Microstructural Design for High-Strain-Rate Superplastic Oxide Ceramics

Keihiro HIRAGA, Byung-Nam KIM, Koji MORITA, Tohru S. SUZUKI and Yoshio SAKKA

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

酸化物系高速超塑性セラミックスの組織設計

平賀啓二郎・金 炳男・森田孝治・鈴木 達・目 義雄

物質・材料研究機構材料研究所, 305-0047 つくば市千現 1-2-1

Factors limiting the strain rate available to superplastic deformation in oxide ceramics are discussed from existing knowledge about high-temperature plastic deformation and cavitation mechanisms. Simultaneously controlling these factors is essential for attaining high-strain-rate superplasticity (HSRS). This is shown in monolithic tetragonal zirconia and composite materials consisting of zirconia, α -alumina and a spinel phase: at strain rates higher than 10^{-2} s^{-1} , tensile ductility reached 300–600% in the monolithic material and 600–2500% in the composite materials. Post-deformation microstructure indicates that certain secondary phases should be effective in suppressing cavitation damage and thereby enhancing HSRS.

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1. Introduction

Substantial superplasticity is defined as the ability of a material to exhibit tensile ductility (elongation) larger than 200%, where the ductility is defined as $e_f = 100(l_f - l_0)/l_0$ for the initial (l_0) and the final (l_f) lengths of the material. In ceramic materials, this ability was first found by Wakai *et al.*¹⁾ and has provided a unique opportunity of net shaping and joining of non-metallic materials. In ceramic materials, however, industrial applications of superplasticity have been highly limited, in contrast to superplastic metallic materials.^{2)–4)} This is because superplasticity in most ceramics occurs at low strain rates around $10^{-5} - 10^{-4} \text{ s}^{-1}$ even at high temperatures of 1400–1650°C. At a strain rate of 10^{-4} s^{-1} , for example, it takes about 2.8 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 unallowable in industry. The forming time can be reduced to shorter than 100 s, when the material is formable at a strain rate higher than 10^{-2} s^{-1} . In metallic materials, superplasticity at a strain rate higher than 10^{-2} s^{-1} , namely high-strain-rate superplasticity (HSRS) is a key of commercial net-shaping,^{3),4)} and so should be in ceramic materials.

This paper addresses HSRS in oxide ceramics and discusses earlier and recent results obtained in this field. First, factors necessary for attaining HSRS are extracted from existing knowledge about superplasticity and relating phenomena. In the light of the extracted factors, discussion is given to the results of earlier studies on superplastic oxides. Finally, an overview of our recent trials is given with discussion about some noticeable aspects newly found in the trials.

2. Prerequisites for attaining HSRS in oxide ceramics

2.1 Creep equation

Since a ceramic material can be regarded as an aggregate of rigid grains, a couple of grain-boundary sliding and grain switching accommodated by diffusion (Fig. 1) has been regarded as the main mechanism of superplastic deformation.^{5),6)} If the processes of accommodation occur ideally uniform and successive, then superplastic deformation takes place also uniformly and successively without intergranular

Fig. 1. A 2-D model⁷⁾ for grain-boundary sliding and grain switching during superplastic deformation.

cavitation. For such an ideal case, the conventional creep equation (Eq. (1)) tells that the strain rate, $\dot{\epsilon}$, for a given combination of stress, σ , and temperature, T , can be heightened by a reduction in the grain size, d , and an increase in the $A \exp(-Q/RT)$ term.

$$\dot{\epsilon} = A \exp(-Q/RT) \sigma^n d^{-p}, \quad (1)$$

where A is a material constant, Q is the activation energy, R is the gas constant, n is the stress exponent and p is the grain-size exponent. An increase in $A \exp(-Q/RT)$ can be attained by enhanced grain-boundary and/or lattice diffusion; doping of some aliovalent cations is empirically known to be effective for this purpose.

In actual materials, however, the accommodation processes do not take place ideally. We should also note that Eq. (1) does not give any information on the following dynamic phenomena. Superplastic deformation is inherently accompanied by accelerated grain growth (dynamic grain growth)⁸⁾ and intergranular cavitation.^{9)–12)} The former increases the stress level for a given strain rate and enhances the latter, leading to premature failure and degradation in post-deformation strengths.¹³⁾ Consideration to these phenomena is essential for the attainment of HSRS and its application.

