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Creep behaviour of two sintered silicon nitride ceramics

J.J. Meléndez-Martínez[a,*], M. Jiménez-Melendo[a],
A. Domínguez-Rodríguez[a], G. Wötting[b]

[a]*Department de Física de la Materia Condensada, University of Seville, Seville, Box 1065, 41080 Spain*
[b]*CFI, Ceramics for Industry, Rödental, Germany*

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Abstract

The high temperature mechanical properties of two sintered silicon nitride—based ceramic materials with different microstructural features, labelled N7202 and N3208, are presented. The mechanical behaviour was examined by creep tests in compression, at temperatures between 1450 and 1700 °C in argon atmosphere. The results, analysed in terms of the creep equation, yield $n = 0.6 \pm 0.1$ and $Q = 470 \pm 20$ kJ/mol for N7202, and $n = 0.6 \pm 0.1$ and $Q = 530 \pm 10$ kJ/mol for N3208. The microstructural observations allow identify a possible microscopic deformation mechanism compatible with the set of creep parameters obtained experimentally. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Creep; Deformation mechanisms; Silicon nitride

1. Introduction

Due to their excellent mechanical and thermal properties (high strength, creep resistance and thermal expansion coefficient, etc.), the technological applications of silicon nitride ceramics are numerous:[1,2] from vessels for chemical reactions to heat exchanger and gas turbine or engines components. In this context, it is of primary interest the study and understanding of the mechanical properties of these materials at high temperatures.

Different studies devoted to this end[3] have revealed that the particular grain morphology of β-silicon nitride is partially responsible for the high creep resistance of these materials. It has been also demonstrated that the secondary glassy phases which appear during the sintering have a strong influence in the creep behaviour of silicon nitride-based ceramics. Finally, silicon nitride ceramics may exhibit a superplastic behaviour, with ductilities exceeding several hundred per cent.[4,5]

In compression, the creep properties have been explained in terms of various deformation mechanisms: viscous flow,[6] grain boundary sliding,[7] solution–eprecipitation,[8,9] etc. There have also been developed models ex profeso, oriented to explain some particular properties of silicon nitride ceramics: concretely, Chen and Hwang[10] have developed a model accounting for stress exponents $n < 1$. This work constitutes a preliminary investigation of the high temperature compressive creep of two sintered silicon nitride ceramics.

2. Experimental procedure

Two silicon nitride-based materials were fabricated by Bayer AG (Krefeld, Germany). The material labelled N7202 was processed from commercial α-Si_3N_4 powders by sintering at 1750 °C under nitrogen pressure of 10 bar (low pressure sintering) with 5 wt.% Al_2O_3, 5 wt.% Y_2O_3 and 1 wt.% MgO as sintering aids. The material labelled N3208 was sintered at 1780 °C under nitrogen pressure of 100 bar (high pressure sintering), with 5 wt.% Al_2O_3 and 5 wt.% Y_2O_3 as sintering aids. According to Bayer, the residual porosity is about 1 vol.% in both cases. The density of both materials was $3.2 \cdot 10^3$ kg/m^3.

From the as received materials, parallelepipedical samples of approximate dimensions $5 \times 3 \times 3$ mm^3 were cut and ground for tests. Compressive creep tests were

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* Corresponding author. Present address: Department de Física, University of Extremadura, Avda. de Elvas, s/n. 06071 Badajoz, Spain. Tel.: +34-95-455-0964; fax: +34-95-461-2097.
E-mail address: melendez@unex.es (J.J. Meléndez-Martínez).

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carried out in argon atmosphere, at temperatures ranging between 1450 and 1700 °C and under nominal stresses between 5 and 90 MPa, approximately. The details of the experimental device can be found elsewhere.[11] The results are analysed in terms of the creep equation:

