High Temperature Mechanical Behavior of Silicon Nitride Ceramics

Tanguy ROUXEL

Laboratoire de Recherche en Mecanique Appliquee de l'Universite de Rennes 1 (LARMAUR), UPRES-EH 2310
University of Rennes 1, Comte de Beaulieu, 35042 Rennes Cedex, France

The temperature dependences of Young's modulus (E) and fracture toughness (Kic), as well as the flow behavior, including stress relaxation, creep and superplasticity of several silicon nitride-based materials, monoliths and composites, are reviewed. A transition range between a low softening rate and a higher one, which coincides with the onset of creep ductility, is observed between 1080 and 1150°C on the E(T) curves and is attributed to the behavior of the secondary glassy phases. The higher the Y/Al ratio or the SiC content, the higher the transition temperature. The Kic(T) curves exhibit four different stages which were discussed and interpreted through a theoretical analysis, warning against the frequent confusion between the intrinsic and the apparent (experimentally accessible) toughness. Reliable creep resistant- or inversely superplastic-ceramics are now available. However, the high temperature deformation mechanisms are not well understood yet. Non-Newtonian flow regimes and the pronounced tension/compression flow asymmetry are still intriguing. Today, it can be anticipated that with the development of materials containing low amounts of highly refractory grain boundary phases, ceramists are facing a situation that places them closer to metalurgists, and which should allow them to derive more benefit from the exceptional intrinsic properties of covalent crystals such as Si3N4. Consequently, grains should play a more and more important role on the high temperature mechanical behavior.

Key-words: Silicon nitride, Mechanical behavior, Elasticity, Fracture toughness, Creep, Superplasticity

1. Introduction

The suitability of a silicon nitride ceramic to a peculiar application (energy conversion systems, automotive industry, refractory industry...) depends on its high temperature mechanical performance, which is intimately linked to the amount and nature of the sintering additives. Nowadays, after years of intensive research focussed on processing methods and microstructure control, a relatively wide range of materials with different properties is available. In comparison with materials prepared in the 70s which generally contained over 10 vol% sintering additives, and were restricted for use at temperatures lower than 1200°C, the last generation of silicon nitride grades, sintered with low amounts of — and eventually no — additives, consists of materials with well-controlled microstructures, designed to meet some specific requirements, and with potential applications above 1300°C.

The study of the high temperature behavior of silicon nitride ceramics is particularly difficult because of the various dynamic microstructural changes that may occur upon testing. For instance, the intergranular glassy phases may experience a glassy transition phenomenon at around 1000°C, crystallization sequences may start above this temperature, additional secondary liquid phases may form from — and above — 1300°C, and decomposition occurs at higher temperature. All these changes have a direct incidence on the strength, the fracture toughness, the creep rate or the thermomechanical stability in general. Silicon nitride ceramics sintered with additives may soften at temperature as low as 900°C. Materials synthesized in the 70s and containing many impurities softened even at temperatures below 850°C.1,2) By contrast, model materials of the late 90s3,4) and sintered with high purity powders and no sintering additive, consists of materials with well-controlled microstructures, designed to meet some specific requirements, and with potential applications above 1300°C.

Note in Fig. 1 that the crystallization of the intergranular phases might have detrimental effects on the mechanical resistance. For instance, such a situation is encountered when some of the quaternary compounds in the Y-Si-O-N system form, with a concomitant volume expansion leading to microcracking.5,6) Furthermore, although the oxidation resistance come into play above 1200°C, it is not considered here. The onset temperature for the formation of additional liquid phase is assumed to coincide with the lowest liquidus temperature with respect to the material composition, and more specifically with the intergranular phase composition. For instance, lowest liquidus temperatures of 1350 and 1660°C were identified in the SiO2-Al2O3-Y2O3 and SiO2-Y2O3 phase diagrams, respectively. It is also likely that the addition of nitrogen decreases these temperatures.7,8)