2.2 Stress concentrations and cavity nucleation

Existing theories and models for intergranular cavitation^{14),16)} tell that cavity nucleation occurs owing to stress concentrations that relate closely to the inhomogeneity of

Fig. 2. Cavitation damage accompanying superplastic tensile deformation in a 10 vol% ZrO_2 (3Y) dispersed Al_2O_3 : (a) cavity nucleation at multiple junctions and phase boundaries and (b) microcracking due to coalescence of micrometer-sized voids grown from cavity nuclei and preexistent defects. Tensile axis is horizontal.

microstructures and chemical compositions. Even in a monolithic material, there are distributions of grain size, grain shape and chemical composition. Owing to this fact, stress distribution and chemical potential, and hence grain-boundary sliding and grain switching coupled with diffusion also become 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 situation means equivalently that in such portions, stress concentrations caused by grain-boundary sliding cannot always be relaxed sufficiently by diffusion.^{14),15)} Typical examples of such portions are multiple grain junctions and phase boundaries, where cavity nuclei have frequently been observed after superplastic deformation (Fig. 2(a)).

Although the detailed relationship among stress concentrations or relaxation, diffusion and cavity nucleation has not been established yet in superplastic ceramics, estimation is available to this issue. For an aggregate of a tetrakaidecahedron having a facet length of $d/3$, the existing models give the following estimation to the critical grain size, d_c , that can be relaxed by grain-boundary diffusion. We define the critical size as $d_c = 3\Lambda$, where Λ is given by Eq. (2) and represents the length over which grain-boundary diffusion relaxes the stress concentrations caused by deformation.¹⁴⁾

$$\frac{\Lambda}{d} = \left(\frac{L}{d} \right)^{\frac{1}{[1-s(n-1)/3]}}, \quad (2)$$

where L is the characteristic diffusive length given by Eq. (3) and s is the extent of stress singularity at the triple point.

Fig. 3. Estimation of the critical grain size over which grain-boundary diffusion can relax stress concentrations caused by deformation.

$$L = \left(\frac{\delta D_{gb} \sigma \Omega}{k_B T \dot{\epsilon}} \right)^{1/3}, \quad (3)$$

where $\delta D_{gb} \propto \exp(-Q/RT)$ is the grain-boundary diffusion coefficient, Ω is the atomic volume and k_B is the Boltzmann constant. Using the diffusion data for a Ce-doped tetragonal ZrO_2 ¹⁷⁾ and assuming $n=3$, $\sigma=30$ MPa and a dihedral angle of 120° , for which s becomes 0.45, we obtain Fig. 3. When d_c is smaller than the grain size, stress relaxation becomes insufficient, leading to active cavity nucleation. In an extreme case of $d \gg d_c$ at large σ , instantaneous de-bonding may occur at grain-boundaries or interfaces.

Figure 3 indicates that the critical grain size decreases steeply with an increase in the strain rate. At 1400°C , for example, the estimation predicts that a grain size of $0.26 \mu\text{m}$ is sufficient to obtain ordinary superplasticity at 10^{-4} s^{-1} , whereas a grain size of $0.06 \mu\text{m}$ is necessary to attain HSRS at 10^{-2} s^{-1} . For a grain size of $0.2 \mu\text{m}$, a temperature higher than 1600°C is necessary to attain 10^{-2} s^{-1} . Grain-size reduction and suppressed grain growth are thus essential for sufficient stress relaxation and suppressed cavity nucleation during high-strain-rate deformation. The estimation also indicates that an increase in the diffusivity by a factor of 10 and 50 corresponds to an increase in the temperature by about 100°C and 200°C , respectively. In the latter, stress relaxation at 10^{-2} s^{-1} is expected to become sufficient for $d=0.2 \mu\text{m}$ even at 1400°C . Thus, enhanced diffusion for a given grain size is also essential for attaining HSRS at a lower temperature.

