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A Two-Step Method to Obtain Superplastic Silicon Nitride with High Thermomechanical Properties

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Abstract

Due to its microstructure, composed of very fine equiaxial grains and some amorphous phase, hot pressed α-Si_3N_4 *was superplastically deformed by bending at relatively low temperature (1540°C) and stress (15 MPa) and at high strain rate* (6×10^{-2} h^{-1}).

Afterwards, a thermal treatment was applied to the deformed samples in order to promote the α *to* β *silicon nitride phase transformation and to recrystallise the residual amorphous phase. Such a treatment leads to a significant increase in the mechanical properties* ($\sigma_F = 770 \rightarrow 880$ *MPa;* $K_{IC} = 3 \rightarrow 5$ $MPa\sqrt{m}$) *resulting in the presence of newly formed acicular grains of* β-Si_3N_4.

The modulus of rupture measured at high temperature (between 800 and 1200°C), as well as the creep strength, are also significantly improved compared to a reference β-Si_3N_4 *material hot pressed with the same sintering aids* (Al_2O_3/Y_2O_3). *Therefore, it can reasonably be assumed that the residual amorphous phase allowing superplastic deformation to occur is almost fully recrystallised after annealing. © 1996 Elsevier Science Limited.*

Grâce à sa microstructure composée de grains équiaxes de petite taille et d'une certaine quantité de phase amorphe, du nitrure de silicium α *pressé à chaud a pu être déformé superplastiquement en flexion à une température et sous une contrainte relativement basses (1540°C, 15 MPa) et à une vitesse de déformation élevée* (6×10^{-2} h^{-1}).

Ensuite, un traitement de recuisson a été appliqué aux échantillons déformés pour induire la transformation du nitrure de silicium de la forme α *à la forme* β *et pour recristalliser la phase amorphe résiduelle.*

Ce traitement a permis d'ameliorer de façon significative les propriétés mécaniques ($\sigma_F = 770 \rightarrow 880$ *MPa;* $K_{IC} = 3 \rightarrow 5$ $MPa\sqrt{m}$) *grâce à la cristallisation de grains aciculaires de* β-Si_3N_4. *Le module de rupture mesuré à haute température (entre 800 et 1200°C), ainsi que la résistance au fluage sont nettement améliorés par rapport à un matériau de référence en* β-Si_3N_4, *pressé à chaud en présence des mêmes additifs de frittage* (Al_2O_3/Y_2O_3). *Dès lors on peut émettre l'hypothèse que la phase amorphe résiduelle permettant la déformation superplastique est presque entièrement cristallisée après le cycle de recuisson.*

Introduction

Since the discovery of superplasticity of zirconia in 1986, most of the works have been focused on oxide ceramics and more especially on zirconia-based materials. However, some authors[1-3] proved that ceramic with covalent bonds (SiC, α-Si_3N_4, α-Sialon,...) can also display such superplastic behaviour. Among these covalent materials, β-Si_3N_4 can be regarded as the most promising ceramic for high temperature structural applications such as valves or turbochargers. In order to manufacture such complex shapes, the hot forging techniques derived from superplasticity[4,5] could become especially useful.

Unfortunately, superplastic behaviour is also associated with equiaxial grains microstructure, which means, for silicon nitride, relatively low thermomechanical properties and a weak creep resistance.

However, as suggested in the present paper, this problem can be overcome thanks to a two-step method consisting, first, of superplastically hot forging to its net shape an α-Si_3N_4 material and, secondly, annealing the as-obtained part to recover a high refractory ceramic without inducing dimensional changes.

Experimental Procedure

It is known that silicon nitride grain growth proceeds following an Ostwald's ripening mechanism and, according to this process, β grains initially present in the starting raw materials behave like nuclei promoting the β-phase at the expense of the α one.[6] Taking into account, the above consideration, a very fine powder, almost fully composed of α-phase (99 wt%), was chosen in order to prepare the α-Si_3N_4 material.

The main characteristics of the starting raw material are reported in Table 1.