2. Young’s modulus

The temperature dependence of Young’s modulus has been investigated by ultrasonic-echography in the [20–1400 °C] range for different oxynitride glasses, silicon nitride
ceramics, and SiC/Si$_3$N$_4$ particulate composites (Fig. 2). An ultrasonic technique was used to follow the change in Young's modulus as a function of temperature. The principle of the method consists in calculating $E$ from the velocity of an ultrasonic pulse propagating in a long, thin and refractory wave-guide sealed to a specimen (about 1 x 3 x 40 mm$^3$). A magnetostrictive transducer (300 kHz) was used and experiments were performed under argon atmosphere with a heating rate of 5°C·min$^{-1}$ from room temperature and up to 1400°C. In the present case, the longitudinal wave velocity is about 10 km·s$^{-1}$, and it follows that the wave-length is about 33 mm, that is much greater than the characteristic dimension of the specimen cross section. The condition of very long wave length, in comparison to the scale of the microstructure, is thus satisfied, and the material response is governed by the effective properties of the equivalent homogeneous medium. Furthermore, in this case, the long beam mode approximation holds, so that $E$ can be calculated from the density ($\rho$) and the longitudinal wave velocity ($V_L$) according to:

$$E = \rho V_L^2 \quad (1)$$

The room temperature elastic moduli were first accurately measured by means of piezoelectric transducers (10 MHz) in direct contact with the specimen.

Most curves in Fig. 2 exhibit transition ranges between a slow softening rate and a faster one. In the case of glasses this transition corresponds to the glass transition range, and is located between 840 and 920°C for oxynitride glasses. Transition temperatures are reported in Table 1. The changes in Young's modulus as a function of temperature as measured on a pure SiO$_2$ glass and on a bulk SiOC glass containing 12 at% covalently bonded carbon atoms were also replotted from the literature. Such glasses are of interest here because high purity silicon nitride ceramics might contain glassy intergranulary films with composition close to SiO$_2$, and because it is still unclear whether or not some carbon atoms may diffuse into the glassy phase during processing or high temperature testing of SiC-containing materials.

In the case of Si$_3$N$_4$ ceramics (material references are indicated in Table 1), the slow decrease ends near 1000-1200°C with slopes ranging from -13 MPa·°C$^{-1}$ for the high purity Si$_3$N$_4$ grade, to -29 MPa·°C$^{-1}$ for ceramics with more than 6 vol% additives (or intergranulary phase). Above 1150°C, a rapid softening regime is observed, with $dE/dT$ between -90 (pure Si$_3$N$_4$) and -258 (Si$_3$N$_4$+10 vol% glass) MPa·°C$^{-1}$. The higher the glassy phase content, or the higher the alumina/yttria ratio, or the lower the SiC particle content is, and the faster the softening becomes. SiC particles located at two-grain interfaces are known to hinder sliding and to increase the cross-linking degree of three-dimensional granular network. Whereas the first effect leads to a remarkable creep resistance, the second one would explain why SiC particles greatly reduce the rapid softening observed above the transition in the $E(T)$ curves. Noteworthy, the decrease in the elastic modulus above the transition follows the same trend as the decrease in viscosity, or as the increase of the creep rate, e.g. materials exhibiting the fastest softening are also those experiencing the highest apparent activation energy for flow.

In order to clarify the role of the amorphous pockets on the ultrasonic testing results, a silicon nitride material was sintered at relatively low temperature (at $T_g$ + 150°C) with the aid of 10 vol% of an oxynitride glass of known rheological behavior. The transition range of the ceramic is located 200°C above the glass transition temperature of the parent glass. Since the densification temperature was between $T_g$ and $T_c$ (crystallization) of the glass, the intergranulary glassy pockets in the ceramic should be of the same composition as the starting glass powder, whereas the intergranulary films certainly have slightly different compositions and structures. Hence, the temperature shift observed strongly...
suggests that, at least for materials with no more than 10 vol% secondary glassy phases, ultrasonic echography is more sensitive to the intergranulary films than to the amorphous pockets. Note that in Fig. 2, the increase in Young’s modulus above 1150°C, before cooling to room temperature stems from the crystallization of the amorphous phases (to form yttrium silicates for instance). In relatively pure silicon nitride ceramics, the intergranulary films might consist of pure amorphous silica, with a special molecular structure (angle distortions near the interfaces) in order to accommodate the neighboring grain surface structures. The observed transition range, around 1140°C, e.g. near the glass transition of amorphous silica (≈1190°C), would corroborate this interpretation.