The existing models¹⁴⁾⁻¹⁶⁾ also predict the following characteristics of cavity nucleation. The probability of cavity nucleation depends on the level of flow stress, the grain-boundary diffusivity, the surface energy γ_s , the grain-boundary energy γ_b and geometrical factors such as the dihedral angle between the grain facets. For a given grain size, for example, the probability of cavity nucleation decreases with increasing δD_b and γ_s and with decreasing σ and γ_b . Since the rate of nucleation depends on $\exp(-1/\sigma^2)$, reduction in the flow stress level is of particular importance.

2.3 Cavity growth and tensile failure

During superplastic deformation, fine defects remaining after sintering and cavity nuclei grow into micrometer-sized voids (Fig. 2), and the interlinkage of the voids causes cracking along a direction perpendicular to the stress axis (Fig. 2(b)).^{9),10),12),18)} In this process, there appears a close similarity

to that of ductile failure in metallic materials containing microvoids or hard inclusions.¹⁸⁾

In zirconia¹⁹⁾ and alumina-based^{12),19),20)} materials, the growth of micrometer-sized voids has been observed to obey $dD/d\varepsilon = \eta D$, where D is the cavity diameter and η is a constant taking a value of about unity. This growth law means that the voids are grown by the plastic flow of the material.^{14),21)} Such a plastic 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 mechanism, the increment of void volume during deformation is determined by the increment of plastic strain. For this reason, the void growth can hardly be controlled by the modifications of chemical compositions and microstructure. For the suppression of damage accumulation arising from the void growth, it is essential to reduce the number of residual defects in the sintered body and to suppress cavity nucleation during deformation.

2.4 Dynamic grain growth

The major importance of suppressed grain growth is to keep the flow stress in a low level during superplastic loading (Eq. (1)). A lowered level of flow stress is necessary for suppressed cavity nucleation as described above. A model²²⁾ derived from a diffusion mechanism gives the following equation for constant displacement-rate loading.¹²⁾

$$d = \left[d_0^m \exp(\alpha m \varepsilon) + \frac{k \{ \exp(\varepsilon) - \exp(\alpha m \varepsilon) \}}{\varepsilon_0 (1 - \alpha m)} \right]^{1/m}, \quad (4)$$

where d_0 is the initial grain size, α 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, $d^m - d_0^m = kt$, where t is the heating time. Equation (4) indicates 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 α for superplastic deformation is rather insensitive to chemical compositions: about 0.5–0.6 for some oxide materials ($\text{ZrO}_2\text{--Al}_2\text{O}_3$,^{12),22)} $\text{ZrO}_2\text{--MgAl}_2\text{O}_4\text{--Al}_2\text{O}_3$,²³⁾ $\text{ZrO}_2(3\text{Y})$ ²⁴⁾) and superplastic metals (Zn--Al)²²⁾). The outline of dynamic grain-growth can thus 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.

2.5 Minor additives

In superplastic ceramics, deformation behavior and tensile ductility are known to be sensitive to some minor additives or impurity elements.^{25)–27)} This fact has typically been observed in monolithic 3Y-TZP^{28)–34)}: tensile ductility for a relative density of $\geq 99\%$ depends strongly on minor additives, although the additives do not introduce any solid or glass phases along grain-boundaries nor at multiple junctions.

To explain the experimental data, Sakuma *et al.*^{27),30)–34)} have taken an approach based on a first-principle molecular-orbital calculation for model clusters. They found a close relationship between tensile ductility at $\sim 10^{-4} \text{ s}^{-1}$ and the total bond-overlap population (BOP) that represents the strength of covalent bonding among the constitutive ions: increasing ductility with increasing BOP. For additions of Ti^{4+} and/or Ge^{4+} to 3Y-TZP, they have also found a close relationship between flow stress and the average product of net charge, Θ , calculated for a model cluster consisting of zirconium ion, doped cation and oxygen ion. Since the level of flow stress reflects diffusivity for a fixed combination of the grain size, strain rate and temperature, the above result also

indicates a close relationship between Θ and diffusivity. This approach has an essential merit of positioning the additives in the $\Theta\text{--}\sigma$ and BOP- e_f fields through the molecular-orbital calculation. Although the minute relationship with the classical parameters such as γ_b , γ_s and δD_b are not clear at this moment, a study³⁴⁾ on Y-TZP doped with Ge^{4+} , Ti^{4+} or Ba^{2+} have indicated a close relationship between the covalence and γ_b .

