

Effect of a Liquid Phase on Superplasticity of 2-mol%-Y₂O₃-Stabilized Tetragonal Zirconia Polycrystals

Chin-Mau James Hwang** and I-Wei Chen*

Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136

A small addition of CuO to 2-mol%-Y₂O₃-stabilized tetragonal zirconia polycrystals significantly enhances superplasticity by forming an amorphous grain-boundary phase containing primarily Cu⁺, Y³⁺, Zr⁴⁺, and O²⁻. This phase apparently melts at around 1130°C, but it already provides a fast diffusion path even below the melting temperature. There are abrupt changes in stress exponent, activation energy, and grain size exponent across the melting temperature. Superplasticity is diffusion-controlled below the melting temperature and is interfaced-controlled above that. [Key words: yttria-stabilized tetragonal zirconia polycrystals, plasticity, liquid phase, creep, grain boundaries.]

I. Introduction

CERAMIC superplasticity has been investigated in recent years by many researchers,¹⁻¹⁰ most notably Wakai and co-workers.²⁻⁴ Large tensile ductilities were demonstrated in a few cases,²⁻⁶ raising the hope that superplastic forming of crystalline ceramics may be technologically feasible someday. Presently, yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) and their composites can be superplastically deformed at a strain rate of 10⁻⁴/s, temperatures above 1400°C, and stress around 25 MPa, but the flow stress increases rapidly to well above 100 MPa as the temperature is lowered to 1250°C.^{2-4,7,10} We believe that the prospect for superplastic forming of ceramics will become brighter if the forming temperature and the flow stress can be lowered to say, 1200°C and 50 MPa, which are comparable to hot working conditions for metallic alloys such as superalloys and molybdenum.^{11,12}

We have speculated that a lower forming temperature and a lower flow stress might be realized in ceramics sintered at low temperatures. If so, then there are two obvious approaches which might be taken to achieve this goal. The first one is a processing approach, using colloidal techniques to lower the sintering temperature. A classical example of this type was given by Rhodes on a yttria-stabilized zirconia which was sinterable at 1000°C.¹³ The second one is a chemical approach, using additives which lead to liquid-phase sintering.^{14,15} In this study, we have explored both approaches in Y-TZP and obtained a very substantial improvement in the superplastic forming conditions.

The benefit of low-temperature sintering made possible by colloidal processing should be apparent. Ceramics processed in this way are known to have smaller grains with a narrower

size distribution.^{13,16,17} These microstructural features can facilitate diffusional creep which is akin to superplasticity. Evidence for liquid-enhanced creep has also been documented in silicon nitride,^{18,19} glass-ceramics,^{20,21} other polycrystalline ceramics,²²⁻²⁴ and metal.²⁵ In theory, for this to happen, the liquid has to wet grain boundaries fully and support a normal stress. In addition, the surrounding grains must be able to dissolve in this liquid. Under such circumstances, mass transport along and across grain boundaries will largely take place within the liquid film, which remains between grains regardless of the local stress state. This is the so-called solution-precipitation mechanism.

Without a liquid phase, diffusional creep via grain boundary is described by the Coble equation²⁶

$$\dot{\epsilon} = A_1 \sigma \Omega \delta_{gb} D_{gb} / k T d^3 \quad (1)$$

In the above, $\dot{\epsilon}$ is the strain rate, A_1 is a constant, σ is the stress, Ω is the atomic volume, δ_{gb} is the effective thickness of the grain boundary, D_{gb} is grain-boundary diffusivity, k is the Boltzmann constant, T is the temperature, and d is the grain size. The presence of a liquid phase at the grain boundary can alter the above equation in several ways. The following two cases are of special interest to the present study.^{20,21,27,28}

(A) Diffusion control: If the mass transport through and across the grain boundary is rate-controlling, then Eq. (1) is modified by substituting $C_l \delta_l D_l$ for $\delta_{gb} D_{gb}$. Here C_l and D_l are the solubility and the diffusivity, respectively, of the rate-controlling species in the liquid film, and δ_l is the liquid film thickness. Since δ_l is proportional to the volume fraction of the liquid, V_l , and the grain size, the following rate equation obtains:

$$\dot{\epsilon} = A_2 \sigma \Omega V_l C_l D_l / k T d^2 \quad (2)$$

In the above, we have introduced a new constant A_2 .

(B) Interface control: If the solute diffusion rate far exceeds the interface reaction rate required for atom attachment and detachment, then diffusional creep is controlled by the latter and the strain rate is proportional to the rate of the interface reaction. Quite commonly, such reactions have a nonlinear, threshold type of dependence on the driving force, which is $\sigma \Omega$ in our case (for example, if nucleation of a surface step is required).²⁹ The average strain per grain, from the deposition and removal of materials at its grain boundary, is inversely proportional to the grain size. Taking these considerations into account, the following rate equation obtains:

$$\dot{\epsilon} = A_3 (\sigma \Omega)^n / k T d \quad (3)$$

In the above, we have introduced a new stress exponent $n > 1$ and another constant A_3 .

It should be obvious that the presence of an amorphous, and, indeed, any low-melting-point grain-boundary phase, has an effect similar to using liquid. This statement is supported by reports of enhanced kinetics sometimes observed below the melting (eutectic) temperature of the grain-boundary phase.¹⁵ We believe the above mechanistic picture leading to Eqs. (2) and (3) for liquid-enhanced creep is applicable below

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*Member, American Ceramic Society.

