compositions and microstructure. The growing voids interlink to each other, resulting in cracking in the direction perpendicular to the stress axis and premature failure. For suppressing damage accumulation by the void growth, it is necessary to reduce the number of residual defects in the sintered body and to suppress cavity nucleation during deformation.

2.3 Dynamic grain growth

Suppressed grain growth is necessary to keep the flow stress in a low level (Eq. (1)). A low stress level is essential to suppressed cavity nucleation and industrial plastic forming. A model derived from a diffusion mechanism gives the following equation for usual tensile under constant displacement-rate loading:

$$d^m - d_0^m = kt,$$

where $d_0$ is the initial grain size, $\dot{\varepsilon}$ is the initial strain rate, $\alpha$ is a constant depending on the grain shape and the grain-size distribution, $m$ and $k$ are the grain-growth exponent and the kinetic constant, respectively, of the static grain-growth law, and $t$ is the heating time. Equation (2) predicts that the grain size for a given strain becomes smaller with a reduction in the initial size and an increase in the deformation rate. In addition, experimental data indicate that the value of $\alpha$ for superplastic deformation is rather insensitive to chemical compositions: about 0.5–0.6 for some oxide materials ($\text{ZrO}_2$–$\text{Al}_2\text{O}_3$), ($\text{ZrO}_2$–$\text{MgAl}_2\text{O}_4$–$\text{Al}_2\text{O}_3$), ($\text{ZrO}_2$–$\text{Y}_2\text{O}_3$) and superplastic metals ($\text{Zn–Al}$). Such data and Eq. (2) indicate that the outline 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 is expected in a microstructure consisting of three or more phases where the amount of each phase is similar. Such a multi-phase structure decreases the frequency of the grain boundaries between the same phases or increases the separation distance between the phases. This situation is of benefit to suppressed grain growth, since grain growth occurs by the migration of such grain boundaries and/or by the ripening of grains through interphase boundary diffusion.

2.4 Microstructural design for attaining HSRS

From the above-described discussion, factors necessary or desirable for attaining HSRS are extracted in the first column of Table 2. The second column summarizes the relationship between these factors and superplastic deformation or cavitation. The third column indicates the dependence of these factors on processing (P), chemical compositions (C) and phases (Ph). For a given combination of chemical compositions and phases, factors (a), (b), (d) and (e) are strongly processing-dependent, particularly in composites. Even for a fixed combination of chemical composition and grain size, superplastic properties may be different. A typical example has been found in 10-vol% $\text{ZrO}_2$-dispersed $\text{Al}_2\text{O}_3$ fabricated from the same raw materials. Tensile ductility for an initial grain size of 0.45 $\mu$m was a factor of $\sim 2.0$ larger in a material prepared by colloidal processing than in a material prepared by conventional dry processing. This result can be attributed to a difference in the size distributions of fine defects and dispersed $\text{ZrO}_2$ particles. The former affects the accumulation of micrometer-sized voids and the latter concerns the rate of cavity nucleation through the rate of dynamic grain growth.

In Table 2, we should also note that some factors may 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 for cavity nucleation. A solution of this problem is the grain-size refinement of the second phase or of both the second and matrix phases, namely a decreased distance that should be relaxed by diffusion (Figs. 3 and 4). A minor additive that enhances diffusion also appears to bring about conflicting effects: the additive should simultaneously enhance stress relaxation and dynamic grain growth. Discussion about Eq. (2) indicates, however, that the weight of this problem is reduced as the strain rate is heightened and grain-size refinement combined with second-phase pinning may give a solution. Factors (a), (c) and (g) listed in Table 2 may have been noted in studies on conventional superplasticity, whereas there have still been very limited studies that consider factors (a) through (h) simultaneously. The present discussion indicates that simultaneously controlling these factors is essential to attain HSRS.