3. Fracture toughness

With rising temperature, from – and above – $T_g$, it becomes more and more difficult to initiate crack propagation from a preexisting flaw, because energy dissipation occurs through viscoelastic flow in the vicinity of the flaw. Eventually, the ceramic parts will never break and the lower bound of the (temperature, strain-rate) range suitable to net-shape forming techniques is met. The relevant problem is the one of the behavior of a crack near its tip, in a material undergoing a transition from pure elastic to viscoelastic and further to pure viscous behavior. In particular, the role of the temperature and strain-rate in the transition range and on the duality between both parameters must be examined. The intrinsic fracture toughness relates to Young’s modulus and to the fracture surface energy, $\gamma$, according to:

$$K_{C_{intrinsic}} = \sqrt{2\gamma E\epsilon}$$

where $E’ = E$ in plane stress and $E’ = E/(1-\nu^2)$ in plane strain. $\nu$ is Poisson’s ratio.

With rising temperature, except in the case of anomalous materials (such as pure SiO$_2$ glass), both $E’$ and $\gamma$ are expected to decrease, so that the intrinsic toughness decreases too (stage I in Fig. 3), with a rapid drop beyond $T_g$ (stage II). However, an increase of the apparent fracture toughness is generally observed above $T_g$ (stage III), in a temperature range which shifts toward higher and higher temperatures as the imposed strain-rate increases ($T_g$, $T_d$) (stage IV). Dusza et al. observed that the toughness measured at a given temperature decreases with increasing loading rates, and that the rate sensitivity is significantly smaller in a Si$_3$N$_4$/SiC nanocomposite than in a monolithic Si$_3$N$_4$ ceramic. Indeed, the temperature dependence of the toughness of a Si$_3$N$_4$/SiC (33 vol%) nanocomposite exhibits no peak. Again, these latter observations indicate that Si$_3$C particles reduce the role of the intergranulary glassy phases on the mechanical properties. Also, the higher the glassy phase content is and the higher the maximum apparent toughness peak becomes. This behavior can be readily interpreted from the time dependence of the crack tip stress $\sigma$. As soon as stress relaxation and blunting phenomena take place in the crack tip area, the time at fracture becomes much larger than the time predicted on the basis of a pure elastic loading of a sharp crack (stage III). In other terms, if we assume that the behavior in the far field remains elastic, the fracture stress, and so the fracture toughness, would appear much higher than in the brittle range. It is noteworthy that above the brittle to ductile transition (BDT), beyond a critical temperature that depends on the imposed strain rate, the cracked specimen breaks no more, so that the far field stress might reach the equilibrium value $\sigma_c$ corresponding to the viscous flow regime (stage IV). Under such circumstances, any fracture toughness measurement becomes meaningless.

To get ductility, it is necessary that healing or stress relaxation processes develop at a crack tip, or within the most critical flaw in an uncracked structure, before the maximum tensile stress exceeds the cohesive stress, $\sigma_c$. The physics of the BDT has been explored both for a pure glass and for a Si$_3$N$_4$/SiC composite, starting from the Irwin expression for the crack tip singularity, assuming that the actual material structure at the crack tip near $T_g$ can be approximated by a continuum solid with a finite radius of curvature, $\rho$. Fracture occurs, if such should be the case, at the macroscopic scale, the fracture criterion writes $K_1 = K_{C_{app}}$, where $K_{C_{app}}$ is the apparent fracture toughness. For a monotonic loading, $K_0$ is constant and the apparent toughness is then given by: $K_{C_{app}} = K_{C_{intrinsic}}$. Note that the local stress intensity factor at a
crack tip, \( \dot{K} \), which depends on the loading history and geometry and on the crack shape and size only, is usually less than the applied stress intensity factor (far field loading), \( K_c \), due, for instance, to stress relaxation or to bridging of the crack surfaces. Crack-tip healing processes may be either kinetic in nature, as far as the rate at which \( \dot{K} \) may relax due to viscous flow in the crack tip process zone is concerned, or geometric in nature, when considering the contribution due to change of crack length or shape and blunting. These different parameters were investigated experimentally in Ref. 17 in order to set up an explicit model allowing for the prediction of the BDT range. The obtained expression for the actual value of the crack tip stress writes:

\[
\dot{\sigma}(t) = 4\varepsilon Y \sqrt{\frac{a}{\pi r}} (1 + \frac{I}{r}) \exp \left(-\frac{1}{I} \right) (3)
\]

where \( a \) is the critical flaw size, \( Y \) is a shape factor and \( r \) is the characteristic relaxation time constant (experimentally measurable).