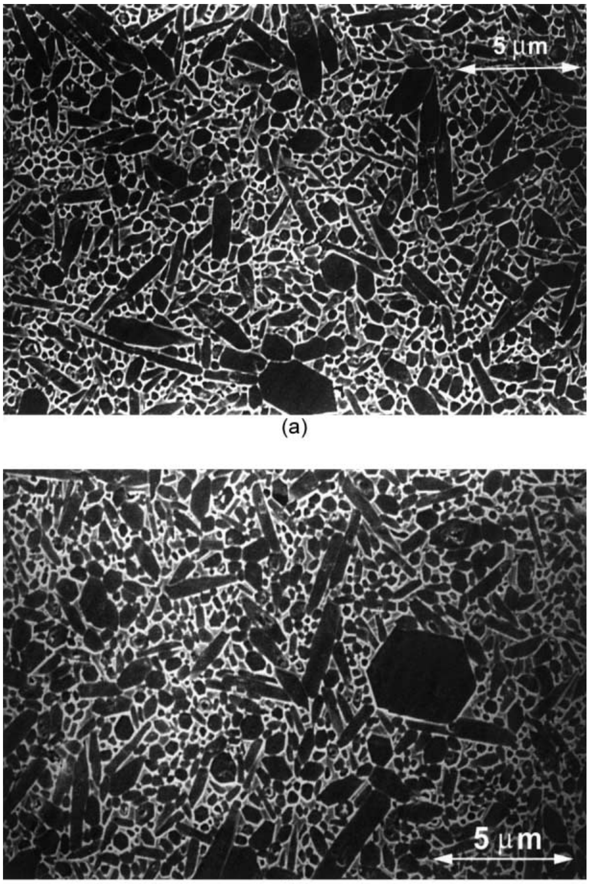
$$\dot{\varepsilon} = A\sigma^n \exp\left(-\frac{Q}{RT}\right) \tag{1}$$

where $\dot{\varepsilon}$ is the steady strain rate, A is a constant, σ is the applied load, T the absolute temperature and R the gas constant. n and Q are, respectively, the stress exponent and the apparent activation energy for creep. Two types of creep tests were performed: (1) at constant temperature and different stresses, in order to evaluate the stress exponent n; and (2) at constant load and different temperatures, to evaluate the apparent activation energy Q. All the tests were finished without evidence of macroscopic failure.

The microstructure of the as received and deformed materials was studied by SEM. To this end, the observation surfaces were ground and polished with diamond paste, and then CF_4-plasma etched to reveal the grain boundaries. In the case of crept materials, the samples were cut in a plane rotated 45° with respect to the compression axis. The SEM observations were carried out in a Philips XL-30 microscope (Servicio de Microscopía Electrónica, University of Seville). The morphologic parameters were measured with a semiautomatic image analyser (Kontron MOP 30) on no less than 300 grains.

3. Results and discussion

Fig. 1 shows SEM micrographs of as received N7202 (Fig. 1a) and N3208 (Fig. 1b). Both materials have similar microstructural features. In these images, the characteristic acicular β-grains are observed. The acicular grains were found to be randomly oriented. These grains interlock to form a three-dimensional network, which is partially responsible for the excellent mechanical properties of silicon nitride-based ceramics. In both materials, the remnant porosity appears in form of isolated pores, located mainly in triple points, with sizes much smaller than the grain diameter in each case. The grain diameters measured for N7202 and N3208 (taken



Figs. 1. SEM micrographs of (a) N7202 and (b) N3208.

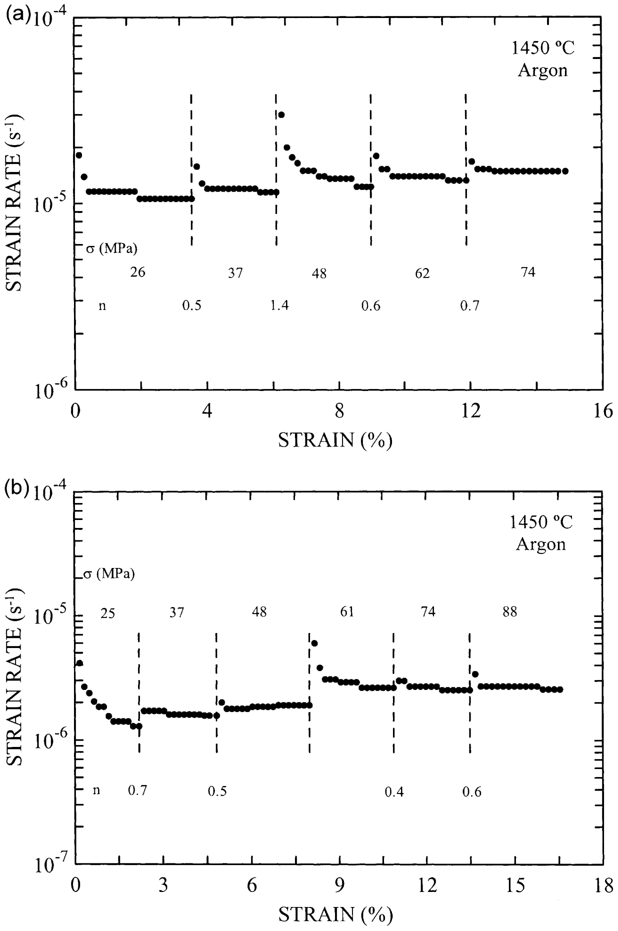


Fig. 2. (a) Creep curve for N7202 obtained at 1550 °C and under stresses ranging between 26 and 74 MPa; (b) *Idem* for N3208, obtained at 1450 °C and under stresses ranging between 25 and 88 MPa.

as equivalent planar diameters) were 0.47±0.19 and 0.36±0.13 μm, respectively; the aspect ratios were $f=2.8\pm1.2$ and $f=2.3\pm0.7$ for N7202 and N3208, respectively.