3. Earlier studies in the light of Table 2

Substantial high-strain-rate superplasticity, namely tensile elongation exceeding 200% at a strain rate of $\geq 10^{-4}$ s$^{-1}$, was reported by Chokshi et al. for a commercial 20-mass%...
Development of High-Strain-Rate Superplastic Oxide Ceramics

Table 2. Necessary Conditions for Attaining High-Strain-Rate Superplasticity

<table>
<thead>
<tr>
<th>prerequisite</th>
<th>relationship with superplastic deformation or cavitation</th>
<th>note*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) reduced initial grain size</td>
<td>Strain rate, stress relaxation, cavity nucleation (processing-dependent)</td>
<td>P, C, Ph</td>
</tr>
<tr>
<td>(b) suppressed dynamic grain growth</td>
<td>Stress concentrations, cavity nucleation (second-phase pinning and dragging; processing-dependent)</td>
<td>P, C, Ph</td>
</tr>
<tr>
<td>(c) enhanced diffusivity</td>
<td>Strain rate, stress relaxation, cavity nucleation (doping of aliovalent cations)</td>
<td>C, Ph</td>
</tr>
<tr>
<td>(d) homogeneous microstructure</td>
<td>dynamic grain growth, cavity nucleation (processing-dependent)</td>
<td>P, Ph</td>
</tr>
<tr>
<td>(e) reduced residual defects</td>
<td>damage due to micrometer-sized cavities (processing-dependent)</td>
<td>P, C, Ph</td>
</tr>
<tr>
<td>(f) low γb and high γs</td>
<td>cavity nucleation (grain-boundary segregation)</td>
<td>C, Ph</td>
</tr>
<tr>
<td>(g) enhanced accommodation (by a viscous phase)</td>
<td>cavity nucleation (glass-phase dispersion, intergranular Si segregation)</td>
<td>C, Ph</td>
</tr>
<tr>
<td>(h) additional accommodation (by limited intragranular plasticity**)</td>
<td>cavity nucleation (relates to (c) and (d))</td>
<td>C, Ph</td>
</tr>
</tbody>
</table>

* dependence on processing (P), chemical compositions (C) and phases (Ph).

** see section 4.4.

Table 3. Oxide Ceramics Exhibiting High-Strain-Rate Superplasticity

<table>
<thead>
<tr>
<th>Material</th>
<th>Prerequisites</th>
<th>ε₀×10⁻⁴</th>
<th>ε₁ × 10⁻⁴</th>
<th>T /°C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Al₂O₃-ZrO₂(3Y)</td>
<td>(b), (c)</td>
<td>0.04</td>
<td>300</td>
<td>1650</td>
<td>17</td>
</tr>
<tr>
<td>5SiO₂-ZrO₂(2.5Y)</td>
<td>(b), (c)-(g)</td>
<td>0.01</td>
<td>360</td>
<td>1400</td>
<td>39</td>
</tr>
<tr>
<td>2CaO·2TiO₂-ZrO₂(3Y)</td>
<td>(b), (c)</td>
<td>0.01</td>
<td>400</td>
<td>1400</td>
<td>40</td>
</tr>
<tr>
<td>0.2Al₂O₃-ZrO₂(3Y)</td>
<td>(a), (c)-(e)</td>
<td>0.03</td>
<td>370</td>
<td>1450</td>
<td>41</td>
</tr>
<tr>
<td>3(Y₂O₃,MgO)-97(ZrO₂,TiO₂)</td>
<td>(a), (c)-(e)</td>
<td>0.01</td>
<td>220</td>
<td>1350</td>
<td>48</td>
</tr>
<tr>
<td>0.2MnO₀·0.3Al₂O₃-ZrO₂(3Y)</td>
<td>(a), (c)-(e)</td>
<td>0.01</td>
<td>600</td>
<td>1450</td>
<td>49</td>
</tr>
<tr>
<td>40ZrO₂(3Y)-30MgAl₂O₄</td>
<td>(a)-(d), (h)²</td>
<td>0.01</td>
<td>500</td>
<td>1500</td>
<td>50-52</td>
</tr>
<tr>
<td>1.0</td>
<td>2500</td>
<td>1650</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30Al₂O₃-ZrO₂(3Y)</td>
<td>(a)-(d), (h)²</td>
<td>0.02</td>
<td>660</td>
<td>1450</td>
<td>53-56</td>
</tr>
<tr>
<td>0.7</td>
<td>250</td>
<td>1550</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a mass%, b mol%, c vol%. d See Table 2.

Al₂O₃-dispersed ZrO₂(3Y), by Kajihara et al.39 for a 5-mass%-SiO₂-doped ZrO₂(2.5Y) and by Oka et al.40 for a ZrO₂(3Y) co-doped 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 a particular advantage for HSRS, since grain growth in Y-TZP is inherently sluggish as compared to that in other materials such as Ce-TZP, cubic zirconia and alumina.42 In the light of Table 2, the materials have additional advantages for attaining HSRS, which are noted in Table 3.

