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Superplasticity in silicon nitride through the α to β phase transformation

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Résumé. — La superplasticité du nitrure de silicium se manifeste entre 1500 et 1600 °C pour des matériaux à grains submicroniques présentant une bonne résistance à l'endommagement. Dans ce domaine de température la microstructure évolue rapidement. Cette étude montre qu'il est avantageux de partir d'une céramique principalement constituée de la phase α -Si₃N₄ afin de bénéficier de la forme équiaxe des grains α ainsi que de la phase liquide transitoire qui se forme au cours de la déformation durant le processus de transformation $\alpha \rightarrow \beta$. La cinétique de cette transformation est analysée et son incidence sur les courbes de déformation à chaud (allongement > 80%) est mise en évidence.

Abstract. — Superplasticity is observed in silicon nitride for temperatures ranging between 1500 and 1600 °C in damage resistant materials with a submicron grain size. The microstructure evolves rapidly in this temperature range. This study shows that it is an advantage to start with an α -Si₃N₄ rich ceramic in order to derive benefit from both the equiaxed α -grain shape and the transient liquid phase that forms during deformation at an intermediate stage of the $\alpha \rightarrow \beta$ transformation. The kinetics of this transformation is analyzed and direct correlation is made with the deformation curves (elongation > 80%).

1. Introduction

Since the discovery in the early 90' of superplasticity in a SiC/Si₃N₄ composite [1], the superplastic behavior of covalent ceramics has become an active research area [2-6], with the result that different approaches may be undertaken to achieve large elongations. Generally speaking, superplasticity can be enhanced either by designing suitable grain-boundaries (low viscosity intergranular phases for instance) or by minimizing the grain size. So far, two methods were successfully employed to design silicon nitride based ceramics for superplastic forming. The

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first method consists in dispersing second phase particles in the Si_3N_4 matrix to reduce grain growth during both the sintering and plastic forming stages. A material containing up to 30 wt% SiC was hence superplastically deformed with elongations over 150% for temperatures in the range 1600 – 1650 °C and strain-rates between 10^{-5} and 10^{-4}s^{-1} , corresponding to flow stresses from 15 to 40 MPa [1,3]. The second approach consists in preparing glass-phase rich materials, with up to 50 vol.% intergranular glass, to enhance grain-boundary sliding, providing that at high temperature the glassy phase acts as an efficient lubricant between the highly refractory Si_3N_4 crystals. An elongation of 230% was obtained in a SiYAlON ceramic with about 45 vol.% of sintering additives (AlN , Al_2O_3 and Y_2O_3) [4] in the 1550 – 1600 °C temperature range with strain-rates between 10^{-4} and 10^{-3}s^{-1} , corresponding to initial flow stresses lower than 5 MPa. Advantages of the second method stem from more attractive forming conditions (lower temperatures and higher deformation rates) and from easier material processing in comparison with that of the $\text{Si}_3\text{N}_4/\text{SiC}$ composite (prepared from an ultra-fine Si-C-O-N powder derived from an organo-metallic precursor) [7]. However, the glass-rich silicon nitride would exhibit relatively poor high temperature mechanical properties due to a high volume fraction of secondary phases, whereas the $\text{Si}_3\text{N}_4/\text{SiC}$ composite proved to have remarkable mechanical strength and oxidation resistance up to high temperatures [8].

A new route to achieve superplasticity in silicon nitride is presented in this short communication. The basic principle is to start with an equiaxed α -grain microstructure and to use the transient liquid phase which forms during the α to β phase transformation to enhance the high temperature viscoplastic flow. The kinetics of this transformation and its incidence upon the deformation curves are discussed.