The plasma etching process erodes the crystalline phases, but the glassy phases are etching-stable. The white regions in Figs. 1(a) and 1(b) correspond to the secondary phase. XRD patterns of N7202 and N3208 are reported elsewhere:[12] these demonstrate that, for both N7202 and N3208, this secondary phase has a glassy nature, and its formation may be attributed to the reaction, during the sintering, of the oxide additives with residual SiO_2 existing at the surfaces of the powder particles. The glassy phase is located mainly in pockets at triple points of the grain structure. It is also remarkable that the distribution of glassy phase is homogeneous both in N7202 and N3208.

Fig. 2 displays log $\dot{\varepsilon}$ vs. ε plots (creep curves) for N7202 [Fig. 2(a)] and N3208 [Fig. 2(b)], obtained respectively at 1550 and 1450 °C and at stresses between 25 and 74 MPa (N7202) and between 25 and 88 MPa (N3208). Final strains of about 15% were achieved. The steady state is reached almost immediately after each stress change: no significant transient states are present. Figs. 2(a) and 2(b) show the stress exponent values obtained from every stress change. These values lie below $n = 1$, with an average value $n=0.6$. Fig. 3 display creep curves for N7202 obtained at 1550 °C by changing the applied stress between 40 and 50 MPa. The extrapolating values after each change are indicative that the microstructure remains unchanged during the deformation. From all the creep experiments, an average stress exponent of $n=0.6\pm0.1$ was evaluated for N7202 and N3208 in the entire range of temperatures and stresses used in this study.

On the other hand, Fig. 4 represent creep curves for N7202 [Fig. 4(a)] and N3208 [Fig. 4(b)], obtained at a constant stress (74 MPa) and at 1550 °C and 1600 °C. From these set of tests, average activation energies of $Q=470\pm20$ and $Q=530\pm10$ kJ/mol are obtained for N7202 and N3208, respectively; again, it was possible to extrapolate the strain rate levels before and after each temperature change, which also supports the idea that the microstructure is stable. Although, in silicon nitride ceramics, it is difficult to ascribe the apparent activation energy to difusional processes due to the presence of the intergranular glassy phase, the results obtained for N7202 and N3208 lie within the typical range of activation energies for silicon nitride ceramics tested in compression (Q ~300–750 kJ/mol).[8,13]

Fig. 5 shows a SEM micrograph of a N7202 sample after creep to a final strain $\varepsilon=25\%$ ($T=1450$ °C, $\sigma=90$ MPa). Measurements of the grain diameter and aspect ratio after creep indicated that no dynamic grain growth occurred during the deformation. However, creep damage is observed. In some grains, there appear microcracks perpendicular to the long axis, but the damage consists mainly in cavities developed along the grain boundaries, which partially coalesce into microcracks. There is no evidence of formation of intra-granular cavities.

The short transient regime in the creep curves and the relatively high macroscopic strains achieved, together with the microstructural features of the crept samples,