Enhanced ductility will be observed if the maximum of \( \dot{\sigma} \) is less than the critical stress leading to unstable fracture. Otherwise, the time to fracture is given by solving the equation:

\[
\dot{\sigma}(t) = \sigma_c.
\]

If the dependence of \( \rho \) on time is unknown, one can assume a constant value for \( \sigma_c \). This allows to get a lower bound for the time – or strain – at fracture. In this latter case, \( K_c \) can be used instead of \( \dot{K} \) as the key fracture parameter and the condition to get full ductility writes:

\[
2\varepsilon Y \sqrt{\frac{a}{\pi r}} < K_c.
\]

It is noteworthy that in the viscous flow regime, the strain-rate relates to the flow stress through:

\[
\dot{\varepsilon} = \frac{2\sigma}{3\varepsilon_y \eta}. \quad \text{Hence, further stating that} \quad \eta = 2\mu \varepsilon \sigma \quad (\mu \text{ is the shear modulus}, (3)), \quad \text{the asymptotic limit for} \quad \dot{K} \quad \text{is expressed as}
\]

\[
\dot{K}(\infty) = \sigma_c Y \sqrt{a} \quad (4)
\]

Enhanced ductility will be observed if the maximum of \( \dot{\sigma} \) is less than the critical stress leading to unstable fracture. Otherwise, the time to fracture is given by solving the equation:

\[
\dot{\sigma}(t) = \sigma_c.
\]

If the dependence of \( \rho \) on time is unknown, one can assume a constant value for \( \sigma_c \). This allows to get a lower bound for the time – or strain – at fracture. In this latter case, \( K_c \) can be used instead of \( \dot{K} \) as the key fracture parameter and the condition to get full ductility writes:

\[
2\varepsilon Y \sqrt{\frac{a}{\pi r}} < K_c.
\]

It is noteworthy that in the viscous flow regime, the strain-rate relates to the flow stress through:

\[
\dot{\varepsilon} = \frac{2\sigma}{3\varepsilon_y \eta}. \quad \text{Hence, further stating that} \quad \eta = 2\mu \varepsilon \sigma \quad (\mu \text{ is the shear modulus}, (3)), \quad \text{the asymptotic limit for} \quad \dot{K} \quad \text{is expressed as}
\]

\[
\dot{K}(\infty) = \sigma_c Y \sqrt{a} \quad (4)
\]

4. Flow behavior

4.1 Dislocation activity

Quite a few study of dislocation activity in silicon nitride were reported so far. What seems clear is that even in highly deformed specimens, a relatively low dislocation density is observed. In \( \beta \)-Si\(_3\)N\(_4\) crystals, most dislocations move in prismatic planes, and the \([0001]\{10\overline{1}0\} \) slip system is by far the most common. Dislocations with \( 1/3\{11\overline{2}0\} \) and \( 1/3\{10\overline{1}0\} \) Burgers vectors were also observed, but again, according to the values for the Peierls potential, slip occurs in 1st and 2nd kinds prismatic planes.\(^{30,31}\) Deformation experiments at high temperature micro-hardness or compression under hydrostatic pressure, show that, between 20 and 850°C, all the dislocation substructures resulting from plastic deformation are mainly built with screw dislocations with [0001] Burgers vector (Fig. 5). This type of dislocation activity should prevail up to 1550°C. It was recently proposed that the occurrence of ductility in compression for temperature higher than 1550°C, for imposed strain rates lower than 8.10\(^{-4}\) s\(^{-1}\) and 6.10\(^{-3}\) s\(^{-1}\) at 1550 and 1750°C, respectively, correlates with the appearance of \((-2\overline{1}1\overline{3}\overline{1})\{11\overline{2}1\} \) pyramidal slip.\(^{32}\) Yield stresses between 50 and 250 MPa were measured at 1700°C by changing the strain-rate between 9.10\(^{-8}\) s\(^{-1}\) and 6.10\(^{-5}\) s\(^{-1}\). These stresses compare well with those applied in compression in the same temperature range to study superplasticity. Furthermore, a rough estimation from the general expression for the Peierls–Nabarro stress,

\[
\tau_{PN} = 2\mu \varepsilon \sigma \exp \left(-\frac{2\pi h}{(1-v) b} \right) (5)
\]

where \( \mu, \varepsilon, h \) and \( b \) are the shear modulus, Poisson’s ratio, the spacing between the slip planes and the length of the Burgers vector, respectively, also supports the possibility for dislocation motion during high temperature deformation in silicon nitride-based ceramics.