In a first stage, the powders were mixed in methanol with a classical sintering additive mixture (5·5 wt% Y_2O_3/1·5 wt% Al_2O_3). Afterwards, the homogeneous slurries were dried under constant stirring in order to avoid any sedimentation. The as-obtained powders were sieved under 50 μm and finally hot pressed under argon in the following conditions: temperature = 1600°C, pressure = 40 MPa.

The sintered bodies were machined into bars (4 mm × 3 mm × 35 mm) for mechanical testing. The Young's modulus (E) was measured by a resonance method and the flexural strength (σ_F) by three-point bending with a span of 15 mm and a constant crosshead speed of 0·1 mm/min. Prior to the bending test, the tensile surface of the bars was mirror polished using a 1-μm grade diamond paste at the final stage and the edges were chamfered. The critical stress intensity factor (K_{IC}) was also determined in bending according to the SENB method and the critical flaw size (a_c) calculated assuming a semi-spherical crack located near the surface.[7]

In order to assess the creep strength of the annealed Si_3N_4 material intended to be used for thermomechanical applications, flexural tests were carried out using this time another device with a wider span (30 mm). For such experiments, the specimen deflection at its centre was measured thanks to a linear variable differential transformer (LVTD) transducer.

Results and Discussion

Characterisation of the hot pressed α-Si_3N_4 material

Despite the relatively low hot pressing temperature, a full density (3·15 g/cm^3) was achieved. It must be pointed out that the temperature has been chosen to decrease the α-Si_3N_4 → β-Si_3N_4 phase transformation rate. In such a manner, the α-phase content of the fully dense Si_3N_4 material measured by XRD analysis still reaches about 93% in weight.

The XRD spectrum emphasizing peaks broadening as well as an unusually high background also suggests that the α-Si_3N_4 contains a large amount of glassy phase which, in turn, is able to explain the high sensitivity of the material to chemical etching (dipping in fused sodium hydroxide for a few seconds is enough to reveal the microstructure).

However, the presence of a certain amount of residual glassy phase is suitable in this case, first, to enhance grain boundary sliding and rearrangement following which the superplastic deformation generally proceeds[4,5] and, second, to promote during the subsequent thermal treatment the α-Si_3N_4 → β-Si_3N_4 phase transformation which is well know to occur by a solution-diffusion through a viscous phase-precipitation mechanism.[8]

The microstructure of chemically etched α-Si_3N_4 is presented in Fig. 1. This SEM micrograph clearly shows that the microstructure is mainly composed of α grains having a size less than one micron. A few elongated grains of the β-phase can also be locally observed (indicated by an arrow), but these β-grains remain of micronic size even along their C-axis direction so that they cannot reasonably reduce or impede the grain boundary sliding involved in the superplastic deformation process.

The main mechanical characteristics of the α-Si_3N_4 material are summarized in Table 2. The strength value of the α-Si_3N_4 material appears quite high in spite of the relatively low K_{IC} value which is a consequence of its equiaxed microstructure yielding direct crack toughening mechanisms (crack deviation, crack bridging,..[9]) inoperative. As the calculated critical flaw size appears small, which is a necessary condition in order to avoid premature failure during deformation, the ability of the hot pressed α-Si_3N_4 to behave superplastically was assessed. The experiments were conducted in bending at a temperature of 1540°C for a crosshead speed of 50 μm/min. This crosshead speed corresponds to a strain rate $\dot{\varepsilon}$ of 6×10^{-2} h^{-1} which exceeds by several orders of magnitude the

Table 1. Main characteristics of the raw material

Impurity content (wt%)						*β-phase content (wt%)*	*Surface area (m²/g)*	*Agglomerate size (μm)*	*Crystallite size (μm)*
C	*O*	*Al*	*Fe*	*Ca*	*Mg*				
0·90	2·00	0·20	0·01	0·01	0·01	≈ 1	8·7	0·9	≤ 0·3

