

THE EFFECT OF GLASS COMPOSITION ON CREEP DAMAGE DEVELOPMENT IN SILICON NITRIDE CERAMICS

F. Lofaj¹, S.M. Wiederhorn², F. Dorčáková¹ and M.J. Hoffmann³

¹Institute of Materials Research of the Slovak Academy of Sciences, 043 53 Kosice, Slovakia

²National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

³Institut für Keramik im Maschinenbau, Universität Karlsruhe, 76131 Karlsruhe, Germany

ABSTRACT

Creep damage development during tensile creep in two different commercial silicon nitride ceramics, SN88 and SN 281, was measured using precise density measurement and anomalous ultra-small X-ray scattering (A-USAXS) techniques. The study revealed that cavitation at multigrain junctions is the main creep damage type and creep mechanism in SN88 which contains Yb/Y-based additives. However, it was fully suppressed in SN281 containing Lu-based additives. Suppression of cavitation resulted in an increase in creep resistance of almost 4 orders of magnitude and more than 200 °C higher operational temperatures in comparison with SN88. The analysis of creep behavior of the ceramics suggests that the transformation from a cavitation to non-cavitation creep mechanism may be related to the changes in viscosity of the residual glass at the grain boundaries due to the presence of Lu. A subsequent viscosity study on the model bulk lanthanide-containing oxide and oxynitride glasses showed that the replacement of Yb by Lu can increase the glass transition temperature, T_g , maximum by 25 °C to 36 °C and viscosity increases only by a factor of $\times 25$ to 100. This is insufficient to explain changes in the creep resistance of SN281. However, the incorporation of nitrogen has an independent and considerably stronger effect than the lanthanides; adding 24 e/o N in the corresponding oxide increased T_g by 84 °C to 100 °C and viscosity by a factor of 10^5 . Thus, the suppression of cavitation and a significant increase in creep resistance in SN281 can be related to the simultaneous effects of a higher degree of cross-linking due to the presence of 3-coordinated N and better packing of glass structure containing Lu modifier with smaller ionic radius on residual glass viscosity.

1 INTRODUCTION

Numerous creep studies carried out on various vitreous bonded ceramics revealed that creep cavitation is the dominant type of creep damage [1-8]. Cavitation is intrinsic to the tensile creep deformation [3-6, 8], whereas in compression cavitation is considerably reduced [3, 5-6]. Creep cavities form predominantly inside the amorphous boundary phases at multigrain junctions [3-4, 9] and each cavity is directly transformed into an increment of tensile strain [5]. The differences in the amount of cavitation were concluded to be responsible for a strong creep asymmetry in vitreous bonded ceramics and unusually high stress exponents compared to the stress dependence in compression [2, 4-5]. Since cavitation is also the main cause for creep failure, suppression of cavitation is the most effective for ways for the improvement of creep resistance, lifetime and reliability of structural silicon nitride components at high temperatures.

Tailoring the microstructure via control of a grain size distribution and especially via composition of the secondary phases using oxides of different rare-earth, *i.e.*, the lanthanide (Ln) family of elements, resulted in new generations of silicon nitride ceramics with greater creep resistance [7, 10]. However, the effects of Ln_2O_3 additives were usually described in terms of the formation of more refractory crystalline secondary phases. Their effect on creep damage accumulation and viscosity of the intergranular residual glassy films (IGF) was not understood and the correlations between creep properties of silicon nitride and viscosity of the bulk glass with the

comparable composition as that of IGF are not available until now. The current study investigates creep behavior and creep damage development in two commercial silicon nitride ceramics containing Yb/Y and Lu-based additives. The aim of the work is to determine the role of the lanthanide type on creep-resistance and creep-mechanisms in silicon nitride ceramics, and to correlate these effects with the Ln and N effects on the viscosity of the bulk oxynitride glasses.