2. Materials Preparation and Experimental Procedure

The studied silicon nitride is a mixture of α and β SiAlON grains embedded in a vitreous YSiAlON phase. A Si_3N_4 powder (UBE SNE-10) was mixed with 6 wt% Y_2O_3 (Rhône-Poulenc) and 3 wt% Al_2O_3 (LONZA) as sintering aids and sintered at 1550 °C for 2 hours under a uniaxial stress of 35 MPa in a graphite die under nitrogen flow [9]. The sintered pellets are fully dense and contain some iron traces as a major impurity. The as sintered ceramic, hereafter referred as 70/30, is constituted with 70 and 30 vol.% α and β phases respectively. The α to β phase transformation kinetics was studied by heat treating 70/30 specimens between 1500 and 1600 °C for different times. In addition, 15/85 and 45/55 grades (α/β ratios in vol.%) were prepared for comparison purposes by sintering the same powder mixture for 2 hours at 1650 and 1570 °C respectively. X-ray diffraction analysis using the $\text{CuK}_{\alpha 1}$ radiation was performed to identify the phases and to estimate the phase volume fractions by comparing the peak intensity ratios (the {201} and {200} diffraction peaks were used for α and β - Si_3N_4 respectively). The phase analysis and the materials preparation, including the incidence of the hot pressing temperature on the α/β ratio and on the mechanical properties, have been reported in a previous paper [10].

An ultrasonic technique was employed to follow the change in Young's modulus (E) as a function of temperature. The principle of the method [11,12] consists in calculating E from the velocity of an ultrasonic pulse propagating in a long thin and refractory waveguide sealed to a specimen located inside a furnace under argon atmosphere. A magnetostrictive transducer (300 kHz) was used and experiments were performed with an heating rate of 5 °C/mn from room temperature to 1500 °C. The room temperature elastic moduli were first accurately measured by means of piezo-electric transducers (10 MHz) in direct contact with the specimen.

The mechanical testing machine as well as the experimental procedure have been described in detail in a previous paper [6]. The compressive tests were performed on parallelepipedic

bars $4 \times 4 \times 7$ (height) mm^3 . Dog-bone shaped specimens with 15 mm long cylindrical gauges were used for the tensile tests. Specimens were tested in a gas tight chamber, under a high purity nitrogen atmosphere. The nitrogen gas was introduced into the chamber after a vacuum with pressure less than 0.1 Pa was achieved. A load cell of 1 kN capacity was set up inside the chamber in order to avoid load fluctuations during either the pumping or the testing stages. SiC fixtures, pipes and pistons were used. A differential measurement device, by means of a LVDT and mechanical contacts with the specimen, was designed to accurately measure the elongation during testing. The true strain ε was calculated from the following expression:

$$\varepsilon = \ln(L/L_0) \quad (1)$$

where L_0 and L are the initial and the present gauge lengths respectively.

The nominal strain or elongation is therefore given by:

$$(L - L_0)/L_0 = \exp(\varepsilon) - 1 \quad (2)$$

The true stress was calculated on the basis of a constant specimen volume throughout deformation, using:

$$\sigma = (P/S_0) \exp(\varepsilon) \quad (3)$$

where P and S_0 are the load and the initial cross-section area respectively.

Compressive experiments were preceded by an isothermal hold of 5 hours in order to get sufficient thermal stability (i.e. to avoid the deformation curves being affected by thermally induced geometrical changes). Such a long time was necessary because of the use of both a relatively massive testing assembly and rather low displacement rates (due to a small specimen size and a relatively low testing temperature). In the case of the tensile experiments, an isothermal hold of 30 mn allows the system to reach a satisfactory thermal equilibrium.