The following consideration based on the cavitation models^{14)–16)} suggests that the above explanation relates closely to the ability of cavity nucleation. For a fixed combination of the major chemical composition, initial grain size, grain shape, size distribution of residual defects and loading conditions, the cavitation models predict that tensile ductility should strongly be controlled by the rate of cavity nucleation. The nucleation rate in this case should depend mainly on γ_b , γ_s and δD_b , since the other parameters are fixed. When γ_b , γ_s and δD_b are sensitive to some cations with valences and/or ionic radii different to those of the matrix cations,²⁵⁾ so should be the cavity nucleation rate and hence superplastic ductility. Since the kinetic constant of grain growth (Eq. (4)) depends on γ_b and δD_b , the doped cations may additionally influence cavity nucleation through varying the rate of dynamic grain growth that affects the flow stress of Eq. (1).

2.6 Guide for attaining HSRS

From the above-described discussion, factors necessary or desirable for attaining HSRS can be summarized as **Table 1**. We should note that some of the factors may concomitantly produce positive and negative effects. For example, although second-phase pinning should be effective in suppressing dynamic grain growth, it may provide a site of stress concentrations for cavity nucleation. A minor additive that enhances diffusion is also the case: the additive should simultaneously enhance stress relaxation and dynamic grain growth. We should also note that some factors are strongly processing dependent. A study¹²⁾ on ZrO_2 -dispersed Al_2O_3 showed that ductility for a given initial grain size was a factor of ~ 2.5 larger in a material prepared by colloidal processing than in a material prepared by conventional dry processing. This result is attributed to differences in the size distributions of fine defects and dispersed 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.¹²⁾ Each factor listed in Table 1 has often been discussed in studies on conventional superplasticity, whereas there have still been few studies that consider these points simultaneously.

3. Earlier studies on HSRS in oxide ceramics

In earlier studies on ceramics, tensile elongation exceeding 200% at a strain rate of 10^{-2} s^{-1} , namely HSRS was reported by Chokshi *et al.*¹⁰⁾ for a commercial 20-mass% $\text{--Al}_2\text{O}_3$ -dispersed $\text{ZrO}_2(3\text{Y})$, by Kajihara *et al.*³⁵⁾ for a 5-mass% --SiO_2 -doped $\text{ZrO}_2(2.5\text{Y})$ and by Oka *et al.*³⁶⁾ for a $\text{ZrO}_2(3\text{Y})$ co-doped with 2 mol% TiO_2 and 2 mol% CaO . Noticeable points in the materials are summarized in **Table 2**. The materials have fine grain sizes of about $0.3 \mu\text{m}$ and the matrices consist of yttria-stabilized tetragonal zirconia (Y-TZP). The latter is a particular advantage in attaining HSRS, since grain growth in Y-TZP is sluggish as compared to that in other materials such as Ce-TZP, cubic zirconia and alumina-base materials.²⁵⁾

Although the data on the Al_2O_3 -dispersed ZrO_2 ¹⁰⁾ was reported without any comment on HSRS, tensile elongation reached $\sim 300\%$ at 1650°C and at a strain rate of $4 \times 10^{-2} \text{ s}^{-1}$. In the light of Table 1, the material has two additional advan-

Table 1. Guide for Attaining HSRS

necessary or desirable factors	relating factors or phenomena
(a) reduced initial grain size	strain rate, stress relaxation, cavity nucleation (processing-dependent)
(b) suppressed dynamic grain growth	Stress concentrations, cavity nucleation (second-phase pinning and dragging: processing-dependent)
(c) enhanced diffusivity	strain rate, stress relaxation, cavity nucleation (doping of aliovalent cations)
(d) homogeneous microstructure	dynamic grain growth, cavity nucleation (processing-dependent)
(e) reduced residual defects	damage due to micrometer-sized cavities (processing-dependent)
(f) low γ_b and high γ_s	cavity nucleation (grain-boundary segregation)
(g) enhanced accommodation (by a viscous phase)	cavity nucleation (glass-phase dispersion, intergranular Si-segregation)
(h) additional accommodation (by limited intragranular plasticity*)	cavity nucleation (relates to (c) and (d))