**Now at Dow Chemical Central Research, Advanced Ceramic Laboratory, Midland, MI 48674.

the eutectic temperature as well, if we simply envision the grain-boundary phase as a short-circuit diffusion path. However, considering the different physical properties of grain-boundary phases above and below the eutectic temperature, we may still anticipate a transition in the enhanced Coble creep behavior near the eutectic temperature.

In this study we report sintering, grain growth, and superplasticity of Y-TZP's, with and without addition of a small amount of a low-melting phase. We wish to demonstrate that a drastic improvement of the superplastic forming conditions can be achieved by such an addition. A better understanding of such practice will be afforded by an examination of the evidence for mechanism changes attributable to the presence of amorphous and liquid grain-boundary phases.

II. Experimental Procedure

(1) Materials

The two systems selected in this study were single-phase zirconia containing 2 mol% Y_2O_3 , designated as 2Y-TZP, and 2Y-TZP containing CuO. Unlike 3Y-TZP (ZrO_2 with 3 mol% Y_2O_3) which typically contains both the tetragonal and the cubic phase, 2Y-TZP is a single-phase tetragonal polycrystal. The eutectic melting temperature of $\text{CuO}/\text{Cu}_2\text{O}-\text{ZrO}_2$ is conveniently located at 1130° and 1090°C in air and in 1 atm (10^5 Pa) of oxygen, respectively.³⁰ The above temperatures are within the range of low-temperature superplasticity for 2Y-TZP. Since the solubility of Cu in zirconia is negligible, Cu is not expected to alter TZP's deformation behaviors by solid solution. To keep the amount of the liquid phase small, only 0.3 and 1 mol% CuO were added to 2Y-TZP.

Highly pure commercial 2Y-TZP[†] and CuO^\ddagger powders were used as starting materials. The powder mixtures of 2Y-TZP and the designated amount of CuO were attrition-milled in an alumina jar using zirconia milling media with a surfactant. The milled slurry was cast, under a pressure of up to 0.7 MPa, into cakes with a diameter of 47 mm, which were dried and isostatically pressed at 400 MPa. The green density after isopressing was between 60% and 65% of the theoretical density.

Sintering studies were performed in air using a sintering dilatometer, at a constant heating rate of 7.5°C/min. For deformation studies, samples were sintered at 1250°C for 1.5 h. The density of the sintered specimen was determined by a water immersion method, and the phase content was analyzed by X-ray diffractometry. Only those specimens with more than 98% of the theoretical density and 100% tetragonal phase were accepted for this study. Annealing at various temperatures and times was also performed to coarsen the grain size when necessary.

(2) Testing

Square bar compression specimens with a height/width ratio of 2.3 were prepared by grinding. Deformation was conducted in uniaxial compression to minimize the effect of cavitation on the constitutive behavior. All tests were conducted in air, between 1000° and 1250°C, with strain rates from 10^{-6} to 10^{-2} /s, in a platinum furnace. The actual specimen temperature during the test was monitored by a thermocouple immediately adjacent to the specimen surface. An alumina hemispherical seat and a set of SiC platens were used in the loading train. With this arrangement, little evidence of end friction was detectable even at very high strain rates. Specimens were allowed to stabilize at the test temperature for 10 to 15 min before the tests began. Deformation was continuously monitored during the test using an extensometer. Most tests were run using a constant displacement rate, and the load and displacement readings were converted into true

stress and true strain rate data reported below. Since steady-state deformation could be reached with strains of the order of a few percent, a single specimen was often used for flow stress determinations at two to three increasing displacement rates. Typically, a test lasted no longer than one-half hour at the test temperature, and testing was terminated after reaching a height reduction of 50%. Under these conditions, very little, if any, grain growth was found in the deformed specimens.

Microstructures and microchemistry of the studied specimens were characterized by electron spectroscopy for chemical analysis (ESCA), SEM, and TEM. The grain size reported was obtained by multiplying the average linear intercept of at least 500 grains by 1.56. Additional micromechanical measurements of hardness and indentation toughness were made by using a Vickers indenter operated at a load over the range of 15 and 40 kg.

III. Experimental Results and Analysis

(1) Sintering and Grain Growth

CuO (0.3 mol%) greatly affected the densification behavior of 2Y-TZP, as evidenced by a shift of the shrinkage curves toward a lower temperature. The maximum shrinkage rate of CuO-containing 2Y-TZP (denoted as 2YZ-0.3 Cu) occurred at 1120°C. Unlike the shrinkage curve of 2Y-TZP, which appears symmetric with respect to the inflection point, at 1165°C, the shrinkage of CuO-containing specimen was much faster above the inflection point. Since the eutectic temperature in the air is 1130°C in the system $\text{CuO}/\text{Cu}_2\text{O}-\text{ZrO}_2$, we may attribute the enhanced sintering to the formation of a liquid phase. This kind of nonsymmetrical shrinkage behavior in sintering has been reported before in other materials when a liquid is generated during heating.¹⁵

We found it possible to obtain specimens with $\geq 98\%$ theoretical density in 2Y-TZP by sintering at 1200°C, and in 0.3% CuO-added 2Y-TZP at 1150°C. Higher densities could be routinely obtained by raising the sintering temperature. For deformation studies described below, samples sintered at 1250°C for 1.5 h were used.