3. Results and Discussion

3.1. THE DUCTILE RANGE AND THE α TO β TRANSFORMATION. — Figure 1, showing the change in Young's modulus versus temperature, gives information on both the brittle to ductile transition (BDT) and the α to β transformation. The curve portion corresponding to the heating stage can be divided into three main regions: in the first region, from 20 to 1150 °C, E decreases slowly with a slope of about $-29 \text{ MPa}/^\circ\text{C}$. Above 1150 °C Young's modulus decreases rapidly, with a slope $dE/dT \approx -174 \text{ MPa}/^\circ\text{C}$, due to the softening of the intergranular amorphous phase. It is thus suggested that the glass transition domain of this phase is close to 1150 °C, which is in good agreement with previous results on silicon nitride [13]. It is found experimentally that ductility is almost negligible below this temperature, which is therefore the lowest limit for the BDT. The third region, corresponding to the isothermal hold at 1500 °C shows a slight decrease of E with time. This decrease is mainly related to the α to β transformation that takes place at this temperature and is rapid in the beginning of the isothermal plateau. The change in glass composition that results from the formation of the β' -SiAlON solid solution (the aluminium content of the glass decreases as aluminium diffuses into the β -Si₃N₄ crystals) might also affect Young's modulus, but the corresponding change should not exceed 1 GPa [14]. Previous indentation studies [15,16] suggested that the α phase is harder and hence presumably stiffer than the β one. Figure 1 provides an experimental evidence for this. A more detailed analysis of the transformation kinetics is given in Figure 2 showing the residual α -Si₃N₄ volume fraction in 70/30 specimens heat-treated between 1500 and 1600 °C as a function of the annealing time. The transformation appears to be strongly thermally activated. Dotted lines refer to deformed specimens and will be used in the discussion of the next section.

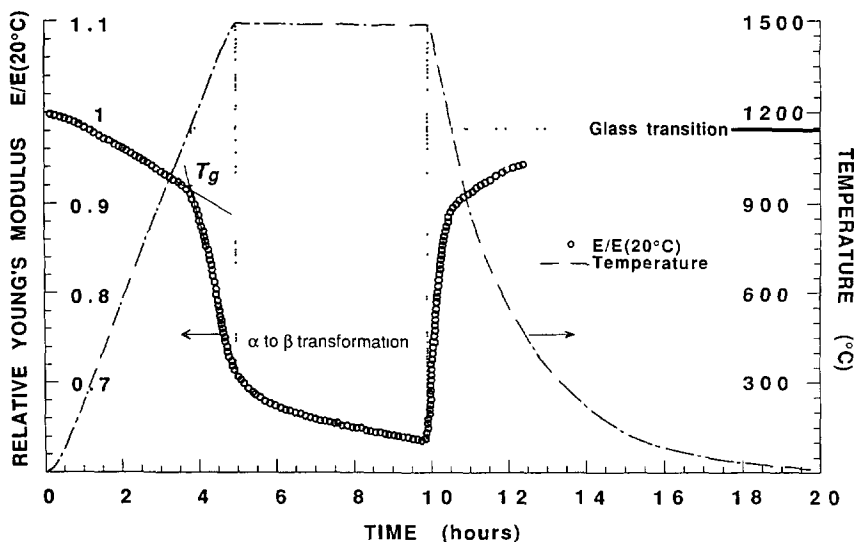


Fig. 1. — Change in Young's modulus as a function of temperature (initial α/β ratio = 70/30); $E(20^\circ\text{C}) = 320$ GPa.

3.2. THE SUPERPLASTIC DEFORMATION. — The deformation curves obtained in compression at 1500°C with a strain rate of 10^{-5} s^{-1} (a and b) and in tension at 1595°C with a strain rate of $2.5 \times 10^{-5}\text{ s}^{-1}$ (c and d) are plotted together in Figure 3. Curves a and c were recorded with 15/85 and 45/55 specimens respectively. Curves b and d concern the initial 70/30 grade. The stress/strain curves can be tentatively divided into 4 regions, related to different deformation regimes. Although these regions are partly overlapping because of the continuous nature of the processes, this description will allow to gain insight into the physics of the deformation behavior.

The first region corresponds to the elastic loading, where it can be noticed that the higher the α content the higher Young's modulus at a given testing temperature, consistent with the results of Figure 1. The elastic domain is limited to strains of less than 0.02.