* see section 4.4

Table 2. Oxide Ceramics Exhibiting High-Strain-Rate Superplasticity

Symbols (Fig. 4)	Material	Necessary or desirable factors ^{d)}	$\dot{\epsilon}_0/s^{-1}$	e_f (%)	$T/^\circ C$	Ref.
■	20Al ₂ O ₃ -ZrO ₂ (3Y) ^a	(b), (c)	0.04	300	1650	10)
◆	5SiO ₂ -ZrO ₂ (2.5Y) ^b	(b), (e)-(g)	0.01	360	1400	35)
●	2CaO-2TiO ₂ -ZrO ₂ (3Y) ^c	(b), (c)	0.01	400	1400	36)
▽	0.2Al ₂ O ₃ -ZrO ₂ (3Y) ^a	(a), (c)-(e)	0.03	370	1450	37)
◇	3(Y ₂ O ₃ , MgO)-97(Zr _{0.95} Ti _{0.05})O ₂ ^b	(a), (c)-(e)	0.01	220	1350	42)
			0.01	300	1450	
◇	0.2Mn ₃ O ₄ -0.3Al ₂ O ₃ -ZrO ₂ (3Y) ^b	(a), (c)-(e)	0.01	600	1450	43)
○	40ZrO ₂ (3Y)-30MgAl ₂ O ₄ -Al ₂ O ₃ ^c	(a)-(d), (h) ^e	0.01	500	1500	44-46)
			0.08	2500	1650	
			1.0	390	1650	
△	30ZrO ₂ (3Y)-30MgAl ₂ O ₄ -Al ₂ O ₃ ^c	(a)-(d), (h) ^e	0.02	660	1450	47,48)
			0.7	250	1550	

^amass%. ^bmol%. ^cvol%. ^dsee Table 1. ^esee section 4.4

tages in attaining HSRS. The dispersed Al₂O₃ particles may contribute not only to the suppression of grain growth, but also to the enhancement of diffusion through supplying Al³⁺ to the ZrO₂ matrix. The latter effect is strongly suggested from studies³⁷⁾⁻³⁹⁾ on Y-TZP doped with a small amount of Al₂O₃.

The doping of 5 mass% pure SiO₂ was intended to enhance superplasticity and attained tensile ductility reaching to 1050% at $1.3 \times 10^{-4} s^{-1}$ and HSRS where elongation reached 390% at $1.3 \times 10^{-2} s^{-1}$.³⁵⁾ High-resolution electron microscopy⁴⁰⁾ combined with energy dispersive X-ray spectroscopy revealed that SiO₂-addition does not introduce intergranular glassy films, but causes intergranular segregation of Si⁴⁺. The molecular-orbital calculation led to a conclusion that the Si-segregation should strengthen the grain-boundary bonding in Y-TZP and thereby enhance superplastic tensile ductility. In the cavitation mechanisms, the explanation may correspond to an increase in γ_s and/or a decrease in γ_b , both of which should lead to suppressed cavity nucleation. In addition, the viscous

flow of ~12 vol% of a silica phase dispersed at multiple grain junctions may suppress stress concentrations around the multiple junctions and hence cavity nucleation. It should also be noted that the silica phase suppresses grain growth.^{40),41)} In the SiO₂ addition, we can thus pick up three additional advantages to HSRS.

The co-doping of CaO and TiO₂ is probably the first example of a design of chemical composition intending to attain HSRS in a ceramic material. The following merits were expected from the co-doping: suppressed grain growth due to dragging from CaO and enhanced diffusivity from TiO₂.³⁶⁾ The co-doping resulted in a dual-phase structure consisting of 22 vol% cubic and 78% tetragonal phases and led to HSRS: tensile ductility reached 404% at $1.1 \times 10^{-2} s^{-1}$. It has not been clarified yet whether the dispersed cubic phase may play a positive or negative role in HSRS. Inspection of these earlier data indicates that, of the necessary factors listed in Table 1, four or more should be satisfied for attaining HSRS.