The addition of CuO enhanced grain growth as well, as evident from the micrographs in Fig. 1, after sintering at 1250°C for 1.5 h. Linear intercept measurement of the two micrographs in Fig. 1 gave a grain size of 0.21 and 0.35 μm for single-phase and CuO-containing 2Y-TZP, respectively. Despite their different sizes, grains in both TZP's remained equiaxed. Thus, we may compare their deformation behaviors without regard to grain morphology.

(2) Superplasticity of 2Y-TZP

The flow behavior of 2Y-TZP of a grain size of 0.21 μm is summarized in Figs. 2 and 3. Figure 2 demonstrates that a strain rate sensitivity m , defined as the slope in the log strain rate–log stress plot, of 0.67 ± 0.05 is obeyed at all temperatures except at the highest stresses. A high strain rate sensitivity is characteristic of superplastic flow. Above 800 MPa (i.e., 1% of the shear modulus) at lower temperatures, the strain rate sensitivity is lower, below 0.1, indicating a change of deformation behavior from superplasticity into obstacle or lattice resistance–limited dislocation glide. The stress exponent n , defined as the reciprocal of m , is 1.6 in the superplastic regime in this material and it increases to over 10 above 800 MPa. Previously reported values of strain rate sensitivity in 3Y-TZP range from 0.33 to 1, all at higher temperatures.^{2-6,31}

The temperature dependence of the superplastic flow is shown in Fig. 3, giving a single activation energy Q of 630 kJ/mol between 1100° and 1250°C. The value is on the high end of the range of activation energies, from 360 to 655 kJ/mol, reported for creep and superplasticity of Y_2O_3 -stabilized tetragonal and cubic zirconia.^{2-6,31-34}

The grain size dependence of superplastic flow of 2Y-TZP during superplastic deformation at 1175°C is shown in Fig. 4,

[†]Tosoh, Tokyo, Japan.

[‡]Alfa Products, Danvers, MA.

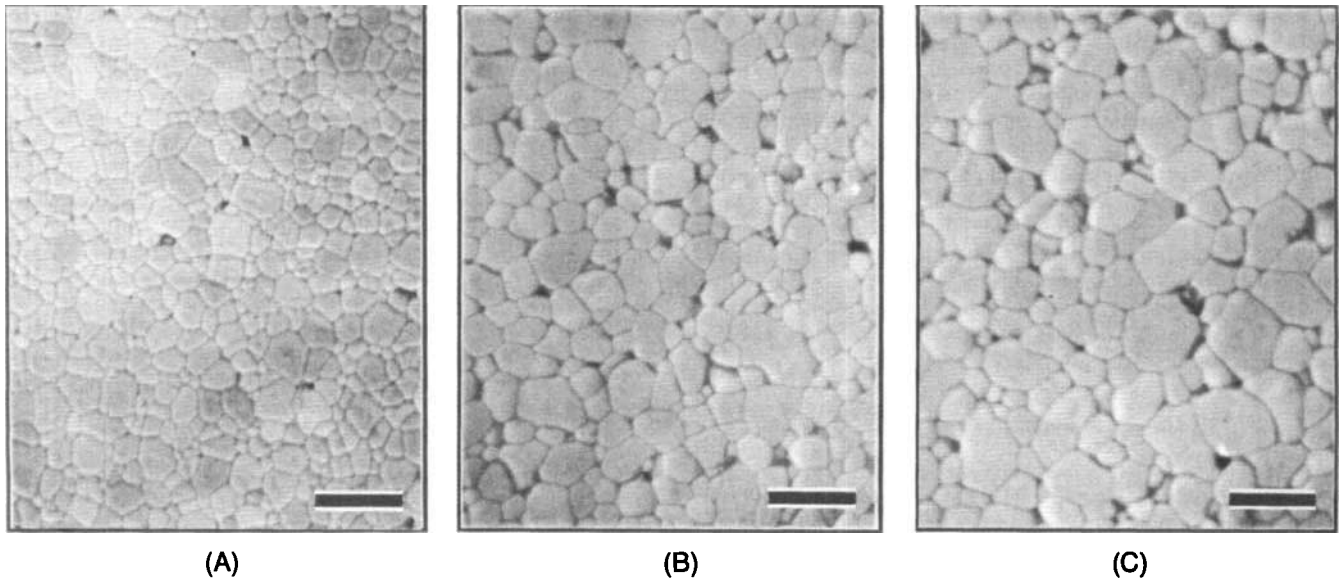


Fig. 1. As-sintered microstructures of three 2Y-TZP's: (A) without additive, (B) with 0.3 mol% CuO, and (C) with 1 mol% CuO; bar = 1 μm.

