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Review
Superplasticity in ceramics

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It is now recognized that superplasticity is a potential deformation process in ceramics. This review summarizes the major characteristics of superplasticity and examines the reports of both transformation and structural superplasticity in ceramic and other non-metallic materials. It is shown that there are both similarities to and differences from metals. Similarities include the variation of strain rate with stress and grain size, but an important difference is the necessity to consider the role of intergranular glassy phases in ceramics. Superplasticity is also important in intermetallic compounds, and in geological materials where there is evidence for superplastic deformation both in laboratory experiments and in natural deformation.

1. Introduction

It is well known that when a metal sample is pulled in tension it usually breaks at a fairly low total elongation. However, some metallic alloys are capable of pulling out to very large tensile extensions of the order of some hundreds or even thousands of per cent. This phenomenon is called *superplasticity*, and it becomes optimized when the flow occurs in a quasi-stable manner so that necking is diffuse rather than localized [1].

The first detailed investigation of the superplastic effect is generally attributed to Pearson [2] in 1934, when an elongation of 1950% was achieved in an aged Bi–44% Sn eutectic alloy. However, as noted by Sherby and Wadsworth [3], there are early indications of superplastic-like behaviour in the work of Bengough in 1912 [4, 5], where a maximum elongation of 165% was recorded in an α/β brass at a temperature of 700° C. Also, there were subsequent reports of superplastic-like behaviour by Rosenhain *et al.* [6], Jenkins [7] and, for the situation where plasticity is associated with a phase change, in the work of Sauveur [8].

In the ensuing years, it has been recognized that the superplastic process has many potential applications in the forming industry and, as a result, considerable attention has been devoted to both the development of new superplastic alloys and new superplastic forming techniques, and to examining the mechanical characteristics of alloys which are known to exhibit superplasticity. Much of this work is summarized in the proceedings of recent meetings devoted to superplasticity [9–13].

Despite the considerable world-wide interest in superplasticity and the recognized technological applications of superplastic materials, it is interesting to note that, with only two exceptions [10, 13], these published proceedings and the most recent reviews of superplasticity [14–18] deal exclusively with metallic alloys; and there is no reference to superplastic behaviour in ceramic materials.

There is a simple reason for this apparent omission. Although there were some limited reports of superplasticity in non-metallic systems in the early 1980s, the first clear demonstration of superplastic behaviour in a ceramic material occurred only in 1986 when Wakai and co-workers [19, 20] reported tensile elongations of over 100% in an yttria-stabilized tetragonal zirconia. This report represents an important contribution to the literature on ceramics, equivalent to the investigation by Pearson [2] on metals, and it has given rise to a considerable interest both in the possibility of attaining superplastic characteristics in ceramics and in the potential utilization of these ceramic materials as components in high temperature applications.

This review was motivated by these very recent developments. The purpose of the review is two-fold: first, to summarize and examine the various reports of superplastic behaviour in ceramics; and second, to examine the possibility of superplasticity in other non-metallic materials, such as under geological conditions. To place this review in perspective, the following section gives a brief summary of the principles of superplasticity, and the next section provides a detailed review of the reports of superplastic deformation in ceramics. There follows a brief outline of the application of superplasticity to intermetallic compounds, rocks and minerals.

2. The principles of superplasticity

There are two basic types of superplasticity, termed *transformation* and *structural* superplasticity,

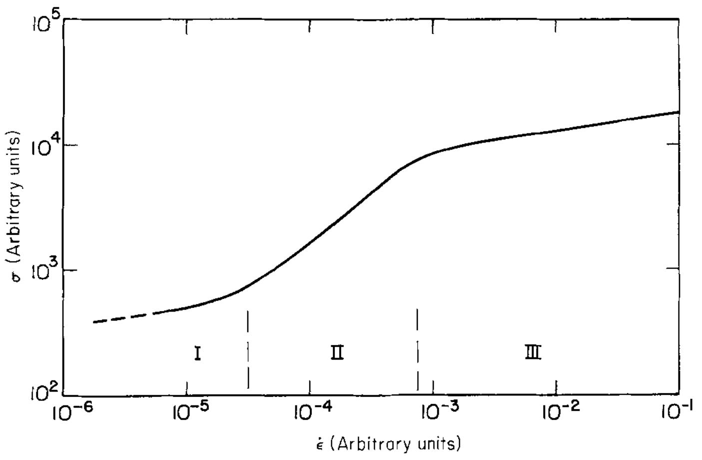

Figure 1 Schematic illustration of steady-state flow stress, σ, against strain rate, $\dot{\varepsilon}$, for a superplastic metal.

respectively. (A third type of superplasticity, termed temperature-cycling superplasticity, refers to the temperature cycling under a small load of a material, such as uranium or zinc, where there is a high degree of anisotropy in the coefficients of thermal expansion [21]. This type of superplasticity is of minor importance and is not considered in this report.) Transformation superplasticity refers to the temperature cycling of a material through a phase change; structural superplasticity refers to attaining superplastic tensile elongations without a phase change and under conditions of constant temperature. Although both types may be important in selected ceramics under certain conditions, technological requirements dictate a major emphasis on the development of ceramics capable of exhibiting structural superplasticity.

There are two important requirements for the attainment of structural superplasticity in metals [22]. First, the grain size must be very small (typically less than 10 μm) and must remain small during plastic deformation. Second, since superplasticity is a diffusion-controlled process, the testing temperature must be high, typically above $\sim 0.5\,T_m$ where T_m is the absolute melting temperature of the material. In general, these two requirements are incompatible because rapid grain growth occurs at elevated temperatures; but the requirements may be fulfilled in metallic alloys by, for example, using a two-phase eutectic or eutectoid alloy (such as Zn–22% Al or Al–33% Cu) or by incorporating particles within the matrix in order to restrict grain growth at elevated temperatures (such as a dispersion of $ZrAl_3$ in Al–6% Cu–0.5% Zr).

The successful development of superplasticity in metals has been a subject of considerable interest in the metal-forming industry. Superplastic metals exhibit high plasticity and low strength at high temperatures, so they can be fabricated into complex parts in a simple forming process. Furthermore, the materials are generally strong and ductile at low temperatures, and additional creep resistance may be introduced by a post-forming heat treatment.