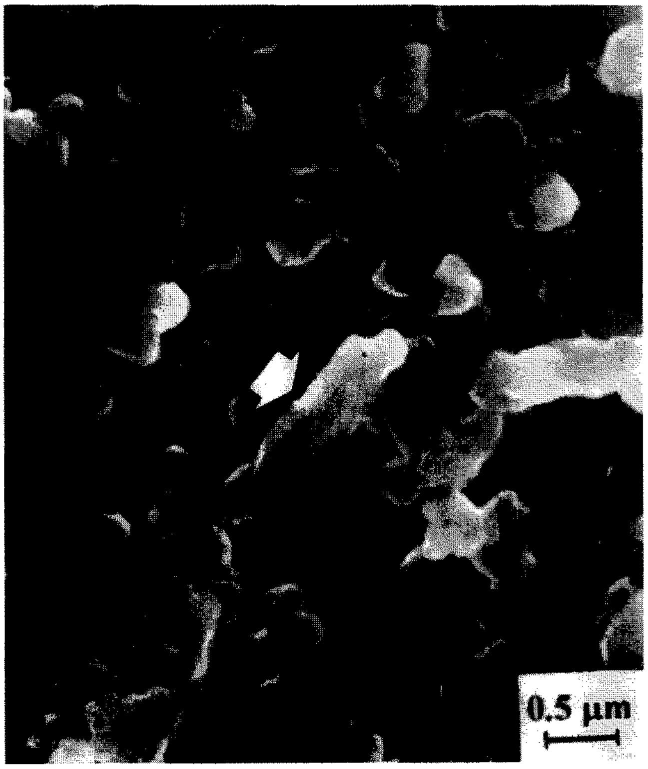

Fig. 1. SEM micrograph of the α-Si_3N_4 microstructure.

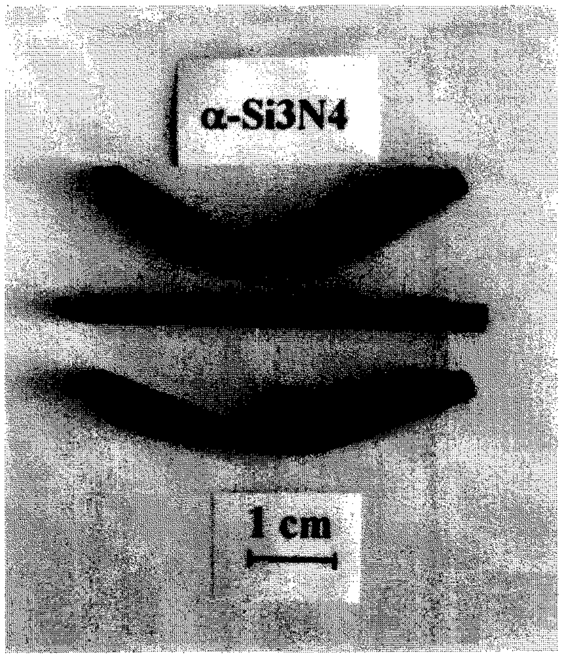

Fig. 2. α-Si_3N_4 superplastically deformed at 1540°C using a crosshead speed of 50 μm/min.

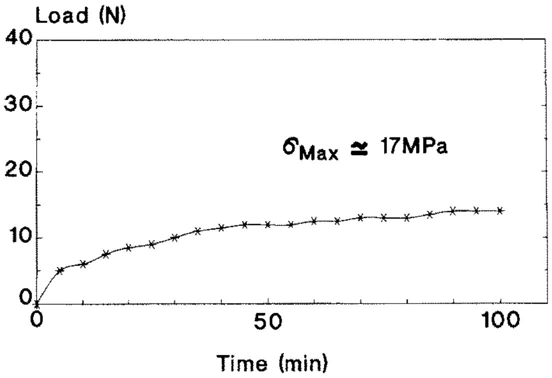

Fig. 3. Load versus time curve recorded during superplastic deformation.

values generally encountered during Si_3N_4 creep.[10] In such conditions, the material effectively displayed a superplastic behaviour (Fig. 2) and the maximal strain reached ($\approx$ 18%) was limited by the geometry of the testing device rather than by specimen fracture.