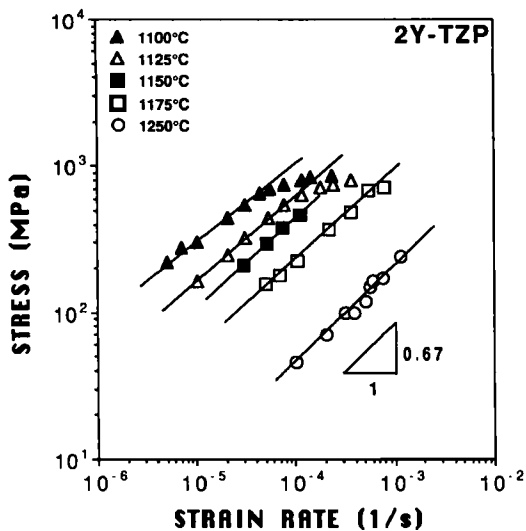


Fig. 2. True stress-strain rate relationships for 2Y-TZP at various temperatures.

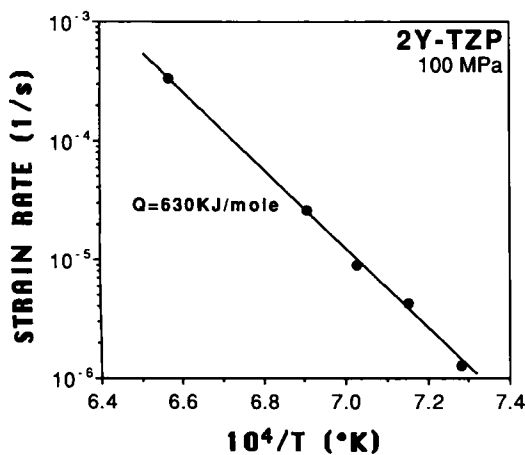


Fig. 3. Temperature dependence of strain rate of 2Y-TZP at 100 MPa.

where the strain rate at a constant stress is plotted versus the grain size in logarithmic scale. The result yielded a grain size exponent p , defined as the negative of the slope in Fig. 4, of 2.7 ± 0.2 . Previously, 2Y-TZP has been studied by Wakai for one grain size only, over the temperature range of 1250° to 1450°C, and by Yoon and Chen in our laboratory for a range of grain sizes over the temperature range of 1250° to 1400°C.¹⁰ Using the activation energy and the grain size exponent reported above, we can compare our data with those of the wo previous studies at 1250°C, for a reference grain size of 0.33 μm. As shown in Fig. 5, these data are reasonably close to each other.

(3) Superplasticity of CuO-Containing 2Y-TZP

Flow behaviors of two CuO-containing 2Y-TZP's, one with 0.3 mol% CuO and a grain size of 0.35 μm and the other with 1 mol% CuO and a grain size of 0.41 μm, are summarized in Figs. 6 to 9. Comparing Figs. 2 and 6, it is obvious that in all cases deformation in the CuO-containing 2Y-TZP's is much faster than that in the single-phase 2Y-TZP, by several orders of magnitude, even though the single-phase 2Y-TZP has the smallest grain size, 0.21 μm.

The strain rate sensitivities of the CuO-containing 2Y-TZP's are high, between 0.5 and 0.8, as evident from Figs. 6(A) and (B). This feature is still characteristic of superplastic flow. However, unlike their counterpart without CuO addition, the

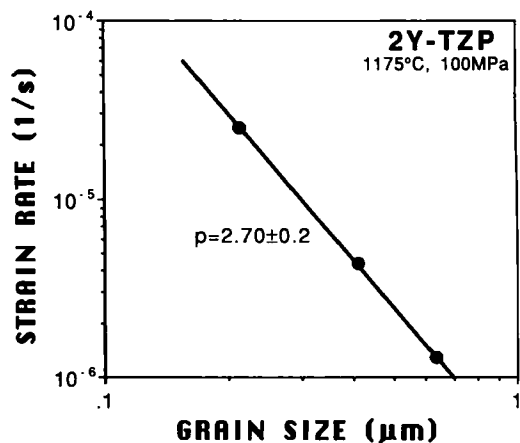


Fig. 4. Grain size dependence of strain rate of 2Y-TZP at 100 MPa and 1175°C.

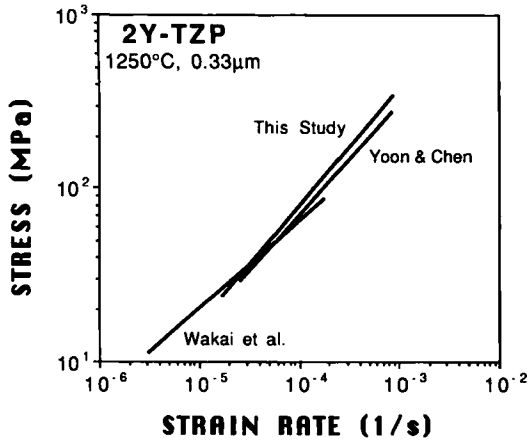


Fig. 5. Superplasticity data of 2Y-TZP by different investigators at 1250°C.