Considering the \([0001]\) \((10\overline{1}0) \) slip system, assuming \( \mu \) a value of 105 GPa, as determined from the Young’s modulus value at 1600°C (extrapolation from Ref. 16) with \(\varepsilon=0.3\) and using \( h=2.91 \) Å (0.291 nm) and \( b=3.29 \) Å (0.329 nm) gives \( \tau_{PN}=107 \) MPa. Hence, it can be speculated that beside mechanisms proposed in the 80s based on grain boundary sliding through viscous flow and solution–migration–precipitation processes, the possibility for dislocation motion should also be considered, especially for the most up-dated creep resistant grades. Nevertheless, owing to the very limited number of active slip systems, dislocations are not expected to give a predominant contribution to the permanent strain.

4.2 Stress relaxation

Typical stress relaxation curves obtained in a material sintered without additives, but using prealloyed powders, are plotted in Fig. 6. With regards to the experimental duration, temperatures above 1350°C are required for relaxation to be observed. Note that the relaxation kinetics does not follow the simple linear Maxwell model corresponding to a Debye-type relaxation. Instead, the experimental data could be remarkably well fitted by the Kohlrausch–Williams–Watt (KWW) equation often quoted in glass science:

\[
\sigma(t) / \sigma_0 = \exp \left[ -\left(t/\tau_r\right)^{\beta} \right] (6)
\]

where \( \tau_r \) is the characteristic relaxation time and, following previous works, parameter \( \beta \) is named correlation factor and can be tentatively related to the mobility of a struct-
tural unit at the atomic or molecular scale. \( b_r \) ranges between 0 (strong intermolecular coupling allowing for pure elastic deformation only) and 1 (weak correlation corresponding to the simple Debye- or Maxwell-relaxation of liquids). Accordingly, the increase of \( b_r \) with temperature (Table 2), from 0.23 at 1400\( ^\circ \)C to 0.67 at 1650\( ^\circ \)C, would reflect a smooth transition between the elastic behavior in the solid state and the viscous behavior in the liquid state. In silicon nitride-based polycrystalline ceramics, intergranular glassy films and pockets are supposed to play a major role in this transition. However, the presence of such films and pockets were not evidenced at room temperature in this material. It is therefore anticipated that the liquid phase that is necessary to promote sintering, crystallizes upon cooling, but partially reforms upon heating above 1150\( ^\circ \)C, and that a significant amount of eutectic liquid may form during testing above 1400\( ^\circ \)C.

Consistently, \( \Delta r \) decreases rapidly with rising temperature, from thousands of hours at 1400\( ^\circ \)C to few minutes at 1650\( ^\circ \)C and a rapid softening is observed above 1500\( ^\circ \)C (Fig. 2). Significant ductility does not show up until the relaxation time (\( \tau_r \)) becomes smaller than the experimental duration at the usual experimental time scale for plastic shaping techniques, from few seconds to few hours. For the presently studied material with improved creep resistance, temperatures above 1750\( ^\circ \)C would be required (1550\( ^\circ \)C for fine-grained superplastic SIYAlON).\(^{32,35}\)

Following the theory of thermally activated deformation, \( \tau_r \) can be regarded as the waiting time of the activation process and depends on \( T \) according to:

\[
\tau_r = \tau_0 \exp \left( \frac{\Delta G_a}{RT} \right)
\]