During the bending test, the load versus time curve was recorded and is shown at Fig. 3. This curve emphasizes the very low stress value ($\sigma \approx$ 17 MPa) sustained by the specimen during bending creep. Moreover, after a given time, deformation arises at a constant load and no further load increase, namely flow hardening,[11] takes place. Therefore, one can reasonably rule out any deep microstructural changes such as for instance recrystallisation or dynamic grain growth which may account for this phenomenon.

Characterisation of the annealed Si_3N_4 initially under the α-phase

After deformation, α-Si_3N_4 materials were heat treated at 1700°C for one hour. Results of XRD analysis reported in Table 3 confirm that annealing allows completion of the $\alpha \rightarrow \beta$ phase transformation and then increase of mechanical properties (especially K_{IC} which is improved by at least 50% compared to the equiaxed α-Si_3N_4).

Moreover, this treatment does not give rise to measurable dimensional changes so that it can be reasonably assumed that hot-forged Si_3N_4 parts will keep their final shape even after annealing.

The microstructure of the annealed sample is presented in Fig. 4 and effectively shows the presence of elongated grains characteristic of the β-phase.

In order to assess if recrystallisation of the residual amorphous phase occurred during thermal treatment, the thermomechanical properties of the

Table 2. Mechanical properties of the α-Si_3N_4 materials

Material	E *(GPa)*	σ_F *(MPa)*	K_{IC} *(MPa$\sqrt{m}$)*	a_c *(μm)*
α-Si_3N_4	310	767	3·1	10

Table 3. Main characteristics of the annealed Si_3N_4 material

	β-Si_3N_4 (wt%)	E *(GPa)*	K_{IC} *(MPa$\sqrt{m}$)*	σ_F *(MPa)*
Annealed Si_3N_4	87	313	4·7	875

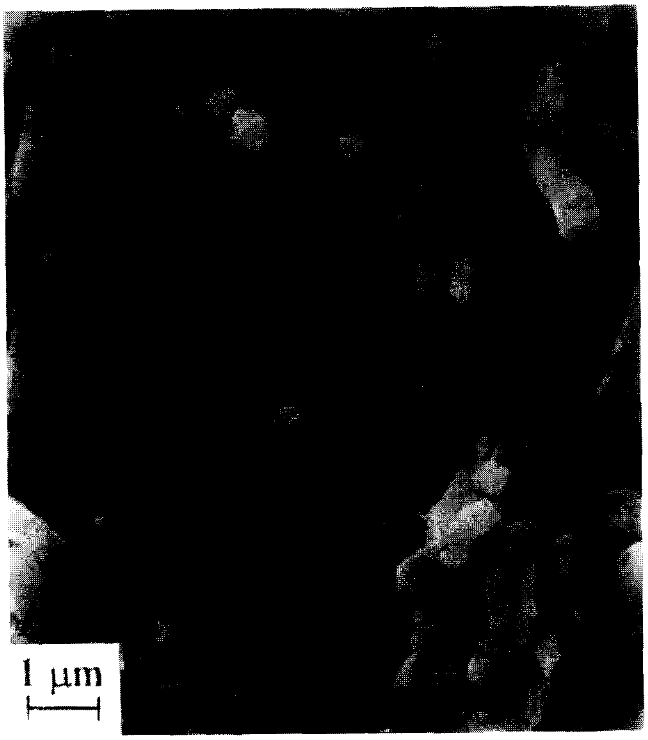

Fig. 4. Microstructure of annealed Si_3N_4 material.