Regions 2 and 3 correspond to permanent deformation regimes. A relatively small hardening rate is noticed in region 2 (in comparison with the third region). It is assumed that deformation in this region is essentially controlled by the α phase whereas it is controlled by the β phase in the third region. This assumption is based on the statement that transitions between region 2 and 3 occur at times ($t_b = 153$ mn, $t_c = 52$ mn and $t_d = 60$ mn) corresponding to roughly similar volume fractions of α phase, between 30 and 40%. A clear illustration of this is obtained by plotting the entire annealing times, calculated by summing the straining times up to the inflexion points with the stabilization times t_s ($t_s = 30$ mn in tension and 300 mn in compression) and plotting the total times in the transformation diagram of Figure 2. A much lower testing temperature in the case of deformation curve b causes t_b to be much greater than t_c and $t_d \cdot t_c$ is smaller than t_d because the specimen used for curve c has a higher initial β phase content (45/55). Furthermore, the transition (inflexion point) is not observed in the deformation curve a, obtained with a 15/85 specimen. The α to β phase transformation proceeds through the dissolution of α grains in the transient liquid phase and the subsequent precipitation of β grain [17]. It is thus believed that both the equiaxed shape of the residual α grains and the transient liquid phase enhance the viscoplastic flow in region 2. It is important to note here that the above discussion is based on a direct comparison between the deformed

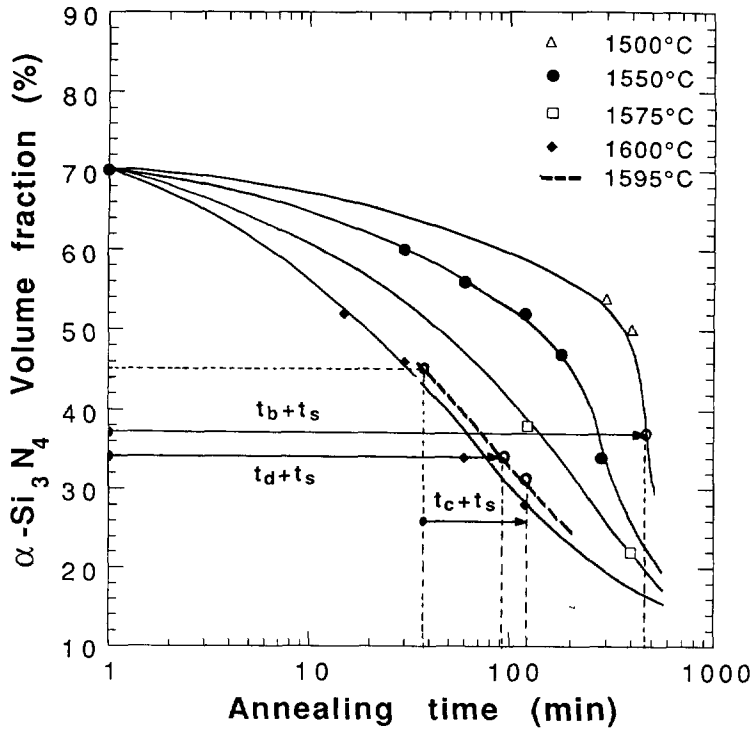


Fig. 2. — $\alpha \rightarrow \beta$ phase transformation diagram obtained from the $\alpha/\beta = 70/30$ grade by heating specimens at 1500, 1550 and 1600 °C with different annealing times (empty circles refer to the experimental data of Fig. 3). Arrows indicate the total running times. The $t_c + t_s$ arrow is associated to a 45/55 starting ratio for α/β . The relatively high β content in this latter grade is illustrated by the shift of the time origin.

microstructures and the simply annealed specimens used to build the diagram of Figure 2. Therefore, the incidence of the mechanical solicitation on the α to β transformation as well as the error on the quantitative phase analysis due to grain alignment toward the tensile axis were not taken into account. A detailed analysis of these factors is far beyond the scope of this short paper and will be reported elsewhere.