When a superplastic metal is pulled in tension, the relationship between the steady-state flow stress, σ, and the imposed strain rate, $\dot{\varepsilon}$, is generally sigmoidal on a logarithmic plot, as illustrated schematically in Fig. 1 [22]. The stress and strain rate are related through the expression

$$\sigma = B\dot{\varepsilon}^m \qquad (1)$$

where B is a constant and m is the strain rate sensitivity ($= \partial \ln \sigma / \partial \ln \dot{\varepsilon}$). In Fig. 1, the behaviour divides into three regions, with low values of m at low and high strain rates in regions I and III, respectively, and a high value of m at intermediate strain rates in region II. Since there is a correlation between the strain rate sensitivity and the total tensile ductility, both experimentally [23] and theoretically [24–27], it follows that maximum elongations occur in region II and there is a decrease in the superplastic effect in regions I and III.

3. Superplasticity in ceramics

3.1. Requirements for superplasticity

As noted in a recent review of the high-temperature creep of ceramics [28], the grain sizes of ceramic materials are invariably substantially smaller than in metals. This is due both to the processing procedures adopted for the production of polycrystalline ceramics, and to their low grain boundary mobilities, so it is generally fairly easy to stabilize, and to maintain, a very fine grain size. The presence of a very small grain size, often $< 10\,\mu$m, and the difficulties of promoting significant grain growth even at high temperatures, indicate the potential for superplastic deformation in ceramics. However this potential is invariably not realized in practice because an additional requirement for superplasticity, not generally important in metals, is a lack of intergranular brittleness. This latter requirement hinders and usually prevents the attainment of true superplastic elongations in ceramic materials.

Nevertheless there have been numerous reports of significant superplastic-like behaviour in ceramics, in the form of both transformation and structural superplasticity, with the latter occurring either in the presence or absence of an intergranular glassy phase. These reports are examined in the following sections.

3.2. Transformation superplasticity

The occurrence of transformation superplasticity is well documented in metals where it arises from thermally cycling a material through an allotropic phase transition [14, 21]. In ceramics, evidence for superplastic-like behaviour was provided by Hart and Chaklader [29] during the monoclinic–tetragonal transformation of ZrO_2. The results are illustrated schematically in Fig. 2 for zirconia tested in three-point bending at a

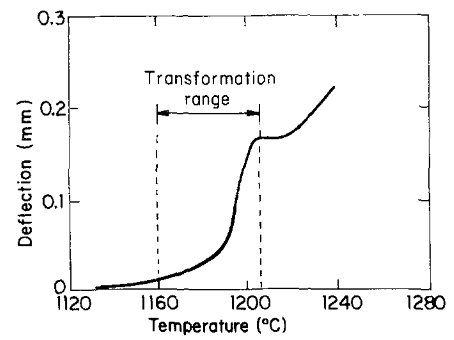

Figure 2 Deflection versus temperature for ZrO_2 tested in three-point bending at a constant heating rate of 5° C min^{-1} [29].

constant heating rate of 5° C min^{-1}. Although the precise curve depended on the specimen density, it was observed that the creep deflection increased rapidly at temperatures above ~1160° C, in the range of the monoclinic to tetragonal transformation. When all of the zirconia was in the tetragonal state, at a temperature of 1205° C, there was a short temperature range of ~20° C wherein no further creep was detected.

The type of behaviour shown in Fig. 2 was a consequence of earlier reports of reactive hot pressing through a phase change, showing evidence of enhanced densification during a decomposition reaction or phase transformation. Much of this early work has been reviewed by Chaklader [30] and Morgan [31], and represents evidence for an enhanced plasticity.

The first clear demonstration of transformation superplasticity in ceramics may be traced to experiments on Bi_2O_3 [32, 33], Bi_2WO_6 [32] and the Bi_2O_3–Sm_2O_3 eutectoid system [33-35]. These results, and more recent investigations, are summarized in Table I, which includes also the maximum reported compressive strain and the equivalent engineering strain.

In the early experiments on Bi_2O_3 and Bi_2WO_6 [32], samples were subjected to compressive creep testing through the monoclinic to cubic phase change at 730° C in Bi_2O_3 or the orthorhombic to tetragonal phase change at 940° C in Bi_2WO_6. Large discontinuous deformation was observed at the transition temperatures, and in practice the transformational strain per cycle was dependent on the applied stress, the heating rate and the initial grain size of the sample.

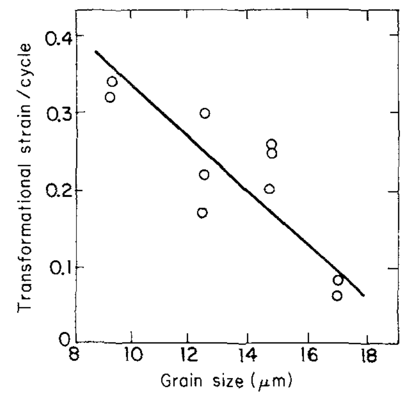

Figure 3 Transformation strain/cycle against grain size for Bi_2O_3 heated at 5° C min^{-1} under an initial stress of 1.38 MPa [32].

The latter effect is shown in Fig. 3 for Bi_2O_3 heated at 5° C min^{-1} under an initial stress of 1.38 MPa. The increase in transformational strain with decreasing grain size indicates the importance of grain boundary effects such as the occurrence of grain boundary sliding.

Transformation superplasticity may be achieved also by using other transformations such as eutectoid decomposition. For example, experiments on the Bi_2O_3–Sm_2O_3 eutectoid system showed transformation superplasticity associated with the eutectoid reaction [34] and a subsequent investigation of Bi_2O_3–4 wt% Sm_2O_3 demonstrated superplasticity in isothermal compression testing [35]. More recently, Panda *et al.* [37] reported the occurrence of large amounts of deformation (> 60%) in a supersaturated fine-grained $MgO \cdot 2Al_2O_3$ spinel when tested in compression at temperatures just below the solvus boundary. This behaviour was explained in terms of precipitation of α-Al_2O_3 from the solid solution, since the precipitation kinetics, as illustrated by the time-temperature-transformation diagram in Fig. 4 [38], were consistent with the deformation behaviour.

3.3. Structural superplasticity

Crystallinity is maintained up to the interfaces in metals, but in ceramics there is the additional possibility of an intergranular glassy phase. Structural superplasticity has been reported in ceramics both

TABLE I Transformation superplasticity in ceramics

Material	Initial grain size (μm)	Temperature (° C)	Strain rate sensitivity	Strain rate (sec^{-1})	Transition	Maximum strain (engineering strain)	Reference
Bi_2O_3	~10	730	–	–	Monoclinic-cubic	–1.15 (68%)	[32]
Bi_2WO_6	~10	940	–	–	Orthorhombic-tetragonal	–0.85 (57%)	[32]
Bi_2O_3-Sm_2O_3 eutectoid	~10	690	0.92	~10^{-4}	Eutectoid decomposition	–0.65 (48%)	[34]
Bi_2WO_6	3	885 ± 5	0.85	–	Not identified	> –0.65 (> 48%)	[36]
Bi_2MoO_6	5	675 ± 5	0.86	–	γ''-γ'	> –0.4 (> 34%)	[36]
$MgO \cdot 2Al_2O_3$	3.0*	1550	0.47	3×10^{-4}	Precipitation of Al_2O_3 from solid solution spinel	–1.0 (63%)	[37]

*Mean linear intercept grain size, equivalent to a spatial grain size of 4.6 μm.