In the Al₂O₃-dispersed ZrO₂, the Al₂O₃ particles may contribute not only to suppressing grain growth, but also to enhancing diffusion through supplying Al¹⁺ to the ZrO₂ matrix. The latter effect is supported by studies41-43 on Y-TZP doped with a small amount of Al¹⁺. The doping of SiO₂ introduces the segregation of Si⁴⁺ along grain boundaries and a glass phase at multiple junctions.44 A study45 on tensile creep in 3Y-TZP containing small amounts of SiO₂, for which the glass phase are absent, shows that the segregation heightens the strain rate for a given stress, that is, enhances superplastic deformation. A molecular-orbital calculation46 indicates that the Si-segregation should strengthen the grain-boundary bonding in Y-TZP and thereby enhance superplastic tensile ductility. In the cavitation mechanisms, this explanation may correspond to an increase in γₗ and/or a decrease in γₘ, both of which should lead to suppressed cavity nucleation. In addition, the viscous flow of the glass phase may suppress stress concentrations around the multiple junctions and hence
cavity nucleation. It should also be noted that the dispersion of the glass phase suppresses grain growth.\textsuperscript{44,47}

The co-doping of CaO and TiO\textsubscript{2} is probably the first example of a design of chemical compositions aiming to attain HSRS in a ceramic material. The following merits were expected in the co-doping: suppressed grain growth due to dragging from Ca\textsuperscript{2+} and enhanced diffusion from Ti\textsuperscript{4+}.\textsuperscript{46} The co-doping resulted in a dual-phase structure consisting of 22 vol\% cubic and 78\% tetragonal phases and led to HSRS. It is not clear whether the dispersed cubic phase may play a positive or negative role in HSRS. Inspection of the earlier data thus indicates that, of the factors listed in Table 2, four or more should be simultaneously satisfied for attaining HSRS.

4. Development of new HSRS materials

4.1 Processing

Placing special attention on factors (a) through (e) of Table 2, we synthesized monolithic\textsuperscript{41,48,49} and composite\textsuperscript{37,50–56} materials, without using glassy phases. We also noted that factors (a), (b), (d) and (e) are processing dependent. This is particularly the case when fine powders were used. Fine powders tend to agglomerate spontaneously owing to van der Waals forces.\textsuperscript{57} The agglomeration forms large pores in green bodies and the pores cannot be eliminated by sintering at a lower temperature. To prevent agglomeration, we applied colloidal processing\textsuperscript{58} to fine oxide powders.

4.2 Monolithic Zirconia

Since grain-growth is inherently sluggish in Y-TZP, factors (a), (c), (d), (e) and (f) are the keys for attaining HSRS. Of these factors, we tried to control (a) and (c) through (e). To enhance diffusion, we doped or co-doped aliovalent cations using commercial high-purity powders of α-Al\textsubscript{2}O\textsubscript{3},\textsuperscript{47} Mn\textsubscript{3}O\textsubscript{4}\textsuperscript{6+} and MgO.\textsuperscript{48} We also used TiO\textsubscript{2},\textsuperscript{49} since earlier data\textsuperscript{59} for grain growth and superplastic properties indicate that diffusion in Y-TZP is enhanced by TiO\textsubscript{2} addition. For the TiO\textsubscript{2}-addition, we co-doped MgO aiming at the stabilization of the tetragonal phase. Using colloidal processing followed by sintering at 1300°C for 2 h, almost fully dense bodies were obtained in an Al\textsubscript{2}O\textsubscript{3}-doped 3Y-TZP and a Y-TZP co-doped with TiO\textsubscript{2} and MgO or with Mn\textsubscript{3}O\textsubscript{4} and Al\textsubscript{2}O\textsubscript{3} (Table 3). The sintered materials consisted of a single tetragonal phase with an average grain size of 0.23 μm, where the size was defined as 1.56 times the average intercept length of the grains. Examinations of sintering behavior and the rate of static grain-growth confirmed enhanced diffusion. As listed in Table 3, the synthesized materials exhibited HSRS at around 1400°C and at a rate of the order of 10\textsuperscript{-2} s\textsuperscript{-1}. By the co-doping of TiO\textsubscript{2} and MgO, the deformation temperature can be lowered to 1350°C. This is the lowest temperature that has reported for HSRS in tension and the temperature locates in a lower limit even for conventional superplasticity in Y-TZP. A maximum tensile elongation of 660% was obtained by co-doping of Mn\textsubscript{3}O\textsubscript{4} and Al\textsubscript{2}O\textsubscript{3}.