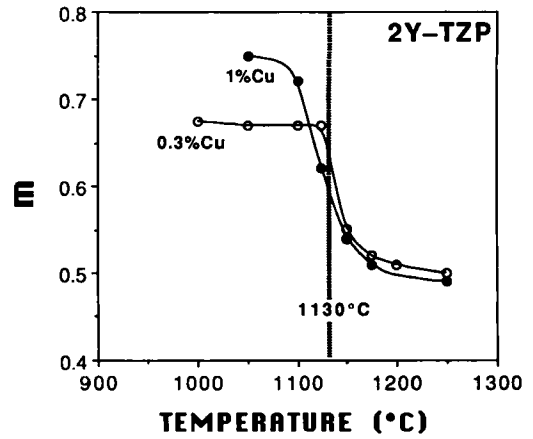


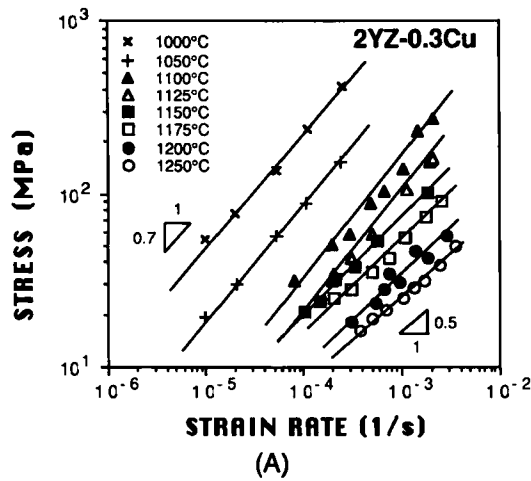
Fig. 7. Temperature dependence of strain rate sensitivity, *m*, in two CuO-containing 2Y-TZP's.

strain rate sensitivities of both TZP's decrease gradually as the temperature increases and then go through a somewhat abrupt transition at the eutectic temperature, as highlighted in Fig. 7.

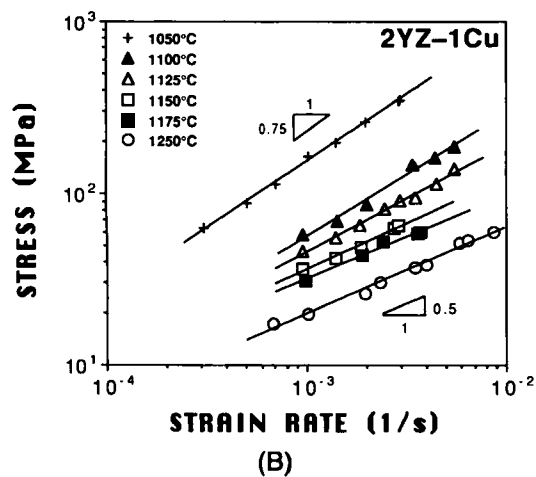
The temperature dependence of superplastic flow of these materials undergoes a corresponding transition at the eutectic temperature, becoming lower at higher temperatures as shown in Fig. 8. This effect is more evident for the higher CuO content. For example, the activation energy decreased from 445 to 415 kJ/mol in 0.3%-CuO-added 2Y-TZP, and from 405 to 233 kJ/mol in 1%-CuO-added 2Y-TZP. In both

cases, the activation energy below the eutectic temperature is already lower than that of 2Y-TZP without CuO addition.

The grain size dependence of 0.3%-CuO-added 2Y-TZP is shown in Fig. 9 for two temperatures, one above and the other below the eutectic temperature. In both cases, the grain size exponents are much lower than that in single-phase 2Y-TZP. In addition, this exponent is higher at a lower temperature, i.e., 1.64 ± 0.15 at 1000°C and 1.23 ± 0.1 at 1175°C.



(A)



(B)

Fig. 6. True stress-strain rate relationships for 2Y-TZP with (A) 0.3 mol% and (B) 1 mol% CuO.

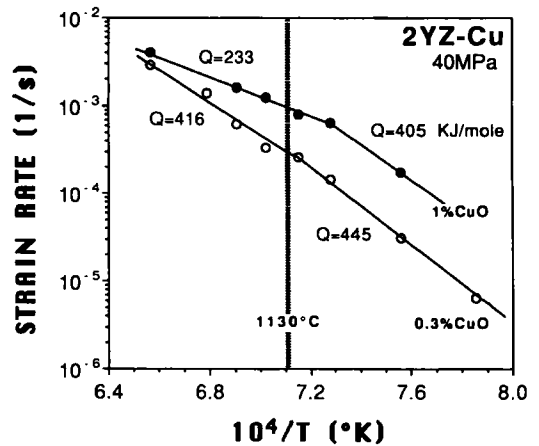


Fig. 8. Temperature dependence of strain rate of two CuO-containing 2Y-TZP's at 40 MPa.

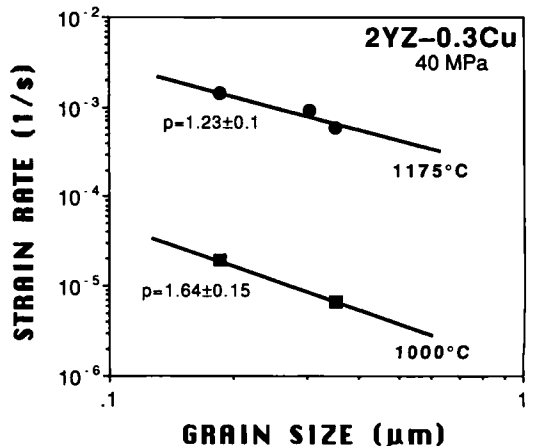


Fig. 9. Grain size dependence of strain rate of two CuO-containing 2Y-TZP's at 40 MPa below and above the eutectic temperature.