where \( \tau_0 \) is temperature independent and \( \Delta G_a \) is the free activation enthalpy. An average value of 1070 kJ/mol was determined by linear interpolation from the data. This value is consistent with the usual values for creep of silicon nitride or viscous flow of oxynitride glasses,\(^{36}\) but is much higher than the values of 406 kJ/mol and 470 kJ/mol obtained the same way in the same temperature range in superplastic ceramics, namely a SIYAlON and a Si_3N_4/SiC nanocomposite,\(^{35}\) for which the fine-grained microstructures allow for a much faster relaxation at a given temperature. However the temperature dependence of the relaxation time constant (Fig. 7) does not follow the Gibb’s equation with a single value for the activation energy over the entire range. In fact, as for most glasses, the activation energy tends to decrease on both sides of the temperature range. For instance, \( \Delta G_a \) decreases from 1100 kJ/mol at 1450\( ^\circ \)C to 465 kJ/mol at 1650\( ^\circ \)C. Thus, \( \tau_r \) would better agree with a Vogel–Fulcher–Tamman type equation commonly used to relate the viscosity of inorganic glasses to the temperature from and above \( T_g \). In the light of these results, it seems difficult to anticipate a physical meaning for the apparent activation energy averaged over the 1400–1650\( ^\circ \)C range. The high temperature value is close to 579 kJ/mol, corresponding to Si diffusion in SiO_2, and close to the value of 500 kJ/mol associated with creep anelasticity in silicon nitride and ascribed to the relaxation of local elastic stress fields at grain boundary asperities, through the redistribution of the viscous phase (SiO_2 films?).\(^3\)

### 4.3 Creep

The creep behavior of silicon nitride ceramics, which are multiple phase materials, is mainly governed by the behavior of the grain boundary phases. However, the rheology of the secondary phases is poorly understood still, and thus the creep mechanism is not completely determined. The most interesting typical features arising from the extensive litera-

---

**Table 2. Stress-Relaxation, Elasticity and Viscosity Parameters for the Studied Silicon Nitride.** At 20\(^\circ\)C, \( E = 322 \) GPa and \( \mu = 127 \) GPa. Values of \( \mu \) at different temperatures are calculated from the corresponding Young’s modulus values, as extracted from the data of Fig. 2. Using \( \mu = E/(2(1+\nu)) \), and assuming a constant value for Poisson’s ratio (\( \nu = 0.27 \)).

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>1400</th>
<th>1450</th>
<th>1500</th>
<th>1550</th>
<th>1575</th>
<th>1600</th>
<th>1625</th>
<th>1650</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_r )</td>
<td>0.23</td>
<td>0.26</td>
<td>0.35</td>
<td>0.53</td>
<td>0.56</td>
<td>0.60</td>
<td>0.62</td>
<td>0.67</td>
</tr>
<tr>
<td>( \tau_r ) (hours)</td>
<td>5600</td>
<td>2016</td>
<td>127</td>
<td>10.6</td>
<td>3.82</td>
<td>1.63</td>
<td>1.07</td>
<td>0.59</td>
</tr>
<tr>
<td>( \mu ) (GPa)</td>
<td>110.9</td>
<td>109.1</td>
<td>107.2</td>
<td>105.3</td>
<td>104.4</td>
<td>103.4</td>
<td>102.5</td>
<td>101.6</td>
</tr>
</tbody>
</table>

---

Fig. 6. Stress relaxation curves obtained in compression under nitrogen atmosphere on a material sintered without additive (from Ref. 33).

Fig. 7. Temperature dependence of the relaxation time constant, \( \tau_r \).
ture on creep of Si₃N₄ are listed hereafter:

1. The earliest creep stage is characterized by a significant delayed elastic- or anelastic-component which stems from the viscoelastic response of the secondary glassy phases and in a lesser extent from the elastic strain stored in the contact areas of adjacent grains.²⁷) (2) The grain-boundary glassy phases are redistributed during creep, mainly during the anelastic transient stage, and changes of the intergranular glass layer thickness follow,³⁰) with the exudation of a significant amount of glassy phase toward the surface of the creeping structure as a consequence;²⁹),³⁰) (3) The steady-state creep stage, if any, requires much time to be observed.³⁶),³⁷) Experiments conducted recently on a creep- and oxidation-resistant material for the next generation gas turbines, showed that the strain rate keeps decreasing over a period longer than a year.³⁸) Under such circumstances, any attempt to give a physical interpretation (through the activation energy for instance) to the apparent steady-state creep rates measured within shorter periods would be vain; (4) It is mostly considered that creep proceeds through solution-migration-precipitation flow mechanisms.³⁹)-⁴²) Such mechanisms involve grain-boundary sliding, with the relative displacement between adjacent grains being accommodated by matter transport through the grain boundary phases, from high pressure areas, where dissolution is favoured, and to low pressure areas, where precipitation or redeposition is enhanced. The rate of dissolution (interface reaction) and the rate of matter transport are the possible rate-controlling processes. The creep kinetics might be governed by the slowest of these. Noteworthy, which of the sliding processes at two-grain interfaces or the redistribution process of the secondary phases at multiple-grain junctions—which is necessary to allow the compatibility of grain displacements—is the rate limiting step still remains a matter of some contention; (5) A pronounced tension-compression asymmetry shows up by lower strain-rates and lower creep exponent in compression (Figs. 8 and 9).