Deformation in the third region is governed by the β phase consisting of acicular grains. A strong hardening phenomenon is observed, with a quasi-linear hardening rate as high as $d\sigma/d\varepsilon = 65$ MPa. This hardening is strain-enhanced and essentially time-independent [6], which suggests that it is mainly related to the increase of the cross-linking degree in the β -grain network and to a lesser extent to grain growth and to crystallization of yttrium melilite at grain boundaries. Curves c and d are almost parallel in region 3 and the strain-shift between both curves is approximately $\Delta\varepsilon = 0.06$ and corresponds to a virtual time-shift equal to 40 mn ($\Delta\varepsilon/\dot{\varepsilon}$) which is precisely the time required for the 70/30 grade to be transformed into a 45/55 grade at this temperature.

Intensive damage shows up in a fourth stage with the appearance of cavitation for tensile stresses higher than 30 MPa. As revealed by SEM observations [6] cavities are less than 3 μm large and tend to align along the tensile axis. A fracture surface analysis showed that fracture

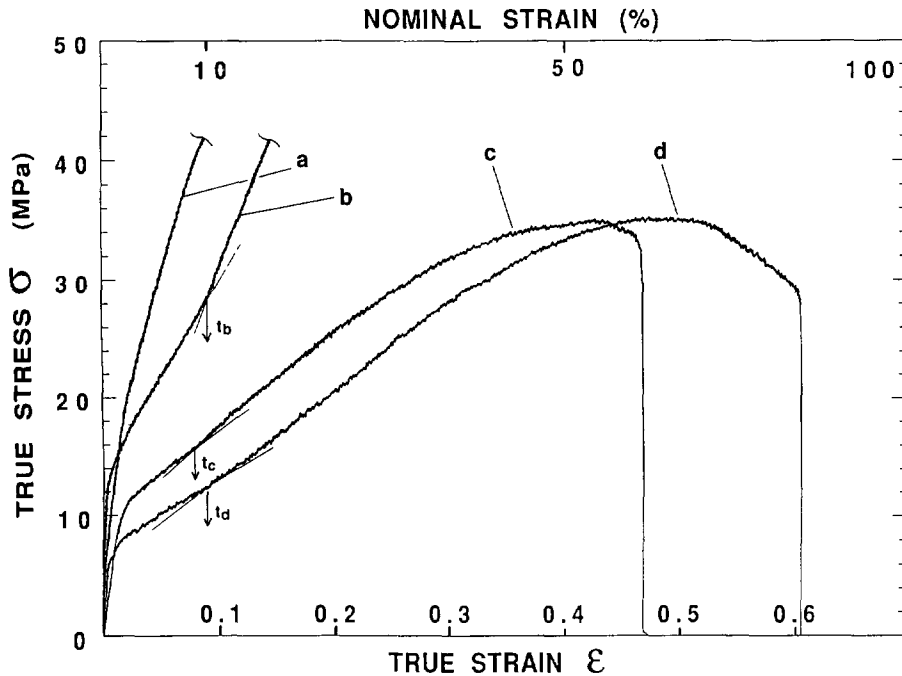


Fig. 3. — Stress/Strain curves: a) compressive test at 1500 °C with a constant strain rate of 10^{-5}s^{-1} , on the 15/85 grade; b) *ibid.* on the 70/30 grade; c) tensile test at 1595 °C with a constant strain rate of $2.5 \times 10^{-5}\text{s}^{-1}$ on the 45/55 grade; d) *ibid.* on the 70/30 grade.