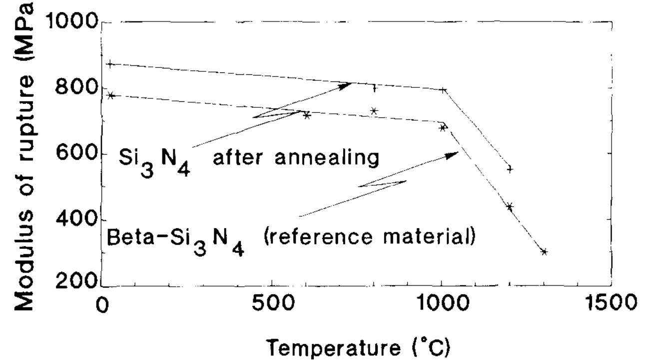

Fig. 5. Evolution of the modulus of rupture with temperature for the annealed Si_3N_4 and the reference β-material.

annealed Si_3N_4 as well as its creep strength were also measured. In both cases, the results were compared to a reference material containing almost the same amount of β-phase ($\approx$ 93 wt%) and low amount of glassy phase.[12]

The evolution of the modulus of rupture as a function of temperature is presented in Fig. 5. This figure clearly shows that the room temperature value of the annealed Si_3N_4 is even higher than for the reference β-Si_3N_4 and, moreover, that this improvement can be maintained with increasing temperature.

Table 4. Steady-state strain rate values calculated after t = 10 hours

Material	$\dot{\varepsilon}$ (h^{1})
α-Si_3N_4	$8{\cdot}7 \times 10^{3}$
Si_3N_4 after annealing	$1{\cdot}6 \times 10^{4}$
β-Si_3N_4 reference material	$2{\cdot}7 \times 10^{4}$

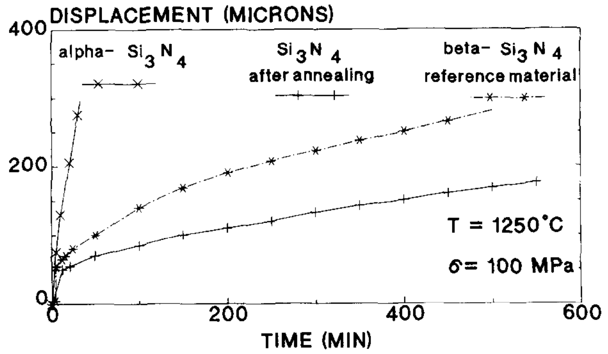

Fig. 6. Creep curves relative to the α-Si_3N_4, to the same material after annealing and to the β-Si_3N_4 reference material.

Creep tests were performed at T = 1250°C under a constant stress of 100 MPa and the steady-state creep rates (given in Table 4) calculated from Hollenberg's equation[13] assuming a stress exponent value equal to 1. Indeed, the observation of recovery creep after unloading (for the annealed Si_3N_4 and the β-Si_3N_4 reference material) agrees with a viscoelastic deformation process characterised by a linear strain rate dependence with stress, i.e. $n = 1$.[14]

The recorded creep curves plotted in Fig. 6 correspond to the α-Si_3N_4, to the same material after annealing and to the reference β-Si_3N_4 material, respectively. From examination of this figure, it must be pointed out that α-Si_3N_4 deforms at the largest strain rate and that the tertiary creep stage is rapidly reached leading to specimen fracture. Conversely, the annealed material is characterised by a high creep resistance as its strain rate value is even lower than for the reference material.

Thus, in spite of its superplastic behaviour, the α-Si_3N_4 material can recover a high refractoriness after thermal treatment and therefore can be again considered as a potential candidate in order to fabricate complex shape parts for thermomechanical uses.

Conclusions

Hot pressed Si_3N_4, mainly as α-phase (93 wt%), was successfully deformed at high strain ($\varepsilon \approx$ 18%) under the following conditions: T = 1540°C, $\dot{\varepsilon} \approx 6 \times 10^{-2}$ h^{-1}. This deformation which belongs to the superplastic range seems to occur without inducing deep microstructural changes as no flow hardening has been detected on the load versus time curve.

The application of a thermal treatment after the deformation process allowed completion of the $\alpha \rightarrow \beta$ silicon nitride phase transformation and recrystallisation at the same time of the residual glassy phase without inducing any dimensional changes.

As a consequence, the thermomechanical properties and the creep resistance were greatly improved and are even better than those corresponding to a reference material having almost the same β-phase content.

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