2 EXPERIMENTAL PROCEDURE

Two commercial silicon nitride ceramics have been investigated: gas-pressure-sintered, self-reinforced nano-composite silicon nitride designated as SN 88 (NGK Insulator Co., Ltd., Nagoya, Japan) and the hot isostatic pressed SN 281 (Kyocera Corp., Kyoto, Japan) [11]. Tensile creep tests were performed on flat, dog-bone shaped samples with the gauge size of 2 mm x 2.5 mm and the gage length of 15 mm. They were loaded via single pin SiC pull rods using a commercial creep machine with dead-weight loading. Tensile strain was measured *in situ* using a laser-extensometer system to detect pair of silicon carbide flags hanging from the specimen. Details of the testing procedure are given elsewhere [3, 6-8, 10]. Specimen density was measured using the sink-float technique [3] on the bars from the gauge and grip section of the specimens after creep testing. Samples were put into a water solution of thallium malonate formate kept at the given temperature using water bath. The density of the solution was adjusted by changing water bath temperature in such a way that it bracketed the buoyancy temperature for each specimen to an accuracy of ± 0.25 °C, which is equivalent to an uncertainty in density of ± 0.05 g.cm⁻³. The density of the specimens was then calculated from the measured buoyancy temperature. The density change from creep strain was assumed to be equivalent to the volume fraction of cavities, determined as the difference between the densities of a sample from the gauge and from the grip [3, 10].

The pairs of samples from the gauge and the grips with dimensions of 2.5 mm x 4 mm x 0.15 mm were also used to obtain cavity size distribution from ultra-small-angle X-ray scattering (USAXS) data on beam line 33ID-D at the Advanced Photon Source at Argonne National Laboratory. Details of the USAXS instrument and evaluation of the anomalous USAXS data, which account for both the secondary phase and the porosity, were reported by Jemian *et al.* [12].

Two oxide and four oxynitride glasses were prepared from the mixture of powders of SiO₂, MgO and RE₂O₃, (RE = Yb and Lu) and α -Si₃N₄. The ratio Mg : RE was 20 e/o : 20 e/o. The amount of silicon nitride powder was calculated in such a way that the N contents were 0 e/o, 20 e/o and 24 e/o. The powders were poured or sintered in gas pressure sintering furnace at 1700 °C [13-16]. Viscosity of the corresponding glass, η , was calculated from the minimum strain rate, $d\varepsilon/dt$, according to the formula, $\eta = \sigma/[2(1+\nu)d\varepsilon/dt]$, where ν is the Poisson's ratio. Creep rates were obtained from compressive creep experiments in the temperature range ≈ 760 °C to ≈ 910 °C under the stress of $\sigma = 10$ MPa to 30 MPa. The glass transition temperature range was determined as the temperature range corresponding to the range of viscosities from 1.10^{12} Pa.s to $1.10^{12.6}$ Pa.s.

3 RESULTS AND DISCUSSION

3.1 Tensile creep: SN 88 vs. SN281

Fig. 1 (A) and Fig. 1 (B) illustrate the differences in creep rates between SN 88 and SN 281 grades. The difference in strain rates at comparable conditions were almost 4 orders of magnitude (>8000 x). Stress exponents in SN 88 are known to change from 1 to ≈ 8 or more (Fig. 2 (A)) depending on the range of the applied stress [6, 17]. In SN281, stress exponent, $n = 5.5 \pm 2.0$, but