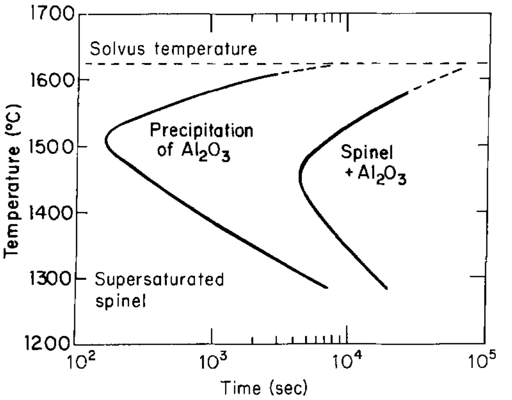

Figure 4 Time–temperature-transformation diagram for precipitation of α-Al_2O_3 from supersaturated $MgO \cdot 2Al_2O_3$ spinel [38].

with and without a glassy phase: these reports are reviewed in this section.

3.3.1. With an intergranular glassy phase

There are early indications of superplastic-like behaviour in the presence of an intergranular liquid phase in sintering experiments with ceramics.

Liquid-phase sintering is often used in ceramics because it permits densification at lower temperatures, thereby minimizing the effect of grain growth, and it is usually easy to obtain a liquid phase by the addition of alkaline and alumino silicates. As discussed in detail by Raj *et al.* [38], the segregation of a liquid phase to the grain interfaces may enhance the grain boundary diffusivity by up to several orders of magnitude. Also, the glassy state is expected to show ideal Newtonian viscous flow, with $m = 1$ in Equation 1, so that the superplastic effect should be optimized.

One of the earliest reports of a superplastic-like behaviour is related to the use of an LiF additive for the hot-pressing of MgO. It is well known that LiF acts as a densification aid for magnesia, initially by acting as a lubricant for the rearrangement of MgO particles and subsequently by forming a thin liquid film between the grains for pressure-enhanced liquid phase sintering [39]. In compressive creep experiments on unannealed hot-pressed MgO containing ~0.25 wt % Li, Hart and Pask [40] reported large increases in the strain rate under constant stress when samples were heated above ~830° C. True strains above 0.25 were recorded without the onset of tertiary creep, and the measured value of m was very close to unity. Since the lithium content was much reduced after creep testing, it was concluded that LiF was evaporated during the test, and it was noted that the exceptional deformation without cracking was, in the broadest sense, an example of superplasticity.

Glass ceramics are ideal materials for the attainment of superplasticity because they consist of fine-grained crystals in a glassy matrix. For example, Bold and Groves [41] reported tensile strains of up to 30% in a lithium aluminosilicate glass ceramic. Many of these early results, and the implications of superplastic behaviour, have been reviewed by Carry and Mocellin [42].

Detailed experiments were conducted on two β-spodumene glass ceramics by Wang and Raj [43] and the results are summarized in Table II. Two different glass ceramics, containing 64.6 wt % and 69.9 wt % SiO_2, respectively, were tested in compression and tension under a constant displacement rate. Both materials exhibited strain-rate sensitivities of ~ 1, and the maximum tensile elongations were ~400 and 135% for the two materials, respectively. It should be noted that the higher elongations occurred in the material having lower flow stresses and faster creep rates for the same grain size.

In the less ductile material with 69.9 wt % SiO_2, Wang and Raj [43] showed that the flow stress in tension was consistently lower than the flow stress in compression. This result is illustrated in Fig.5 in a plot of strain rate, $\dot{\varepsilon}$ against flow stress, σ, at a strain of ± 0.30. Both curves give a slope of ~ 1, so that m is also close to 1. The difference in behaviour between the two testing conditions is probably due to the additional force required to overcome friction between the ends of the specimen and the loading platens in compression testing.

Finally, it should be noted that Wang and Raj [44] performed additional tests on the two glass ceramics and reported that the material with 64.6 wt % SiO_2 could be deformed essentially indefinitely in tension if a sufficiently high hydrostatic pressure (of the order of twice the flow stress) was superimposed during testing.

3.3.2. Without a significant intergranular glassy phase

Metals generally do not contain an intergranular glassy phase, but the situation for ceramics is less clearly defined. As noted by Carry and Mocellin [42], it is appropriate to refer to a wide range of ceramics as nominally single phase even though, due to very low solubility limits, they may contain small pockets of residual impurities or glassy layers at the grain interfaces. In this section, structural superplasticity is examined in ceramics where either there is no

TABLE II Structural superplasticity in ceramics with an intergranular glassy phase

Material	Initial grain size (μm)	Temperature (K)	Strain rate sensitivity	Strain rate (sec^{-1})	Maximum tensile strain	Reference
64.6 wt % SiO_2 glass ceramic	~1	1298	~1	~10^{-4}	~400%	[43]
69.9 wt % SiO_2 glass ceramic	~1	1423	~1	~10^{-4}	135%	[43]

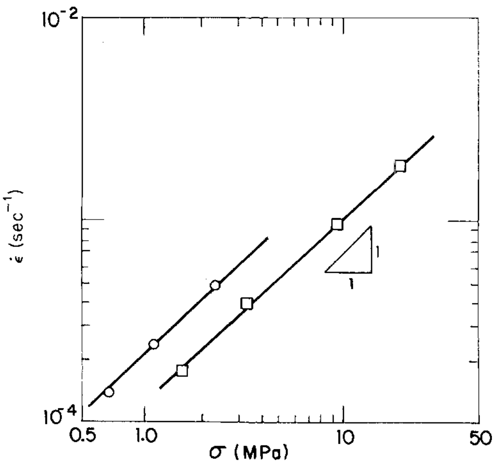

Figure 5 Strain rate against flow stress at a strain of ± 0.30 for tests in ○, tension and □, compression on a 69.9 wt % SiO_2 glass ceramic [43].

intergranular glassy phase or, if a glassy phase is present, it tends to be isolated primarily in pockets at the triple junctions.