4. Recent trials for attaining HSRS in oxide ceramics

4.1 Processing

Placing special attention on necessary factors (a) through (e) of Table 1, the present authors tried to attain HSRS in both monolithic^{37),42),43)} and composite materials,^{44)–48)} without using glassy phases. We also noted that factors (a), (b), (d) and (e) are processing dependent. This is particularly the case, when we use fine powders that tend to agglomerate spontaneously owing to van der Waals forces.⁴⁹⁾ 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 processing⁵⁰⁾ to fine oxide powders.

4.2 Tetragonal zirconia

Since grain-growth is inherently sluggish in Y-TZP, factors (a), (c), (d), (e) and (f) should be 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_2O_3 ³⁷⁾, Mn_3O_4 ⁴³⁾ and MgO .⁴²⁾ We also used TiO_2 ,⁴²⁾ since experimental data^{34),51)} for grain growth and superplastic properties indicate that diffusion in Y-TZP is enhanced by TiO_2 addition. For the TiO_2 -addition, we co-doped MgO aiming at the stabilization of the tetragonal phase.⁴²⁾ Using colloidal processing followed by sintering at 1300°C for 2 h, almost fully densified bodies were obtained in an Al_2O_3 -doped 3Y-TZP and a Y-TZP co-doped with TiO_2 and MgO or with Mn_3O_4 and Al_2O_3 (Table 2). The sintered materials consisted of a single tetragonal phase with an average grain size of $0.23\text{ }\mu\text{m}$, 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 indicated enhanced diffusion.

These materials exhibited HSRS at around 1400°C and at a rate of the order of 10^{-2} s^{-1} . By the co-doping of TiO_2 and MgO , the deformation temperature can be lowered to 1350°C . This is the lowest temperature that has reported for HSRS in ceramics and locates in a lower temperature limit for conventional superplasticity in Y-TZP. A maximum tensile elongation of 660% was obtained by co-doping of Mn_3O_4 and Al_2O_3 .

4.3 Composites

The following merits can be expected in composite materials: strongly suppressed dynamic grain growth and improved fracture strengths.⁵²⁾ When a tetragonal zirconia is dispersed in the composites, transformation toughening can be expected below the transformation temperature. Despite these merits, we should note that strong grain-boundary pinning may simultaneously work to impede grain-boundary sliding. For this reason, enhanced diffusion is indispensable in the matrix. In addition, the elimination of agglomeration in raw materials is of particular importance in composites. For a given value of the relative density, lower extent of agglomeration enables us to sinter the material at a lower temperature and thereby obtain a finer grain size.

Of the factors listed in Table 1, 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 the tri-phase structure, we can expect strongly suppressed grain growth, since the frequency of the grain boundaries is decreased between the same phases and the diffusion distance is accordingly increased between the phases.⁴⁴⁾ 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 examined a sys-

Fig. 4. Tensile ductility as a function of the initial strain rate in undoped 3Y-TZP ($\blacktriangle$), ZrO_2 -dispersed Al_2O_3 ($\blacktriangledown$),¹²⁾ and the materials listed in Table 2. The data for undoped 3Y-TZP were taken from sources listed in Ref. 53.

tem consisting of tetragonal ZrO_2 , α - Al_2O_3 and $\text{MgO} \cdot \text{Al}_2\text{O}_3$ -spinel, where $\text{MgO} \cdot \text{Al}_2\text{O}_3$ -spinel is expected to supply Al^{3+} and Mg^{2+} to the ZrO_2 phase and Mg^{2+} to the Al_2O_3 phase.