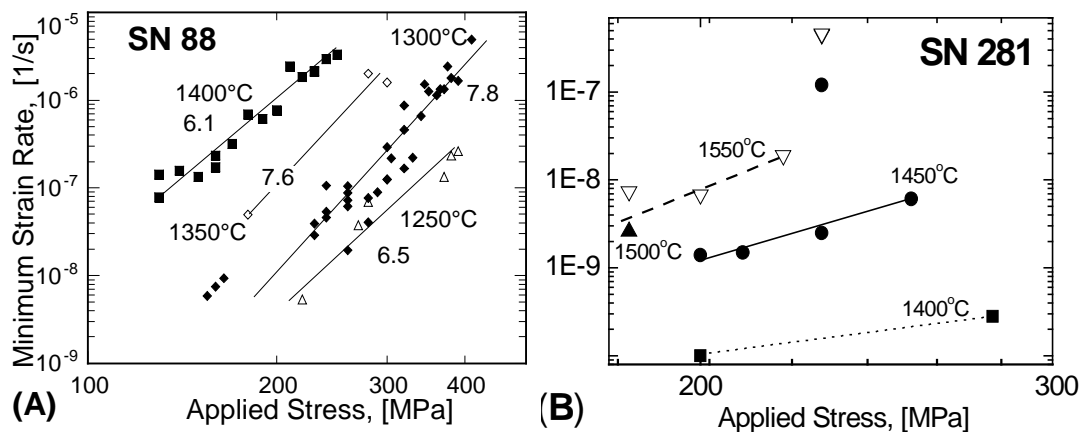


Figure 1: Stress dependence of the minimum strain rate in SN 88 - (A), and SN 281 - (B) [7, 17].

the limited number of tests and scatter in the creep rates between different batches at identical conditions prevented determination of the stress exponents dependence on stress. The maximum failure strains obtained in SN 88 were around 3.5 % [5, 8, 17] whereas in SN 281 exceeded 1 % only at temperatures above 1500°C [7, 10]. The activation energies in SN 88 was in the range from 684 kJ/mol to 830 kJ/mol with the average around 750 kJ/mol [17], compared to 757 ± 117 kJ/mol in SN 281 [7]. The lifetime in SN88 at 1400 °C under stress of 150 MPa was around 80 hours while it exceeded 10 000 h in SN 281. If a maximum allowable strain of 0.5 % in 10 000 h is assumed for the design of structural components, steady-state strain rates $< 1.5 \times 10^{-10} \text{ s}^{-1}$ are required. It was estimated for a stress of 150 MPa that this rate can be achieved in SN 281 at about 1450 °C, which is about 230 °C higher than that for SN 88 [7, 10].

3.2 Cavitation

The contribution of cavitation to tensile strain was determined from a density change and A-USAXS measurements on the same specimens. The results of both techniques for both materials are summarized in Fig. 2. In accordance with previous density and ultrasonic measurements [8], the slope of the fit was around 0.75 which suggests that the contribution of cavitation to tensile strain in SN88 was 75 %. Thus, cavitation is the main creep mechanism in this case. In contrast to SN 88, the data for SN 281 oscillated around zero regardless of the strain. Cavitation contribution to tensile strain was fully eliminated in SN 281 and therefore, creep deformation occurs via volume-conservative mechanisms.

SN 281 differs from other grades of silicon nitride because of the suppression of cavitation. The deformation is in this case non-dilatational, which implies that only solution-precipitation (SP) and grain boundary sliding (GBS) can be active in SN 281. Both SP and GBS depend on the properties of the amorphous boundary phase. At the same time, cavity nucleation and growth occur via GBS and SP, respectively. Cavitation can be suppressed when the grain boundary thickness is reduced and/or the viscosity of IGF is increased. The replacement of Yb by Lu can significantly affect these parameters. However, direct measurement of grain boundary thickness in SN 281 did not show significant thinning of the grain boundaries compared to other ceramics [7]. Thus, the change of the residual glass viscosity seems to be the main reason for enhanced creep resistance. Because