The very small grain sizes inherent in many systems suggest that they may be ideal materials for superplastic deformation but, as discussed earlier, the overall ductilities are generally restricted because of the occurrence of intergranular brittleness through the nucleation and growth of grain boundary cavities. This problem was addressed theoretically by Evans *et al.* [45] in an attempt to identify specific microstructures and strain-rate regimes where superplastic deformation may be favoured. Their analysis shows that cavity nucleation is suppressed in the absence of a grain boundary amorphous phase. It was noted that it would be helpful to identify specific solid-solution additives that lead to rapid grain-boundary diffusion.

There have been numerous reports of structural superplasticity in nominally single phase ceramics; the results are summarized in Table III for all investigations where the maximum strains achieved were reasonably large. (Table III does not include experimental results which were reported as indicative of, and consistent with, superplastic flow but where the tests were terminated at relatively low total strains: examples are Al_2O_3 [63, 64], MgO [65] and TiO_2 [57].)

As indicated in Table III, the first reports of structural superplasticity in a ceramic material may be traced to the work of Chung and Davies [46–48] on UO_2. Subsequently, superplasticity was reported in several different ceramics including Al_2O_3, MgO, α-SiC and yttria-stabilized tetragonal ZrO_2 (Y–TZP).

Inspection of Table III leads to four important conclusions:

1. The grain sizes of superplastic ceramics are consistently extremely small and usually $< 1\ \mu m$. This contrasts with superplastic metals where the grain sizes are usually of the order of 2 to 5 μm.

TABLE III Structural superplasticity in ceramics without a significant intergranular glassy phase

Material	Initial grain size (μm)	Temperature (K)	Testing conditions	Strain rate sensitivity	Strain rate (sec^{-1})	Maximum strain	Reference
UO_2	2	1623	Compression	~1	$\sim 10^{-5}$	68.6%	[46–48]
MgO	0.1–1.4	1327	Compression	~0.83	$\sim 10^{-5}$	> 80%	[49]
Al_2O_3 (+0.05% MgO)	0.75	1723	Compression	~0.75	$\sim 10^{-6}$	> 39%	[50]
α-SiC (+1.5% Al)	1.5–2.8	2173	Compression	~1	$\sim 10^{-4}$	> 40%	[51]
Al_2O_3 (+0.25% MgO)	1.0	1693	Compression	-	$\sim 10^{-4}$	> 45%	[52]
Y-TZP*	0.3–2.2	1723	Compression	~0.5	$\sim 10^{-4}$	> 78%	[53]
Y-TZP	0.3	1723	Tension	~0.5	$\sim 10^{-4}$	> 120%	[19]
Y-TZP	0.3–0.4	1723	Tension	0.53	$\sim 10^{-4}$	> 160%	[20]
			Compression	0.48	$\sim 10^{-4}$	> 78%	
Y-TZP/20% Al_2O_3†	0.9	1772	Compression	0.53–0.83	$\sim 10^{-4}$	> 84%	[54]
$BaTiO_3$	0.45	1423	Compression	~0.5	$\sim 10^{-4}$	> 39%	[55]
Y-TZP	0.5	1570	Compression	-	$\sim 10^{-5}$	39%	[56]
Al_2O_3 (+0.05% MgO)	~1	1723	Compression	0.5–1.0	$\sim 10^{-4}$	> 39%	[57, 58]
Y-TZP	~0.2	1573	Compression	~0.7	$\sim 10^{-4}$	> 41%	[57, 58]
Y-TZP/20% Al_2O_3	~0.5	1723	Tension	~0.5	$\sim 10^{-4}$	> 200%	[59]
Y-TZP	0.3	1823	Tension	~0.3	$\sim 10^{-4}$	350%	[60]
Y-TZP/20% Al_2O_3	0.5	1923	Tension	~0.5	$\sim 10^{-3}$	~500%	[61]
Y-TZP	0.53	1600	Compression	~1	$\sim 10^{-4}$	99%	[62]

*Tetragonal ZrO_2 stabilized with 3 mol % Y_2O_3.

†Composite of Y-TZP with 20 wt % Al_2O_3.

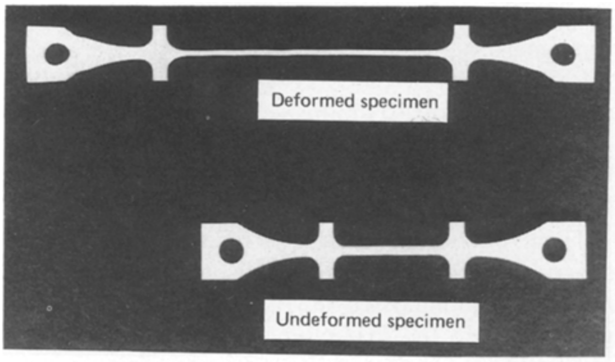

Figure 6 Tensile superplasticity in Y-TZP with an initial gauge length of 30 mm deformed in air to > 120% at 1723 K [19].

2. The value of the strain rate sensitivity, *m*, is generally in the range from 0.5 to 1.0, whereas in metals the superplastic condition is usually characterized by $m \simeq 0.5$ [22].

3. The strain rate for optimum superplasticity is often close to $10^{-4}\,\text{sec}^{-1}$ in ceramics. This is lower than in most metals, but is consistent with the experimental observation on metals that optimum superplasticity occurs at lower strain rates when the grain size is reduced [66].

4. Most of the early claims of superplasticity in ceramics refer to tests conducted in compression rather than in tension. Since this testing mode does not provide a satisfactory check on the occurrence of intergranular brittleness, these reports do not strictly represent true superplastic behaviour.

If attention is restricted specifically to tests in tension, Table III shows five reports of true superplasticity in ceramics.

The first two reports were by Wakai and co-workers [19, 20] on 3 mol % Y_2O_3-stabilized tetragonal ZrO_2 (Y-TZP) with maximum tensile elongations at a testing temperature of 1723 K of > 120 and > 160%, respectively. This remarkable first demonstration of tensile superplasticity in a ceramic is shown in Fig. 6 for a specimen of Y-TZP with an initial gauge length of 30 mm deformed in air to > 120% at 1723 K [19]: it is clear from the appearance of the deformed specimen that the deformation was uniform with no local necking.

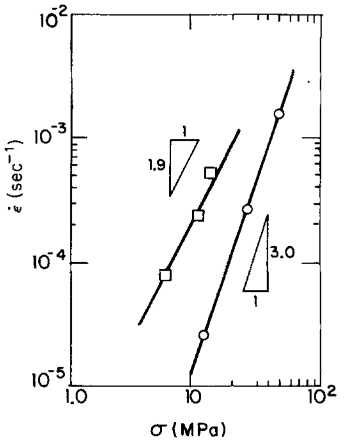

Figure 7 Strain rate against stress for Y-TZP tested in tension at 1723 K, showing the difference between the results of □, Wakai *et al.* [19] and ○, Nieh *et al.* [60].