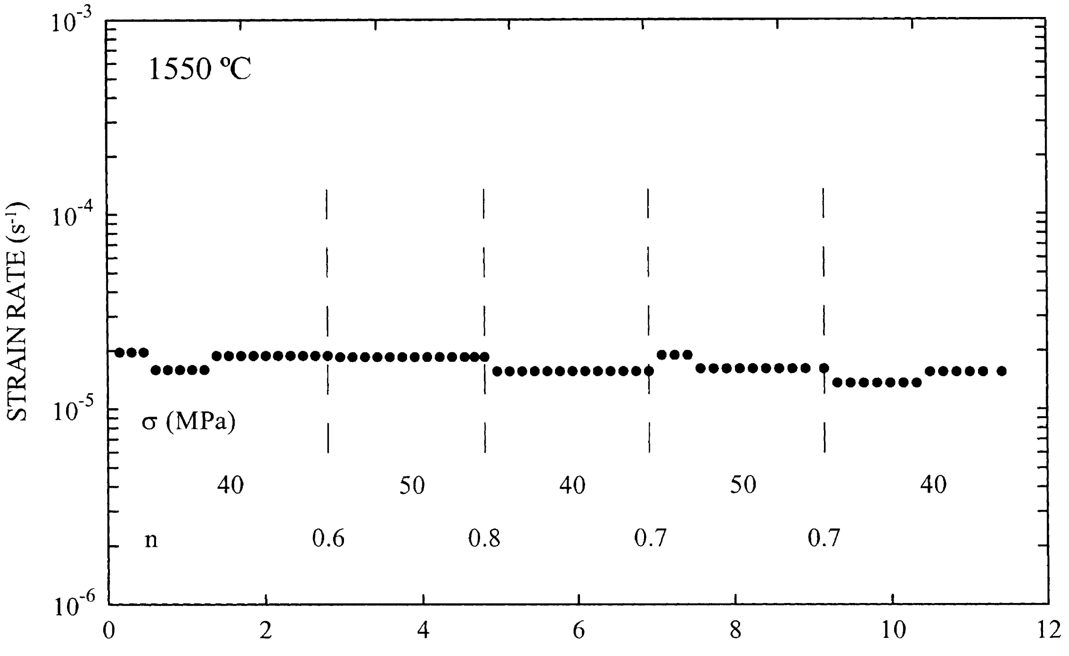


Fig. 3. Creep curve for N7202 obtained at 1550 °C and under two stresses (40 and 50 MPa).

are consistent with a grain boundary sliding (GBS) process as primary deformation mechanism. In glass ceramics, the accommodation of the primary mechanism is mainly provided either by viscous flow of the glassy phase or by solution–reprecipitation.[6,8,14] The current models for both viscous flow and solution–reprecipitation predict $n=1$ or $n=2$, depending on the rate-controlling mechanism. On the other hand, it is also expectable that a partial accommodation is provided by the nucleation of cavities: this is associated normally to $n>2$ in compression.[15] None of these mechanisms can be invoked to explain the experimental results obtained. The stress exponent values obtained for N7202 and N3208 under the experimental conditions used in this study are certainly unusual. To the authors' knowledge, only Chen et al.,[10] Rosenflanz et al.[16] and Burger et al.[17] report stress exponents $n<1$ for silicon nitride-based ceramics.

Chen and Hwang[10] studied the creep behaviour of a hot-pressed SiAlON by constant cross-head speed tests carried out at temperatures between 1500 and 1600 °C. The authors identified a transition from $n=1$ (compatible with the Newtonian viscous flow mechanism or with an accommodated grain boundary sliding mechanism) to $n\sim0.5$ ("shear thickening" regime) at a critical stress $\sigma^* \sim 20$ MPa, which was almost independent on the composition of the secondary phase and the temperature within the experimental range. This transition was observed in compression, but not in tension.

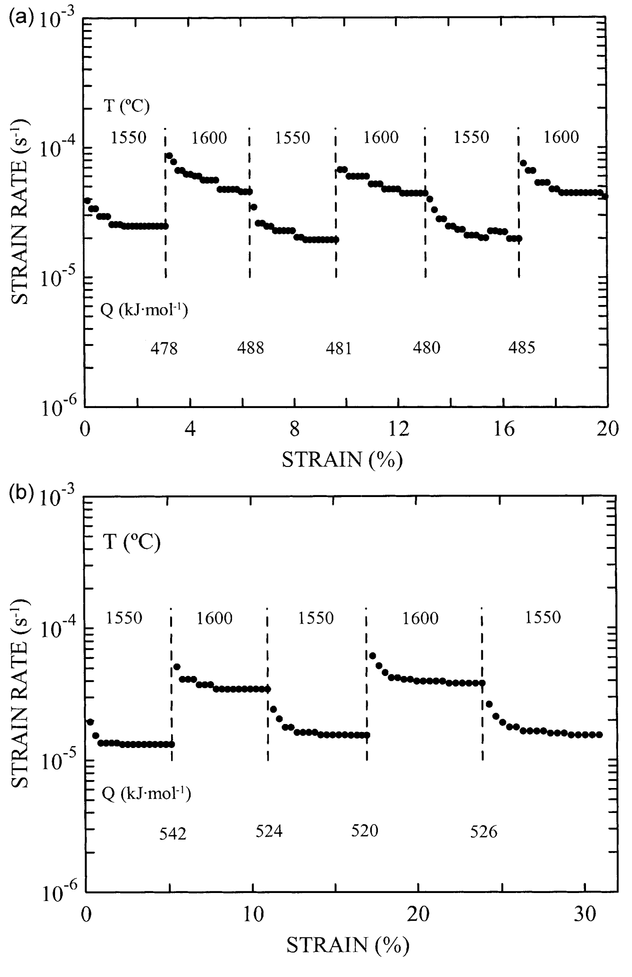


Fig. 4. (a) Creep curve for N7202, obtained at 1550 °C and 1600 °C under an applied stress of 74 MPa.; (b) *Idem* for N3208.