Apparently, the transition behaviors noted previously in strain rate sensitivity and in activation energy also occurred in the grain size exponent at the eutectic temperature. Taken in toto, these results demonstrate clearly that the deformation mechanisms in CuO-containing 2Y-TZP, at both above and below the eutectic temperature, are different from that of pure 2Y-TZP.

Lastly, to make clear the effect of the amount of CuO addition on deformation, we plot in Fig. 10 the ratio of the strain rates, at 40 MPa, of the two CuO-containing 2Y-TZP's for the entire temperature range studied. It is clear from Fig. 10 that, below the eutectic temperature, the strain rate increases rapidly with an increasing CuO addition. Above the eutectic temperature, however, the effect of the CuO amount is much less. Indeed, the strain rate seems to be independent of the CuO amount at temperatures approaching 1300°C. The implication of this and other observations on deformation mechanisms will be discussed further in a later section.

(4) Grain-Boundary Phase

Direct evidence of the presence of a Cu-rich grain-boundary layer was obtained by ESCA and TEM. We found that all the 2Y-TZP's could be fractured nearly intergranularly at room temperature. In the CuO-containing specimens, the fracture surface, according to the ESCA analysis, contained Cu^+ , Y^{3+} , Zr^{4+} and O^{2-} . Since the ESCA signals came primarily from elements on and within a distance of 1 to 2 nm from the surface, to determine the depth distribution of the above species, ion beam sputtering was applied to progressively remove the near-grain-boundary material. This then resulted in a rapid, monotonic decrease of the Cu concentration with the sputtering time, its signal falling below detectability after 3 min. This indicated that Cu was present only within a thin layer at the grain boundary. It should also be noted that Si peaks were searched for but not found in the above experiment. However, when 0.5 mol% of SiO_2 was intentionally added to 2Y-TZP, a Si^{4+} peak was detected on the grain boundary.

A TEM micrograph shown in Fig. 11(A) of the same material sintered at 1250°C revealed this Cu-rich layer to be amorphous. The amorphous layer was of the order of 1 to 2 nm and was distributed relatively uniformly along the grain boundary. The amount of the amorphous phase was too low to give a diffuse scattering halo in the selected area diffraction pattern. An accumulation of the amorphous phase at the triple point was found in a few cases, such as the one shown in Fig. 11(B). In contrast, we found that in single-phase 2Y-TZP, the glassy phase was too limited to be detectable in TEM in most cases.

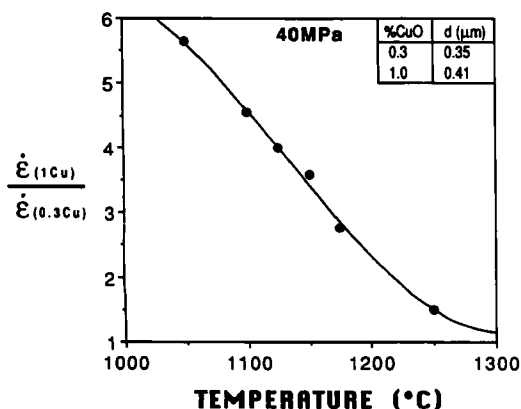
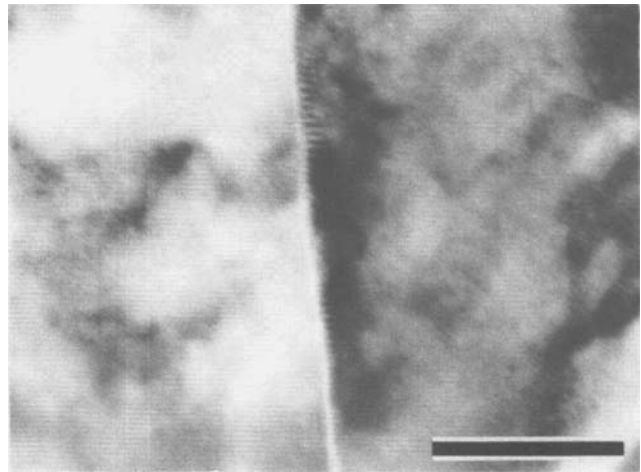
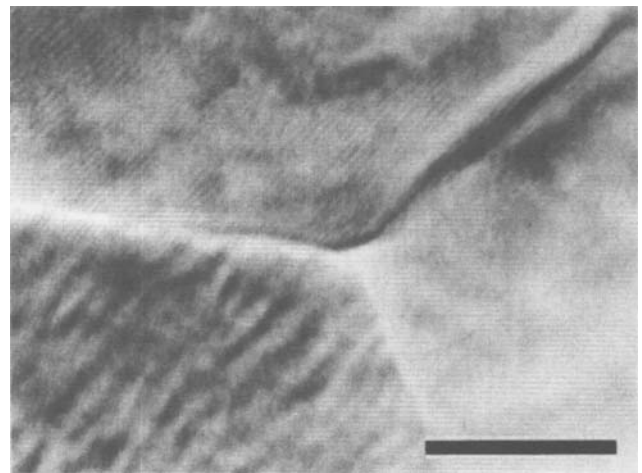


Fig. 10. Ratio of strain rate of two CuO-containing 2Y-TZP's with 1 and 0.3 mol% CuO.