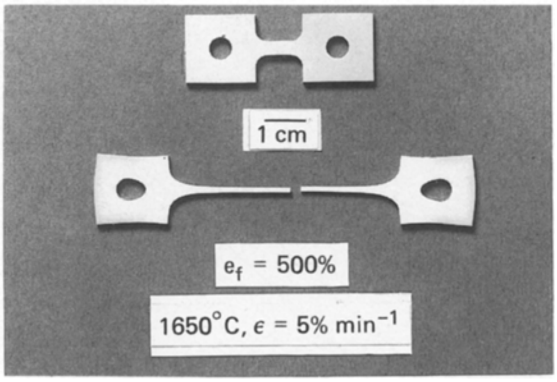

Figure 8 Tensile superplasticity to an elongation of ~ 500% in a Y-TZP/20% Al_2O_3 composite [61].

Later work on Y-TZP by Nieh *et al.* [60] led to a tensile elongation of 350% after testing in vacuum at 1823 K. (There is also an unpublished tensile elongation of over 800% in Y-TZP, as cited by Nieh *et al.* [61].) However, there is a significant discrepancy between the two sets of mechanical data at 1723 K because Wakai *et al.* [19] obtained $m \simeq 0.5$ and Nieh *et al.* [60] reported $m \simeq 0.3$. This difference is illustrated in Fig. 7, where the strain rate is plotted against stress and the slopes of the lines give the values of the stress exponent, $n\ (= 1/m)$.

Nieh *et al.* [60] suggested that the value of $m \simeq 0.3$ obtained in their experiments may be due to viscous glide and the dragging of solute atom atmospheres as in metallic solid solution alloys [67]. This seems unlikely for four reasons. First, superplasticity is usually attributed to a grain boundary process rather than an intragranular dislocation mechanism. Second, Wakai *et al.* [53] reported that the strain rate in Y-TZP is proportional to $(1/d)^{1.8}$ where *d* is the grain size; this is consistent with superplasticity in metals where the strain rate is typically proportional to $(1/d)^2$ [68] but it is not consistent with the viscous glide mechanism where there is no dependence on grain size. Third, it has been shown that a strain-rate sensitivity of ~ 0.3 in ceramics, equivalent to a stress exponent of ~ 3, is generally best interpreted in terms of the climb of dislocations from Bardeen–Herring sources when crystallographic slip is restricted rather than by the mechanism of viscous glide [28]. Fourth, Carry [69] has noted significant changes in the values of *n* in Y-TZP depending on the impurity content and especially the level of Al_2O_3: since it is known that yttria-stabilized tetragonal ZrO_2 tends to contain a glassy grain-boundary phase [70], the effect of Al_2O_3 content is probably associated with the nature and extent of the glassy phase.

More recently, there have been two reports of tensile superplasticity in a Y-TZP composite containing 20 wt % Al_2O_3. The first report by Wakai and Kato [59] gave a maximum tensile elongation of > 200% in air at 1723 K, and subsequently Nieh *et al.* [61] obtained a maximum elongation of ~ 500% by testing in vacuum at 1923 K: the latter result is illustrated in Fig. 8. There is a consistent relationship between strain rate and stress in these two sets of experiments,

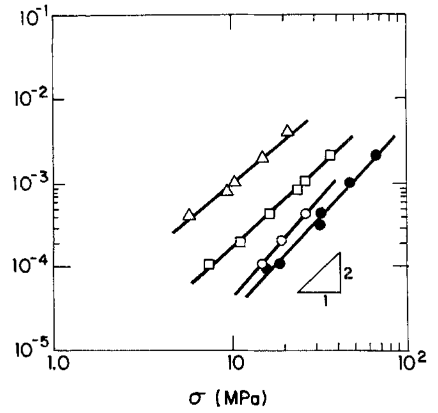

Figure 9 Strain rate against stress for a Y-TZP/20% Al_2O_3 composite. T (K) = ●, 1723 [59]; ○, 1723, □, 1823 and △, 1923 [61].

as shown in Fig. 9 where the strain rate sensitivity is ~0.5.

An important parameter in achieving superplasticity is clearly the ability to fabricate, and to retain during testing, a very fine and fairly uniform grain size. In Y-TZP, the Y_2O_3 additive inhibits grain growth and the sintered material typically contains ~90% of tetragonal phase ZrO_2 and ~10% of cubic phase ZrO_2 [19]. Microstructural observations after testing of Y-TZP show no grain growth at 1523 K [19], minimal grain growth at 1723 K [19, 60], and growth from an initial grain size of ~0.3 μm to a final size of ~1 μm after testing at 1823 K [60]. In the Y-TZP composite, the 20 wt % Al_2O_3 corresponds to a volume fraction of 28%, and the Al_2O_3 grains are dispersed reasonably uniformly throughout the ZrO_2 grains. This suggests that grain growth will be inhibited, even at high temperatures, and this is confirmed by measurements of Nieh *et al.* [61] where there was grain growth from 0.5 to 0.9 μm after testing for 18 h at 1823 K; the microstructures for these two conditions are shown in Fig. 10.

Finally, in view of the obvious importance of Y-TZP and the Y-TZP/Al_2O_3 composite in the superplasticity of ceramics, it should be noted that some summaries are available covering the superplastic data for these materials [71–73].

4. Superplasticity in intermetallic compounds

There is increasing interest in the possibility of attaining superplasticity in intermetallic compounds. These compounds exhibit superior creep, fatigue and corrosion resistance but their use tends to be limited because of low ductility and consequent difficulties in fabrication.

Structural superplasticity has been reported in several intermetallic compounds, as summarized in Table IV. Based on their initial microstructures, the superplasticity of these materials falls into two distinct categories: (i) single phase superplasticity, as in Fe_3 (Al, Si) [74] and the Ni_3Al + Cr alloy [78], and (ii) duplex-phase superplasticity, as in Ni_3Al with a disordered γ phase [75] and the Ni_3Al + Cr + Zr alloy [78].

The first report of superplasticity in an intermetallic compound was by Hanada *et al.* [74] in 1981 using an $Fe_3(Al_{0.35}, Si_{0.65})$ alloy. This alloy is known as Sendust, it is a magnetic head material, and an elongation of 100% was attained at a temperature of 1123 K. Subsequently, single-phase superplasticity was reported in Ni_3Al with an elongation of 160% [76, 77], an Ni_3Al + Cr alloy with an elongation of 100% [78] and TiAl with an elongation of > 100% [79].