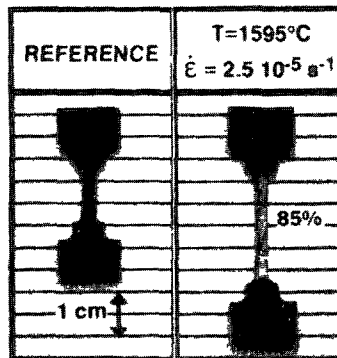


Fig. 4. — Tensile specimen before deformation and after testing at 1595 °C with a constant strain rate of $2.5 \times 10^{-5}\text{s}^{-1}$ (85% elongation).

did not result from cavity coalescence but originated at iron rich impurities introduced during processing. Damage induces a decreasing apparent hardening rate. A maximum elongation of 85% was recorded for the 70/30 grade at 1595 °C, with fracture occurring within the cylindrical gauge (Fig. 4). After deformation, specimens tested at 1595 °C have a final α/β ratio close to 23/77. The corresponding microstructure consists mainly of coarse and elongated β Si_3N_4 grains (Fig. 5).

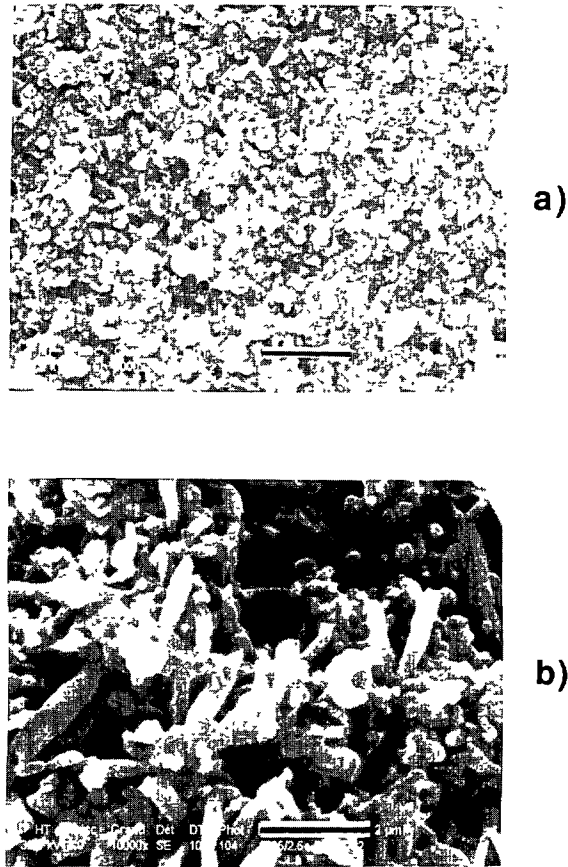


Fig. 5. — Scanning electron micrographs: a) Reference material (as-sintered 70/30 grade); b) After 85% elongation at 1595 °C (curve d). Bar is 2 microns.

4. Conclusions

The deformation behavior of a monolithic silicon nitride sintered with 6 and 3 wt.% yttria and alumina respectively has been studied in tension and in compression between 1500 and 1600 °C. In this temperature range, a superplastic-like behavior is observed for strain rates between 10^{-5} and $4 \times 10^{-5} \text{s}^{-1}$, corresponding to flow stresses from 10 to 35 MPa.

The stress/strain curves reveal a transition between two flow regimes, which has been related to the α to β phase transformation. The transformation kinetics has been analyzed and discussed in close relation to the deformation curves to give a physical interpretation of the deformation behavior.

The analysis shows that the superplastic forming ability can be improved by starting from a fine grained α -rich grade and by carefully selecting the temperature/strain-rate forming conditions to reduce the β -phase controlled deformation stage (region 3) to the benefit of the α -phase controlled one (region 2). A promising result of 85% elongation was obtained at 1595 °C with a 70 vol.% α phase grade.