Different explanations were proposed so far.²⁸),³⁵),³⁶)-⁴⁰) In a small scale creep approach³⁵) that was extended to non-

![Fig. 8. Temperature dependence of the strain-rate for monolithic silicon nitride materials. To allow comparison, experimental results from various references have been normalized for a flow stress of 100 MPa. Empty and filled marks refer to compressive and tensile tests, respectively (see Ref. 35 for details).](image)

![Fig. 9. Stress sensitivity exponent as a function of the flow stress. Most of the plotted data refer to experiments conducted above 1000°C. Horizontal bars indicate the stress range investigated by each author (see Ref. 35 for details).](image)
Newtonian flow\(^{46}\) the deformation rate under uniaxial loading is expressed from the rate of approach (in compression) or separation (in tension) of two adjacent grain facets and the maximum achievable strain corresponds to the situation where there is no longer any fluid left between two facets under compressive normal strain (i.e. lateral facets in tension). The asymmetry between tension and compression derives from different values for the maximum strain in compression and in tension and is therefore a direct consequence of this hypothesis. Although this model accounts both for a flow stress higher in compression than in tension and for a lower hardening rate in the latter case, consistently with the observations, it results in values for the maximum strain corresponding to the very early loading stages, i.e. well before any pseudo-stationary deformation regime is reached. Furthermore the model does not account for the transition from shear thinning (tension) to shear thickening (compression) and stands for non-deformable and equiaxed grains only. A continuum approach, by means of a self-consistent scheme was also proposed,\(^{47}\) accounting for grain alignment either toward the stress axis in tension or in planes normal to the stress axis in compression, so that a lower flow stress is predicted in tension. The shear thickening flow observed in compression was also interpreted by the model, considering that two adjacent grains form a rigid entity when the compressive stress normal to the grain–grain interphase exceeds a critical value, hence resulting in an increase in the effective rigid phase volume fraction. The last proposal is based on a detailed analysis of cavitation during tensile and compressive creep tests,\(^{48,49}\) and concludes that cavitation contributes to a large amount of the permanent strain (over 70% in some cases) and that cavitation is the main factor for the creep asymmetry. This is because cavitation is greatly impeded in compression as the Si\(_3\)N\(_4\) grains get in contact and interlock so that sliding is no longer possible, with a macroscopic negative volume change upon loading, whereas tensile stresses induce dilating regions, into which the flow of the glassy (or liquid) phase is not fast enough to prevent against cavitation. This explains higher values for \(n\) in tension (\(n>2\)) than in compression (Fig. 9). (6) Creep damage shows up through the occurrence of cavitation. Two types of cavities are generally observed: lenticular cavities, which may coalesce to form microcracks, appears in two-grain interfaces that lie normal to the applied stress, whereas larger interstitial cavities grow in the glassy pockets at multiple grain junctions. Noteworthy, the volume fraction of cavities increases linearly with strain in tension,\(^{50}\) accounting for a significant fraction of the total strain, so that it was proposed that the nucleation and growth of cavities control the creep rate. A significant improvement of the creep resistance of silicon nitride was achieved upon the last ten years (Fig. 10). The updated grades exhibit creep rate lower than \(10^{-9} \text{s}^{-1}\) and a creep strain of about 1\% after 10000 h under 150 MPa (tensile stress) at 1500°C in air. The improvement mainly relates to the improvement in microstructure control and to the use of carefully selected sintering additives. In comparison to the materials synthesized in the 80s, lesser amounts of more refractory additives are used today. For instance, MgO was progressively replaced by a combination of rare-earth oxides and alumina, and further by rare-earth oxides such as Y\(_2\)O\(_3\), Yb\(_2\)O\(_3\) and Lu\(_2\)O\(_3\) only.