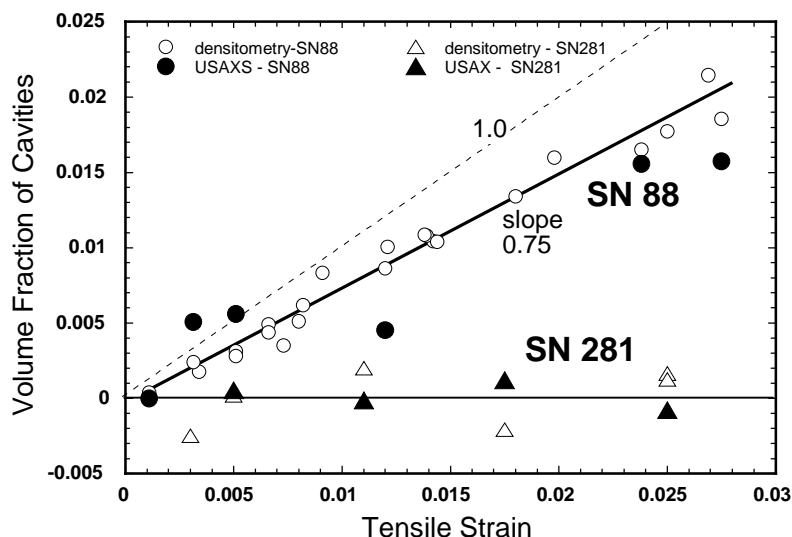


Figure 2: The comparison of the density change and A-USAXS measurements illustrates principal differences in the role of cavitation in SN 88 and SN 281 ceramics.

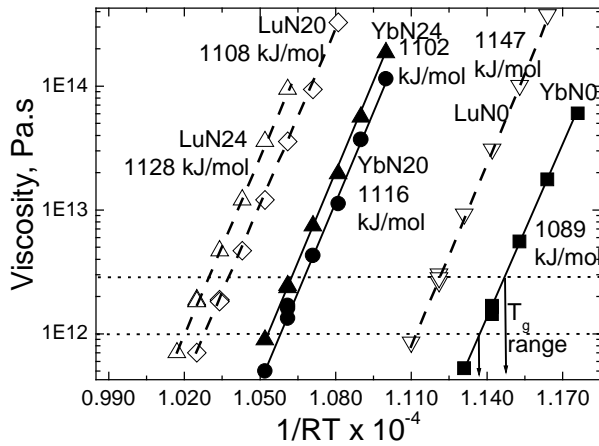
the viscosity of IGF is difficult to measure, the viscosity of the bulk glasses was studied to estimate the effect of lanthanides on the flow behavior of the IGF.

3.3 Viscosity of the bulk RE-oxide and oxynitride glasses

Fig. 3 summarizes glass viscosities as a function of inverse temperature in Yb and Lu oxide and oxynitride glasses with 20 e/o N and 24 e/o N. The difference between Lu- and Yb-containing oxide glasses in terms of viscosity is 17 fold and 26 °C to 33°C in terms of T_g change (see Table). The oxynitride glasses exhibited very similar behavior: their viscosities changed 26 to 32 times due to the exchange of La by Lu; T_g increased by 44 °C to 47°C. The apparent activation energies were in the range from 1089 to 1128 kJ/mol which indicates the absence of Ln and N effects on the activation energy. Stress exponents were always near 1 (see Table), which confirms that the deformation occurs via conventional viscous flow regardless of the N content and the type of lanthanide modifier. The effect of nitrogen on viscosity is much stronger than that of the lanthanides. Addition of 24 e/o N into oxide glass resulted in 85 °C to 100°C increase of T_g and viscosity changed by at least 4 orders of magnitude.

3.4 Lu effect in ceramics and bulk glasses

The suppression of cavitation was accompanied by an increase of creep resistance of SN 281 compared to SN 88 by almost 4 orders of magnitude. A direct comparison with the viscosity change in the bulk glasses shows that the replacement of Yb with Lu produces only 1 to 1.3 orders of magnitude increase in viscosity. Obviously, the high creep resistance in SN 281 cannot be explained only on the basis of the Ln exchange in the intergranular glass. The missing >2.5 orders have to be related to another effect. Additional nitrogen in the intergranular glass seems to be a possibility resulting in the required viscosity change. Three orders of magnitude greater viscosity



Glass system	T _g range, °C	Stress exponent
Yb-N0	772-784	1.2
Yb-N20	851-864	0.7
Yb-N24	856-869	1.0
Lu-N0	797-808	0.9
Lu-N20	882-896	0.9
Lu-N24	894-908	1.0

Figure 3: Arrhenius plot of the viscosity in for Ln-Si-Mg-O-N glasses with Ln = Yb or Lu and N contents 0, 20 and 24 e/o and the summary of T_g range and stress exponents in the studied glass systems. The abbreviation relates to the lanthanide type and N content.