4.3 Composite materials

The following merits can be expected in composite materials: strongly suppressed grain growth and improved fracture strengths.\textsuperscript{50} When Y-TZP is dispersed in the composites, transformation toughening can be expected below the transformation temperature. Despite these merits, grain-boundary pinning may simultaneously work to 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 raw materials is of particular importance, since it enables us to sinter the material at a lower temperature. Of the factors listed in Table 2, we thus tried to control (a), (c), (d) and (e). We examined second-phase pinning and a tri-phase structure where the volume fraction of each phase was similar. In such a structure, we can expect strongly suppressed grain growth, as described before. For a large amount of second-phase dispersion, for which clustering of the phase is unavoidable, we used such a secondary phase that exhibits superplastic or superplastic-like deformation. From these considerations, we synthesized materials consisting of tetragonal Zr\textsubscript{2}O\textsubscript{3}, α-Al\textsubscript{2}O\textsubscript{3} and MgO–Al\textsubscript{2}O\textsubscript{3}-spinel, where MgO–Al\textsubscript{2}O\textsubscript{3}-spinel is expected to supply Al\textsuperscript{3+} and Mg\textsuperscript{2+} to the ZrO\textsubscript{2} phase and Mg\textsuperscript{2+} to the Al\textsubscript{2}O\textsubscript{3} phase.

We prepared 30 vol% MgAl\textsubscript{2}O\textsubscript{4}–ZrO\textsubscript{2} (3Y)\textsuperscript{53–56} and 40 vol% ZrO\textsubscript{2} (3Y)–30 vol% (MgO–1.1Al\textsubscript{2}O\textsubscript{3})–Al\textsubscript{2}O\textsubscript{3}\textsuperscript{50–52} from commercial powders. In the former, we applied colloidal processing to MgAl\textsubscript{2}O\textsubscript{4} and ZrO\textsubscript{2} (3Y) powders. In the latter, we applied conventional processing to ZrO\textsubscript{2} (3Y), MgO and Al\textsubscript{2}O\textsubscript{3} powders. Sintering at 1400°C for 1–2 h resulted in densified bodies with grain sizes of 0.29 μm (ZrO\textsubscript{2}) and 0.42 μm (MgAl\textsubscript{2}O\textsubscript{4}) for the dual-phase composite and 0.28 μm (ZrO\textsubscript{2} and spinel) and 0.45 μm (α-Al\textsubscript{2}O\textsubscript{3}) for the tri-phase composite. In the latter material the spinel phase was formed by chemical reaction between the MgO and Al\textsubscript{2}O\textsubscript{3} powders. The grain size of each phase becomes smaller than that obtained by the sintering of each phase alone, particularly in the Al\textsubscript{2}O\textsubscript{3} and spinel phases. The composite materials sustained noticeably high strain rates (10\textsuperscript{-1}–10\textsuperscript{-3} s\textsuperscript{-1}) and large tensile elongation (390–2500%).\textsuperscript{50,51} As plotted in Fig. 5, the developed monolithic and composite materials attain superplasticity at higher strain-rates as compared to the conventional and HSRS materials reported in the earlier studies.\textsuperscript{11,32,35–39,21–25,32–34,39,40,41}

4.4 New aspects found in the developed materials

The tensile data of Fig. 5 show a difference between the monolithic materials and the composites. The former locate in a region of lower temperature, strain rate and tensile ductility, whereas the latter in a region of higher temperature, strain rate and ductility. The difference may relate to the balance among the resistance against grain growth, resistance against grain-boundary sliding and diffusivity. Further grain-size refine-
Acknowledgements  The author is deeply grateful to Dr. B-N. Kim, Dr. K. Morita, Dr. T. S. Suzuki, Dr. Y. Sakka and Mr. K. Nakano for their contributions to this work. He also thanks to Dr. T. Tanabe, Prof. H. Vehoff of Universität des Saarlandes and Prof. P. Neumann of Max-Planck-Institut für Eisenforchung who encouraged him to study high-temperature deformation and failure mechanisms.

References