We prepared 30 vol% MgAl_2O_4 - ZrO_2 (3Y)^{47),48)} and 40 vol% ZrO_2 (3Y)-30 vol% ($\text{MgO} \cdot 1.1\text{Al}_2\text{O}_3$)- Al_2O_3 ⁴⁴⁾ from commercial powders. In the former, we applied colloidal processing to MgAl_2O_4 and ZrO_2 (3Y) powders. In the latter, we applied conventional processing 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 $0.29\text{ }\mu\text{m}$ (ZrO_2) and $0.42\text{ }\mu\text{m}$ (MgAl_2O_4) for the dual-phase composite and $0.28\text{ }\mu\text{m}$ (ZrO_2 and spinel) and $0.45\text{ }\mu\text{m}$ (α - Al_2O_3) for the tri-phase composite. In the latter material the spinel phase was formed by chemical reaction between the MgO and Al_2O_3 powders. The grain size of each phase becomes smaller than that obtained by the sintering of each phase alone, particularly in the Al_2O_3 and spinel phases. Compared to the monolithic Y-TZP plotted in Fig. 4, although a higher temperature is necessary for sintering and deformation, the composites sustained noticeably higher strain rates and larger tensile elongation. As listed in Table 2, the available strain rate and tensile ductility reached 10^{-1} – 10^0 s^{-1} and 390–2500%, respectively.

4.4 New aspects appearing in deformed microstructure

In the composite materials described above, inspection of deformed microstructure has revealed some noticeable aspects in the ZrO_2 (Fig. 5)^{44),46)} and spinel⁴⁸⁾ grains: dense intragranular dislocations and dislocation-relating substructures such as subboundaries. Elongation along the stress axis was also found in the spinel grains (Fig. 6).^{47),48)} Such dislocation substructures and grain elongation were not found in undeformed materials. Thus, the observed aspects indicate that the grains of these phases are not perfectly rigid, that is, the grains are deformed by dislocation mechanisms to some extent during high-strain-rate loading.

Another notable feature appeared in cavitation behavior.^{44)–46)} As shown in Fig. 7, some cavities were extremely elongated along the stress axis and micrometer sized cavities were rather sparse in the remaining matrix. Such a microstructure should appear when a small number of residual defects grew with plastic flow under strongly suppressed cavity nucleation. If cavity nucleation is active as observed in con-

Fig. 5. A dark field transmission electron micrograph of a ZrO_2 -spinel- Al_2O_3 composite⁴⁴⁾ deformed at 1650°C and at 1 s^{-1} , showing the formation of dislocation substructures in a ZrO_2 grain.

Fig. 6. Grain shapes after superplastic deformation in a MgAl_2O_4 -dispersed ZrO_2 .⁴⁷⁾ While the white zirconia grains are euaxial after deformation, the dark spinel grains are noticeably elongated by deformation. Tensile axis is horizontal.

Fig. 7. Elongated cavities in a ZrO_2 - $\text{MgO} \cdot \text{Al}_2\text{O}_3$ - Al_2O_3 composite deformed to 2500% at 1650°C and at 0.1 s^{-1} .⁴⁵⁾ Comparison with Fig. 2(b) shows suppressed cavitation and the absence of cracking perpendicular to the stress axis.

ventional materials (Fig. 2), a large number of micrometer-sized voids must grow from cavity nuclei during superplastic deformation. The void growth must be followed by coalesce and microcracking^{9),10),12),18)} along the direction normal to the

stress axis (Fig. 2(b)).

Thus, the dislocation substructures and the cavitation behavior indicate that the grains of ZrO_2 and MgAl_2O_4 in the composites should contribute to the relaxation of stress concentrations around the multiple grain junctions and/or phase boundaries. Although further studies are desirable for this issue, the experimental results indicate that the dispersion of some secondary phases may provide a potential way for enhancing HSRS in oxide ceramics. This is an additional factor desirable for HSRS and noted as factor (h) in Table 1.

5. Concluding remarks

High-strain-rate superplasticity is now intentionally attainable in tetragonal zirconia and some composites synthesized from ZrO_2 , Al_2O_3 and MgO . For this attainment, the knowledge about superplastic deformation, cavitation and dynamic grain growth emphasizes the importance of simultaneously controlling the following factors: the initial grain size, the number of residual defects, diffusivity, dynamic grain growth and the homogeneity of microstructure. Recent trials indicate that grains of ZrO_2 and spinel phases dispersed in the composites may contribute to stress relaxation around multiple grain junctions and hence the suppression of cavity nucleation during high-strain-rate deformation. For industrial application, further studies are desirable on lowering the temperature available to high-strain-rate superplasticity in composite materials and on establishing a technology for high-strain-rate plastic forming of ceramics.

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