There are two important differences between the reports of single-phase superplasticity in intermetallic compounds and structural superplasticity in metals and ceramics. First, superplasticity may be attained in intermetallic compounds even when the initial grain size is fairly large, as in Sendust with an initial grain size of 100 μm [74]. Kim *et al.* [77] noted that an extremely small initial grain size is not required in Sendust because of the occurrence during deformation of dynamic recovery within the grains and dynamic recrystallization near the grain boundaries. Second, intragranular dislocation movement is important in the single-phase superplasticity of intermetallic compounds, as demonstrated in, for example, Ni_3Al [77].

5. Superplasticity in geological materials

The concept of superplastic deformation has been applied to rocks and minerals. As in metals and ceramics, there are reports of both transformation and structural superplasticity.

5.1. Transformation superplasticity

The Earth's upper mantle consists primarily of orthorhombic olivine with composition $(Mg_{0.91}Fe_{0.09})SiO_4$, but there is a transition to a dominant spinel phase at

TABLE IV Structural superplasticity in intermetallic compounds

Material	Initial grain size (μm)	Temperature (K)	Testing conditions	Strain rate sensitivity	Strain rate (sec^{-1})	Maximum strain	Reference
Fe_3(Al, Si)	100*	1123	Tension	–	10^{-4}	100%	[74]
Ni_3Al/γ	10*	1373	Tension	–	~10^{-3}	638%	[75]
Ni_3Al	1.6†	973	Tension	> 0.4	10^{-4}	160%	[76, 77]
Ni_3Al + Cr	10	1273	Tension	~0.5	~10^{-3}	100%	[78]
Ni_3Al + Cr + Zr	10	1273	Tension	~0.5	~10^{-3}	280%	[78]
TiAl	60†	1373	Tension	0.2–0.3	10^{-3}	> 100%	[79]
Ni_3Si/α	15	1353	Tension	0.5	~10^{-3}	650%	[80]

*Prepared by powder metallurgy.

†Prepared by hot deformation and recrystallization.

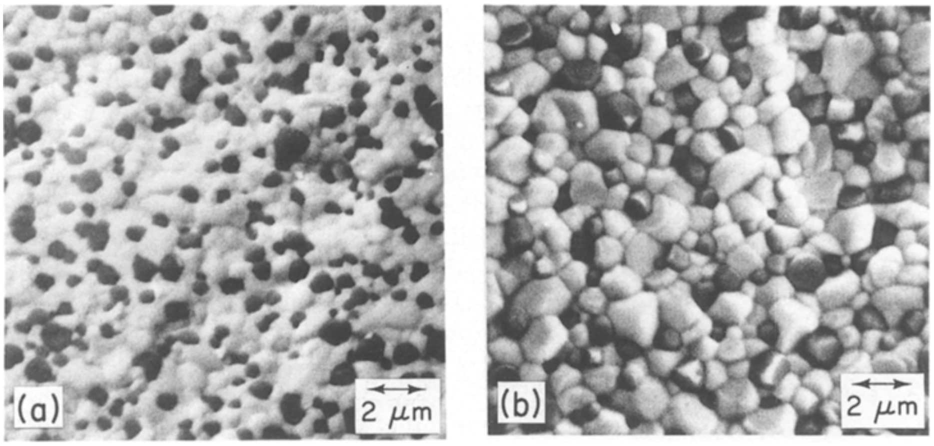

Figure 10 Microstructure of Y-TZP/20% Al_2O_3 composite: (a) before testing; (b) after testing for 18 h at 1823 K [61].

depths below ~400 km. The olivine–spinel transformation is due to pressure and in practice it occurs through a mixed phase region with a thickness of ~30 km.

Following an earlier suggestion by Gordon [81], Sammis and Dein [82] were the first to examine in detail the possibility that the transformation zone may have a low effective viscosity due to the occurrence of transformation superplasticity. By conducting laboratory experiments on polycrystalline CsCl, where there is a phase change from b c c β to f c c α at 460° C, evidence was presented for macroscopic deformation at the phase boundary. Noting that a temperature-induced structural change is analogous to a pressure-induced change, it was concluded that flow is localized at the first-order density discontinuities in the Earth's mantle at depths of ~400 and ~650 km.

Subsequently, transformation superplasticity has been invoked in several geological investigations of phase transitions [83–85], and Poirier [86] has derived the appropriate expressions for the changes in strain rate or stress at a phase transition. (Since very large superplastic elongations are not strictly relevant in geophysical situations, Poirier [86] prefers the term "transformation plasticity".)

5.2. Structural superplasticity

There are two types of data relating to structural superplasticity in geological materials.

First, there are mechanical data from laboratory experiments which may be interpreted as evidence for structural superplasticity based on a high strain-rate sensitivity (or a low stress exponent) and additional observations such as a strain rate which depends on grain size and a large contribution from grain-boundary sliding. For example, rheological data from a fine-grained (d = 1 to 10 μm) limestone gave $n \simeq 2$ (so that $m \simeq 0.5$) at low stresses, and it was concluded by extrapolation that superplasticity may be an important deformation process in rocks [87, 88]. There is also evidence for structural superplasticity in an Mg_2GeO_4 spinel with a grain size of 3 μm, where again $n \simeq 2$ [89].

Second, there is microstructural evidence for the occurrence of structural superplasticity in a wide range of naturally-deformed materials [90–98]. To assist in post-deformation interpretation, Boullier and Gueguen [92] listed six criteria which should be examined in order to confirm that superplasticity has been an active flow mechanism. Briefly, these criteria for superplasticity are a high temperature, very small grain size, low stress and strain rate, essentially equiaxed grains, low dislocation densities with no sub-boundaries, and a high strain-rate sensitivity. Boullier and Gueguen [92] demonstrated the application of these criteria by examining several different natural mylonites.

Attempts have been made to incorporate superplasticity into deformation mechanism maps for geological materials [88, 99], but this is difficult because of uncertainties in the precise flow laws.

Finally, it is interesting to note that a different type of local heterogeneous superplastic deformation has been proposed recently for ice, based on examinations of deep cores from polar ice sheets and evidence for continuous boundary migration and grain growth [100, 101].

6. Discussion

It is clear from the preceding sections that there are many reports of superplastic (or superplastic-like) behaviour in a wide range of non-metallic materials. For technological applications, the most significant development is the recent demonstration of tensile structural superplasticity in ceramics which do not contain a significant intergranular glassy phase: these results are documented in Table III. In this section, attention will be restricted to the mechanisms of structural superplasticity and the applications of superplastic ceramics.