4. Superplasticity

Since the first report of superplasticity (more than 100% elongation) in a Si\(_3\)N\(_4\)/SiC nanocomposite, in the early 90s,\(^{31}\) this property has been observed in different silicon nitride-based ceramics above 1500°C.\(^{15,28-29}\) Indeed, different approaches may be undertaken to achieve large elongations: superplasticity can be enhanced either by designing suitable grain-boundaries (low viscosity intergranular phases for instance), or by minimizing the grain size (adding a second phase such as SiC for instance), or by taking advantage of the transient liquid phase which forms during the \(\alpha\) to \(\beta\) phase transformation.\(^{15}\) In most cases, materials were sintered by hot-pressing, both to get near theoretical density and to minimize the sintering duration in order to reduce grain growth, and have an average grain size of less than 0.5 \(\mu\)m. Maximum elongations of 230%\(^{52}\) and 470%\(^{56}\) were obtained in a \(\beta\)-SiAlON ceramic sintered with about 45 vol\% additives (AlN, Al\(_2\)O\(_3\) and Y\(_2\)O\(_3\)), in the 1550–1600°C range, corresponding to initial flow stresses lower than 5 MPa. Cavitation damage resistant materials lead to flow curves showing a continuous hardening which is mainly due to the alignment of the acicular \(\beta\) grains toward the tensile axis, and to a lesser extent to the crystallization of secondary phases. So far, and in all cases, with regard to our poor state of understanding, the hope for finding a mechanism accounting for the extremely complex nature of the superplastic flow in such materials seems premature. Of interest is the tension-compression asymmetry, which is also observed during creep. Flow in compression is contingent to the problem of packing of a mixture of equiaxed and rod-like particles embedded in a viscous matrix, and data in this area are clearly needed. A pseudostationary flow is observed as soon as the rigidity threshold associated with the consolidation is reached. In compression, the maximum strain might be controlled by the geometry of the packing of the grains and by the ability of the grains to be viscoplastically deformed. The tensile flow has many features in common with the rheology of concentrated suspensions. In this latter area, shear thinning due to the flow destroying aggregates and also to aligning the microstructure with the flow is a well known phenomenon. The feasibility to take advantage of the superplastic behavior for the net-shaping of components is illustrated in Fig. 11. When the microstructure consists in rod-like \(\beta\)-Si\(_3\)N\(_4\) grains, the superplastic deformation results in texture anisotropy and leads to strengthening and toughening effects normal to the postive strain directions.

Acknowledgements Dr. S. Wiederhorn (NIST, Gaithersburg, USA) is gratefully acknowledged for discussion and for providing Fig. 10. The author expresses also deep gratitude to the many stu-
dent, colleagues and friends whose contributions are presented in this article and who encouraged these researches upon the passed ten years. These include most especially Dr. X. Milhet, Dr. F. Rossignol, Dr. S. Testu, Dr. B. Mawari, Prof. J. Rabier (University of Poitiers, France), Prof. J.-L. Besson, Prof. P. Goursat (University of Limoges, France) and the research team at ENSCI (Limoges, France), Prof. F. Watai (TIT, Tokyo, Japan), and Prof. T. Sakuma (University of Tokyo, Japan).

Fig. 11. Hot forging of parabolic and conic shells, at 1595°C in nitrogen atmosphere, using graphite moulds (reprinted from Ref. 20)).

References
Tanguy Rouxel

After obtaining an engineer diploma from the Ecole Nationale Supérieure d'Arts et Métiers, Tanguy Rouxel gained his B. Sc (French DEA) in Mechanics of Materials from the University of Paris XIII, and his Ph. D. (French Doctorate) in Ceramic Science from the University of Limoges. After graduating he became a Post-doctoral Fellow in the Government Industrial Research Institute of Nagoya (then the NIRIN, Japan) for one year and a half. Dr. Rouxel then held a position as a CNRS Researcher in the Ecole Nationale Supérieure de Céramique Industrielle for four years, during which he spent several periods of study leave, in the department of Materials Science at the University of Tokyo, and in the Glasses and Ceramics laboratory in the University of Rennes (France). In 1997, Dr. Rouxel was appointed Professor at the University of Rennes, where he is presently leading a new research laboratory (the LARMAUR) devoted to the study of surface mechanics problems, and flow and fracture in advanced glasses and ceramics.