References

- [1] Wakai F., Kodama Y., Sakaguchi S., Murayama N., Izaki K. and Niihara K., "A superplastic covalent crystal composite", *Lett. Nature* **344** (1990) 321.
- [2] Chen I. W. and Xue L. A., "Development of superplastic structural ceramics", *J. Am. Ceram. Soc.* **73** (1990) 2585.
- [3] Rouxel T., Wakai F. and Izaki K., "Tensile ductility of superplastic $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-Si}_3\text{N}_4/\text{SiC}$ composites", *J. Am. Ceram. Soc.* **75** (1992) 2363.
- [4] Wu X. and Chen I. W., "Exaggerated texture and grain growth in a superplastic SiAlON", *J. Am. Ceram. Soc.* **75** (1992) 2733.
- [5] Wakai F., Kodama Y., Sakaguchi S., Murayama N., Izaki K. and Niihara K., "Superplasticity of non-oxide ceramics", *Superplasticity in Metals, Ceramics, and Intermetallics*, Mayo M. J., Wadsworth J., Mukherjee A. K. and Kobayashi M. Eds., *Mat. Res. Soc. Symp. Proceed.* **196** (1990) 349.
- [6] Rouxel T., Rossignol F., Besson J. L., Goursat P., Goujard J. F. and Lespade P., "Superplastic deformation of a monolithic silicon nitride", *Plastic Deformation of Ceramics*, Roubort J., Bradt R. C. and Brookes C. Eds., *Engin. Foundation Conf. (Snowbird Utah, U.S.A., August 7-12, 1994)*.
- [7] Izaki K., Hakkei K., Ando K., Kawakami T. and Niihara K., "Fabrication and mechanical properties of $\text{Si}_3\text{N}_4\text{-SiC}$ composites from fine, amorphous Si-C-N powder precursors", *Ultrastructure Processing of Advanced Ceramics*, J. D. Mackenzie and D. R. Ulrich Eds. (J. Wiley & Sons, Inc., U.S.A., 1988) p. 891.
- [8] Niihara K., Hirano T., Nakahira A., Ojima K. and Izaki K., "High temperature performance of $\text{Si}_3\text{N}_4\text{-SiC}$ composites from fine, amorphous Si-C-N powder", *Mat. res. Soc. Intern. Meet. Adv. Mat.* **5** (1989) 107.
- [9] Debaig C., Goursat P. and Desmarres J.M., European Patent Application Number 88400323.7 (1988).
- [10] Rossignol F., Goursat P., Besson J. L. and Lespade P., "Microstructure and mechanical behaviour of self-reinforced Si_3N_4 and $\text{Si}_3\text{N}_4\text{-SiC}$ whisker composites", *J. European Ceram. Soc.* **13** (1994) 299.
- [11] McSkimmin H. J. and Fisher E. S., "Measurement of ultrasonic wave velocities for solids", *J. Appl. Phys.* **31** (1960) 627.
- [12] Gault C., "Ultrasonic non-destructive evaluation of microstructural changes and degradation of ceramics at high temperature", *Nondestructive Monitoring of Materials Properties*, Holbrook J. and Bussiere J. Eds., *Mat. Res. Soc. Symp. Proceed.* **142** (1989) 263.
- [13] Rouxel T., Besson J. L., Gault C., Goursat P., Leigh M. and Hampshire S., "Viscosity and Young's modulus of an oxynitride glass", *J. Mat. Sci. Lett.* **8** (1989) 1158.
- [14] Lemercier H., Rouxel T., Fargeot D., Besson J. L. and Piriou B., "Yttrium oxynitride glasses: structure and mechanical properties - elasticity and viscosity", *J. Non Cryst. Sol.*, submitted.
- [15] Greskovitch C. and Gazza G. E., "Hardness of dense α - and β - Si_3N_4 ceramics", *J. Mat. Sci. Lett.* **4** (1985) 195.
- [16] Suematsu H., Petrovic J. J. and Mitchell T. E., "Deformation and toughness of α -silicon nitride single crystals", Chen I. W., Becher P., Mitomo M., Petzow G. and Yen T. S. Eds., *Mat. Res. Soc. Symp. Proc.* **287** (1993) 449.
- [17] Messier D. R., Riley F. L. and Brook R. J., "The α/β silicon nitride phase transformation", *J. Mat. Sci.* **13** (1978) 1199.