This behaviour was attributed to a dependence of the viscosity of the glassy (liquid) phase on the applied stress. Indeed, Chen and Hwang assumed that, above the transition stress σ^*, certain regions of the intergranular phase undergo a sharp increase of the viscosity, becoming "rigid". This effect gives rise to strain rates lower than those expected in the case of "no-shear-thickening", and therefore to apparent stress exponents lower than one. Rosenflanz et al.[16] on a hot-pressed SiAlON, and Burger et al.[17] on a HIP-ed silicon nitride material, found features similar to those described by Chen and Hwang.

From a microscopic viewpoint, the existence of a transition stress σ^* was explained by Chen and Hwang introducing an additional hypothesis, in analogy with the theories of colloidal stability:[18] each grain surface is surrounded by a layer, named Stern layer, in which the intergranular phase is over-condensed, thus having a higher viscosity. The presence of these Stern layers at the surface of each grain decreases the effective thickness of the intergranular phase, thus modifying the forces equilibrium which stabilizes the grain boundaries.[19] The viscous flow of the liquid phase is then impeded when the normal stress at the grain boundaries is high enough to squeeze out the intergranular liquid (no over-condensed) so that only the two Stern layers remain. In this case, it is expected that both viscous flow and grain boundary sliding are partially avoided: it is in this sense that the grain boundaries become rigid. Using Clarke's theory for the stability of the grain boundaries, Chen and Hwang estimated the theoretical value for the

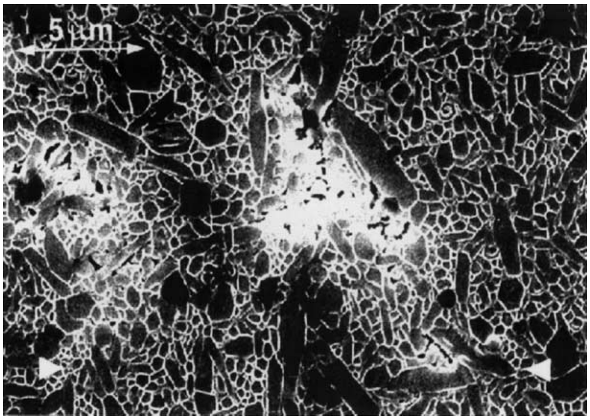


Fig. 5. SEM micrograph of a N7202 sample crept up to a final strain $\varepsilon=25\%$ ($T=1450$ °C, $\sigma=90$ MPa). The arrows indicate the compression axis.

transition stress σ* ~24 MPa, which is in excellent agreement with the experimental results.

Clearly, the physical and chemical properties of the glassy phase dictate the transition-to-shear thickening stress in glass ceramics different than those previously mentioned. In some cases, if the transition stress is very high, a possible shear thickening process may be unidentifiable. Inversely, if the transition stress is very low, the shear thickening regime may be present in a wide range of stresses and temperatures. Therefore, one viable way of explaining the anomalous stress exponents for creep of N7202 and N3208 is to assume that, for the concrete composition and amount of additives present in both materials, a shear thickening phenomenon occurs, characterised by a transition stress lower than about 5 MPa.

To check out this hypothesis it is necessary a further study oriented to characterise the creep behaviour of N7202 and N3208 at stresses below about 5 MPa. This investigation is in progress at the University of Seville.

4. Conclusions

The compressive creep behaviour of two sintered silicon nitride ceramics, labelled N7202 and N3208, has been characterised in the temperature range 1450–1700 °C and at stresses ranging between 5 and 90 MPa. The results have been analysed in terms of the classical creep equation.

- For N7202 and N3208, the average stress exponent was 0.6 ± 0.1 in the entire temperature and stress ranges; the apparent activation energies were $Q=470\pm20$ kJ/mol for N7202 and $Q=530\pm10$ kJ/mol for N3208.
- The SEM observations on crept samples revealed that no dynamic grain growth had taken place. Some cavities along the grain boundaries were observed.
- The primary deformation mechanism seems to be grain boundary sliding, and the anomalous stress exponent values obtained might be explained by assuming that a shear thickening phenomenon (with a transition stress lower than about 5 MPa) takes place during the deformation. The validity of this conclusion remains to be checked out.

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