6.1. Superplasticity with a glassy phase

This type of structural superplasticity is well documented in glass ceramics, as shown in Table II, but it is not found in metals and therefore necessitates the development of a new and unique flow mechanism. There are two major processes for deformation in a polycrystalline material containing a liquid phase.

The first mechanism, by Pharr and Ashby [102], is depicted schematically in Fig. 11. This mechanism of liquid-enhanced creep requires a repetitive cycle of plasticity and dissolution. Initially, the crystal grains press together under a stress σ to produce a zone of plasticity of width $2x$ (Fig. 11a). The liquid removes the neck by dissolution until the dihedral angle reduces to a critical value, ϕ_{EQ} (Fig. 11b). Thereafter, there is further plasticity so that the neck grows

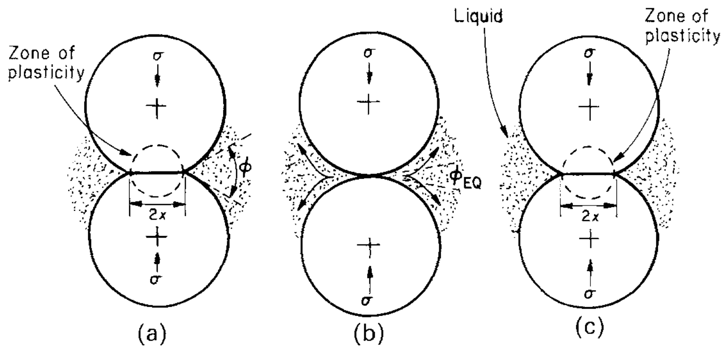

Figure 11 Model for liquid-enhanced creep based on repetitive plasticity and dissolution [102].

(Fig. 11c), and this is again followed by dissolution so that the process is repetitive.

As noted by Wang and Raj [43], it is difficult to apply the mechanism of Fig. 11 to glass ceramics tested in tension because (i) the mechanism requires a compressive principal stress; (ii) if there is a small volume fraction of liquid it will segregate to triple junctions; and (iii) there is no evidence for any dislocation activity. Thus it is appropriate to consider the second mechanism, proposed by Raj and Chyung [103], as depicted schematically in Fig. 12.

This mechanism is based on the concept that the interface between two grains consists of islands, where the adjacent crystals meet, surrounded by an interpenetrating liquid phase. In Fig. 12, the glass layer is of thickness h, the normal traction across the interface is supported by the islands, and the glass provides a path for fast diffusion of the molecules. It has been shown that the creep results documented in Table II for the 69.9 wt % SiO_2 glass ceramic are consistent with the predictions of this model [103].

6.2. Superplasticity without a significant glassy phase

6.2.1. *Mechanical characteristics*

In the superplasticity of metals, Equation 1 is usually expressed in the more explicit form of

$$\dot{\varepsilon} = \frac{ADGb}{kT}\left(\frac{b}{d}\right)^{p}\left(\frac{\sigma}{G}\right)^{n} \qquad (2)$$

where D is the appropriate diffusion coefficient, G is the shear modulus, b is the Burgers vector, k is Boltzmann's constant, T is the absolute temperature, d is the grain size, n is the stress exponent ($= 1/m$) and A and p are constants. An advantage of using Equation 2 is that it provides a direct link with analyses of high temperature creep [28, 104].

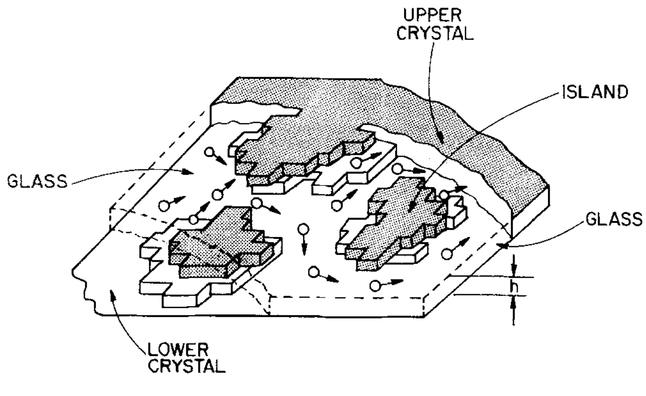

Figure 12 Model for superplasticity in a glass ceramic based on an interface consisting of islands surrounded by a liquid phase [103].

As noted in Fig. 1, superplastic metals usually exhibit a sigmoidal relationship between stress and strain rate, dividing the behaviour into three distinct regions. At high strain rates, region III has many similarities with normal dislocation creep; in the superplastic region II, $n \simeq 2$ (so that $m \simeq 0.5$), $p \simeq 2$ to 3, the activation energies are similar to the values for grain boundary diffusion, and the contributions from grain boundary sliding to the total strain are high (~ 50 to 70%); whereas in the low stress region *I*, $n \simeq 3$ to 5, $p \simeq 2$ to 3, there is an increase in the activation energies to values close to that of lattice self-diffusion, and the measured sliding contributions are low ($\sim 30\%$) [68].

It is difficult to obtain any meaningful information from the measured activation energies for superplastic ceramics because the appropriate values for grain boundary and lattice diffusion are not well documented. However, the values of m given in Table III are in the range ~ 0.5 to 1.0, and for the tests performed in tension the results generally give $m \simeq 0.5$ ($n \simeq 2$) which is consistent both with experimental data for metals [68] and with most of the standard theories of structural superplasticity [105]. In addition, there is experimental evidence for $p \simeq 2$ to 3 in UO_2 [46, 47] and $p = 1.8$ in Y-TZP [20, 53], which again is similar to superplasticity in metals. Finally, Wakai and co-workers reported grain-boundary sliding contributions in the Y-TZP/20% Al_2O_3 composite of 75% [54] and 60 to 80% [59], respectively. This is similar to tabulated data for superplastic metals [106], but it should be noted that Wakai *et al.* [54, 59] used a grain shape technique which is generally considered unreliable in metals because of the tendency for migration continually to spheroidize the grains [107].

One apparent dichotomy between metals and ceramics concerns the relationship between $\dot{\varepsilon}$ and σ: whereas superplastic metals tend to give an S-shaped curve and three regions of flow as illustrated schematically in Fig. 1, the data points for superplastic ceramics tend to lie along reasonably straight lines as in Figs 7 and 9. This difference is probably due to the rather limited range of strain rates usually employed at any single temperature when testing ceramics. Indeed, Carry and Mocellin [55] specifically noted a transition in $BaTiO_3$ from $n \simeq 3$ at low stresses to $n \simeq 2$ at higher stresses, similar to the transition from region I to region II in Fig. 1, and they reported a decrease in activation energy from $\sim 1200\,\mathrm{kJ\,mol^{-1}}$ in region I to $\sim 800\,\mathrm{kJ\,mol^{-1}}$ in region II. This trend is similar to the well-established behaviour in superplastic metals.