(A)



(B)

Fig. 11. TEM micrographs revealing a thin layer of amorphous phase at the (A) grain boundary and (B) triple point of CuO-containing 2Y-TZP; bar = 20 nm.

(5) Microstructural and Micromechanical Observations

Micromechanical properties, including hardness and indentation toughness of 2Y-TZP's with and without CuO additions, are presented in Table I. In comparing these data, it should be noted that the grain sizes of the two materials are not the same and they have not been optimized for best room-temperature properties. It is evident, however, that the CuO addition of a small amount has a negligible effect on mechanical properties at room temperatures.

Deformed microstructures of 2Y-TZP's with and without CuO addition were examined by SEM and TEM. In all cases, no significant cavitation damage or change in grain shape and grain size was found after the compression test was performed, regardless of the temperature, stress, strain rate, total strain, or additive amount. Further examination by TEM of a 0.3%-CuO-added specimen, at a strain of 85%, again showed no sign of cavitation. The lack of cavitation was finally confirmed by the density measurement.

Table I. Mechanical Properties of 2Y-TZP's with and without an Additive

Material	Toughness (MPa·m ^{1/2})	Hardness (GPa)
2YZ	4.34 ± 0.30	11.9
2YZ-0.3% Cu	5.98 ± 0.24	10.6

IV. Discussion

(1) Superplastic Forming Conditions

The flow stress of CuO-containing 2Y-TZP at 1200°C was much lower than those reported previously for 3Y-TZP.^{2-7,31} This is illustrated in Fig. 12, in which all the reported 3Y-TZP strain rate data at 40 MPa are plotted against the reciprocal temperature. The strain rates of this study, also shown in the graph, are significantly higher than the rest. Clearly, then, the addition of a low-melting phase is an effective way to facilitate ceramic superplasticity. Although a uniaxial tensile test was not performed in the present study, our group has reported biaxial shell stretching of the same ceramic, at a strain rate approaching 10⁻³/s at 1150°C, to large strains.³⁵ We found no acceleration of cavitation in those tests and verified that the microstructure remained stable during deformation. Inasmuch as such an experiment is commonly regarded as the most severe formability test in the sheet metal forming field, it has provided, in our view, the most encouraging indication to date that superplastic forming of ceramics would be technologically feasible. It is also important to note that the low-temperature mechanical properties were not significantly affected by the addition of a small amount of low-melting phase.

(2) Grain-Boundary Phase in CuO-Added 2Y-TZP

As confirmed by the TEM and ESCA analyses, there was a low-melting (1130°C), probably amorphous, continuous phase along the grain boundaries of CuO-containing 2Y-TZP. This phase contained Cu,[†] Y, Zr, and O, and it apparently facilitated sintering, grain growth, grain-boundary sliding, and creep. Two prerequisites for such effects are (1) the grain-boundary phase must cover or wet the entire grain boundaries, and (2) the surrounding grains must be able to dissolve in this phase. As evidenced from the TEM and ESCA results, these requirements were apparently satisfied by the Cu-rich grain-boundary phase.

Heating above the eutectic temperature poses an additional requirement for the grain-boundary phase; i.e., it has to support a normal stress in order to be effective in diffusional creep. Otherwise, the liquid would be squeezed out totally by compression and would not be able to promote creep. A thin intergranular liquid phase can fully support a normal stress if its thickness does not exceed the equilibrium thickness determined by the balance of a dispersion attraction between ad-

joining grains and a repulsion due to the structure of the intergranular liquid. (A thicker liquid layer will be squeezed around a bit until a thin film of the above equilibrium thickness is left to support the normal stress.) As both of these interactions are of short range (<10 nm), it is a natural consequence that the equilibrium thickness is of the order of 1 nm.³⁶ This seems to be the case in the present system of CuO-containing 2Y-TZP. Unfortunately, little is known about the structure of the liquid and the dielectric properties of the adjoining grains to allow a quantitative prediction of the equilibrium thickness. However, at the concentrations of CuO that we used, the thickness of the grain-boundary layer is estimated to be 0.3 and 1.0 nm. In the above estimation we have assumed a grain diameter of 0.3 μm and the volume fraction of the liquid to be 0.003 and 0.01, respectively. Since these values are probably smaller than the equilibrium thickness, we believe the grain-boundary liquid in our study can support a normal stress.

(3) Mechanisms of Superplasticity in CuO-Containing 2Y-TZP

The main effects of CuO on the constitutive behavior of 2Y-TZP are summarized in Table II. We now attempt to rationalize these results in terms of the three mechanisms listed in the Introduction, Eqs. (1) to (3). In doing so, we first acknowledge that we still lack a satisfactory micromechanical model which accounts for the stress exponent and other aspects of superplasticity, despite many such attempts in the past two decades.^{37,38} However, there is a general agreement that superplasticity is akin to diffusional creep and involves grain-boundary sliding and grain-boundary migration, but it somehow proceeds at a much faster rate. In the absence of a definitive model, it is difficult for us to make quantitative and absolute predictions of the stress and grain size exponents, etc. at this time. Instead, we have arrived at our rationalization based on the comparison of the qualitative trends in constitutive parameters by invoking the general parallelism between diffusional creep and superplasticity.

We believe that the deformation mechanism in single-phase 2Y-TZP is similar to that of Coble creep, as described by Eq. (1). When CuO is added, below 1130°C, creep is enhanced and controlled by a faster diffusion in the grain boundary, as described by Eq. (2). Above 1130°C, as a liquid phase forms, diffusion is so fast that creep is controlled by interface reactions, as described in Eq. (3). The above picture is consistent with our observations in the following ways.

(1) The stress exponent should remain the same but the grain size exponent should decrease by one as the mechanism changes from Eq. (1) to (2), which was exactly the case with 2Y-TZP and CuO-containing 2Y-TZP below the eutectic temperature.

(2) The stress exponent should increase and the grain size exponent should decrease as the mechanism changes from Eq. (2) to (3), which was exactly the case with CuO-containing 2Y-TZP when the eutectic temperature was crossed.

(3) The diffusion-controlled, grain-boundary-phase-enhanced creep should depend on the amount of the grain-boundary phase, while the interface-controlled, liquid-enhanced creep should not, which was exactly the case observed below and above 1130°C in our experiment, respectively.

(4) Whether it is diffusion control or interface control is dependent on the rates of the two mechanisms. The slower one should be the controlling mechanism. Therefore, the Arrhenius plot of the strain rate should have a concave downward curvature giving a lower activation energy at higher temperatures, which was exactly the case observed below and above 1130°C in our experiment.

Further interpretation of the data of activation energies is difficult at this time for the following reasons. First, even if Coble creep operated in 2Y-TZP, superplasticity would likely

[†]Although CuO was added initially, the more stable state of Cu at high temperatures (above 1000°C) in air is Cu⁺ (Ref. 29). This was confirmed by the ESCA analysis in the sintered materials.

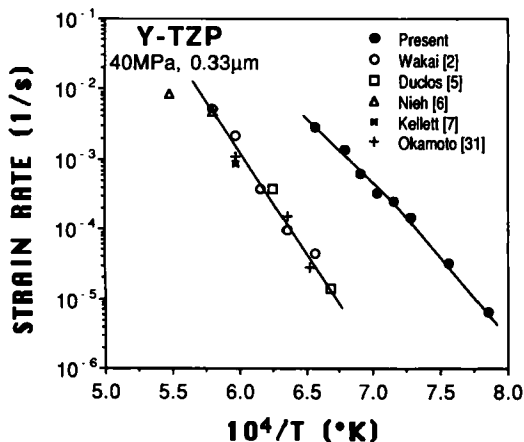


Fig. 12. Comparison of temperature dependence of strain rate of 3Y-TZP from Refs. 2, 5-7, and 31 with 2Y-TZP (this study) at a reference stress of 40 MPa and a reference grain size of 0.33 μm. Except for Ref. 6, all tests were performed in air.

Table II. Summary of Parameters in the Constitutive Equation for Superplasticity ($\dot{\epsilon} = A\sigma^n d^{-p} \exp[-Q/kT]$)

Material	Grain-boundary phase	n	Q (kJ/mol)	p	A
2Y-TZP	None	1.5 ± 0.15	630	2.70 ± 0.2	
2Y-TZP/0.3% CuO (below 1130°C)	Amorphous solid	1.3 ± 0.1	445	1.64 ± 0.15	Proportional to %CuO
2Y-TZP/0.3% CuO (above 1130°C)	Liquid	2.0 ± 0.1	416	1.23 ± 0.1	Independent of %CuO

involve grain-boundary migration which could be controlled by short-range lattice diffusion if solute segregation occurred. (Direct evidence of solute segregation in a wide range of tetragonal zirconia has been reported by our group recently.)^{39,40} The relatively high activation energy of 630 kJ/mol in 2Y-TZP was probably a result of the above. Second, activation energy in Eq. (2) involves both diffusivity and solubility; thus the activation energy of 445 kJ/mol below the eutectic temperature cannot be attributed to a single process. Third, activation energy of the interface process is not well documented; thus it is difficult to judge whether or not the activation energy of 416 kJ/mol above the eutectic temperature was reasonable.

V. Conclusions

(1) The addition of CuO enhances both densification and grain growth because of the formation of a liquid phase. The liquid-forming temperature is consistent with the eutectic temperature, 1130°C, in the system $\text{Cu}_2\text{O}/\text{CuO}-\text{ZrO}_2$. Direct evidence of the grain-boundary phase is provided by TEM and ESCA analyses. The grain-boundary phase contains Cu^+ , Y^{3+} , Zr^{4+} , and O^{2-} , and it apparently wets the grain boundary.

(2) The addition of a suitable, low-melting, grain-boundary phase is an effective means to facilitate superplasticity. In 2Y-TZP it has resulted in a substantial decrease in the flow stress, activation energy, and grain size exponent, while retaining damage tolerance, hardness, and toughness. Based on the present results, it is suggested that superplasticity below 1200°C and 50 MPa can be easily achieved in Y-TZP.

(3) A transition in superplastic flow behavior occurs in the vicinity of the eutectic temperature. Decreases in strain rate sensitivity, activation energy, and grain size exponent have been observed as the grain-boundary liquid phase formed. Coble creep, grain-boundary-phase-enhanced diffusional creep, and liquid-enhanced interface creep are proposed as the dominant deformation mechanisms in 2Y-TZP and in CuO-containing 2Y-TZP below and above the eutectic temperature, respectively.

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