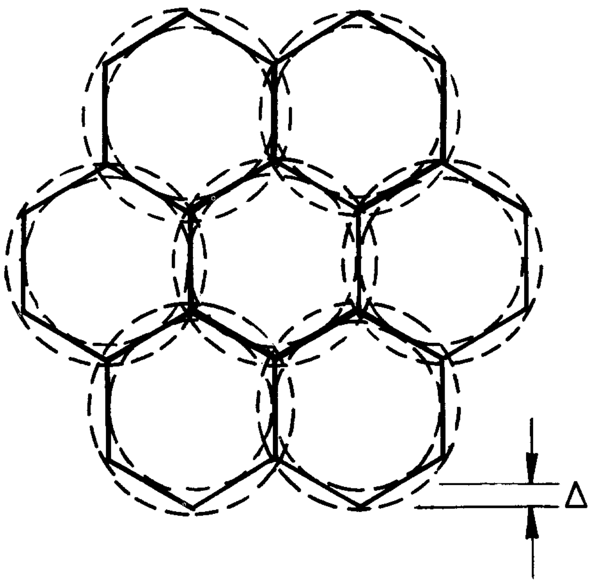

Figure 13 A model for flow in the presence of a glassy boundary phase: Δ is the width of the glass phase for unrestricted rotation.

6.2.2. The flow mechanism

As already noted, Y-TZP tends to contain a glassy boundary phase [70]. It is therefore instructive to examine the significance of this phase in any consideration of the flow mechanism.

It is reasonable to visualize each grain as a central core surrounded by a peripheral mantle [108]. If there is an assemblage of regular hexagonal grains, as shown in Fig. 13, they can rotate without deformation of the central core if the mantle is defined as the area swept out between the apices and mid-points of the sides of the rotating hexagons. This mantle has a width Δ which is given by [105]

$$\Delta = \frac{d}{2}\left(1 - \frac{\sqrt{3}}{2}\right) \qquad (3)$$

Thus, for a typical Y-TZP grain size of 0.3 μm (Table III), the grains can move freely over each other, without grain deformation, if there is a liquid phase at the grain boundaries with a thickness of 0.02 μm. Clearly, this thickness is unrealistically large (note, however, that glassy pockets up to $\sim 0.1\,\mu$m in size have been reported in a zirconia-toughened Al_2O_3 [109]). However, in practice the thickness would be reduced because of (i) non-uniformity in the grain distribution; (ii) the occurrence of grain deformation; and/or (iii) enhanced diffusion associated with the boundary region leading to the easy removal of obstructing asperities. In this connection, there is evidence for enhanced boundary widths for diffusion in both ceramics [110] and minerals [111].

6.3. Applications of superplasticity in ceramics

In the long term, the utility of superplastic ceramics will depend on their success in forming applications. However, since superplastic forming necessitates tensile and compressive stresses, the development of ceramics with reasonably large tensile elongations is a necessary first step.

There have been reports of superplastic forming of Al_2O_3 [58, 63] and Y-TZP [20, 58, 72, 73], and hot forging of ZrO_2 and Al_2O_3/ZrO_2 ceramics [112]. Figure 14 shows an example of a piston ring fabricated from Y-TZP [20], where a Y-TZP bar, with dimensions of 4 × 2 × 187 mm, was bent around an SiC disc with diameter of 60 mm. The finished product was achieved in ~ 10 min by bending in air at 1450° C.

Bulge forming has also been achieved with Y-TZP, and the principle is illustrated schematically in Fig. 15 [20]. A Y-TZP pipe is shown in cross-section in Fig. 15a, and the pipe contains a powder between two SiC loading rams. When the loading rams are compressed under a stress σ, as in Fig. 15b, the Y-TZP is bulge formed into the die. Wakai *et al.* [20] report the successful use of this forming procedure using either SiC or BN powder with a Y-TZP pipe (inner and outer diameters of 7.0 and 10.7 mm, respectively, and a length of 30 mm) and by compressing the SiC rams at 0.2 mm min^{-1} at 1450° C.

Clearly, forming tests of this type will become of increasing importance in the future development and utilization of superplastic ceramics.

7. Conclusions

1. There are numerous examples of both transformation and structural superplasticity in ceramics: these examples are tabulated in this review.

2. Structural superplasticity occurs in ceramics both with an intergranular glassy phase and without a significant glassy phase.

3. Based on the limited data now available, it

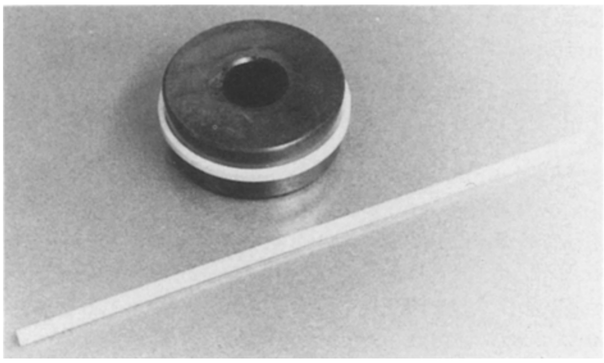

Figure 14 Piston ring fabricated from Y-TZP: the dimensions of the Y-TZP bar are 4 × 2 × 187 mm [20].

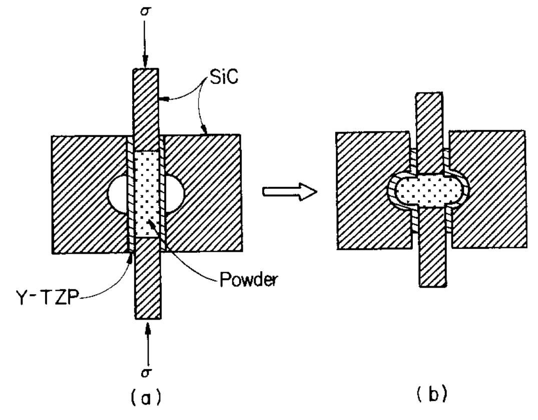

Figure 15 The principle of bulge forming with Y-TZP: (a) initial condition; (b) after compressing the loading rams [20].

appears that many of the characteristics of structural superplasticity in ceramics are similar to metals including the variation of strain rate with stress and grain size and the large contribution from grain-boundary sliding.

4. Superplasticity is becoming increasingly important in intermetallic compounds, and also it has been widely invoked for geological materials both after deformation in the laboratory and in naturally-deformed rocks.

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