would correspond to ≈ 15 e/o N content difference. The observed mechanism change and creep resistance increase would be a result of a higher IGF viscosity due to simultaneous glass structure “tightening” effects of Lu with a smaller ionic radius and an increased “cross-linking” due to the presence of 3-coordinated N. However, the saturation limits for N in both, Yb and Lu oxynitride glasses are about the same because of similar ionic radii. Thus, it is difficult to expect substantially higher N contents in Lu-containing glasses unless the thickness of the IGF influences viscosity. At least two other reasons can be considered the increased creep resistance. Different nitrogen saturation limits in Yb- and Lu-containing glasses may be related to a change in the valence of the Yb [13-16] from +3 to +2, whereas Lu remains at +3. The second reason may be related to the redistribution of the lanthanides with different ionic radii between the triple junctions and intergranular films. The content of RE modifiers with smaller ionic radii in IGF tends to be lower than that with greater atoms [18]. In that case, Lu content in IGF is lower and the viscosity of such glass is closer to that of pure silica than in the IGF with Yb modifier. However, both cases require experimental confirmation.

4 CONCLUSIONS

The transition from cavitation to non-cavitation creep mechanism via suppression of cavitation in the silicon nitride ceramics containing Lu-based additives resulted in a creep resistance increase of almost 4 orders of magnitude and more than a 200 °C higher operational temperature compared to the earlier, Yb/Y- containing ceramics. This effect can be attributed to the changes in viscosity of the residual intergranular glass due to the presence of Lu. However, the tests of the model bulk Yb and Lu-containing oxide and oxynitride glasses indicated that the replacement of Yb by Lu can increase T_g maximum by 25 °C to 36 °C and can account for a viscosity increase of only a factor of 25 to 100. However, adding 24 e/o N in the corresponding oxide increased T_g by 84 °C to 100 °C and viscosity by a factor of 10⁵. Thus, the effect of Lu on the creep of SN281 can be related to the simultaneous effect of Lu and to the presence of 3-coordinated N on viscosity of the residual glass.

Acknowledgement This work was supported by A. von Humboldt Foundation, VEGA Grant No. 2/3206/23, Grant APVT-51-049702, NANOSMART - Centre of Excellence of SAS and a “New materials and technologies in the construction of machines and equipment” program.

5 REFERENCES

1. Lange, F.F., Davis, B.I., Clarke, D.R., Compressive Creep of $\text{Si}_3\text{N}_4/\text{MgO}$ Alloys, Part 1, Effect of Composition, *J. Mat. Sci.*, **15**, 601-10 (1980).
2. Luecke, W.E., Wiederhorn, S.M., Tension/Compression Asymmetry in Si_3N_4 , *Key Eng. Materials*, **89-91**, 587-92 (1994).
3. Luecke, W.E., Wiederhorn, S.M., Hockey, B.J., Krause, Jr., R.F., Long, G.G., Cavitation Contributes Substantially to Tensile Creep in Silicon Nitride, *J. Am. Ceram. Soc.*, **78**, 2085-96 (1995).
4. Luecke, W.E. and Wiederhorn, S.M., A New Model for Tensile Creep of Silicon Nitride, *J. Am. Ceram. Soc.*, **82**, 2769-78 (1999).
5. Lofaj, F., Okada, A., Kawamoto, H., Cavitation Strain Contribution to Tensile Creep in Vitreous Bonded Ceramics, *J. Am. Ceram. Soc.*, **80**, 1619-23 (1997).
6. Yoon, K.J., Wiederhorn, S.M., Luecke, W.E., A Comparison of Tensile and Compressive Creep Behavior in Silicon Nitride, *J. Am. Ceram. Soc.*, **83**, 2017-22 (2000).
7. Lofaj, F., Wiederhorn, S.M., Long, G.G., Hockey, B.J., Jemian, P.R., et al., Non-Cavitation Tensile Creep in Silicon Nitride with Lu-Based Additives, *J. Europ. Ceram. Soc.*, **22**, 2479-87 (2002).
8. Lofaj, F., Blessing, G.V., Wiederhorn, S.M., Ultrasonic Velocity Technique for Non-Destructive Quantification of Elastic Moduli Degradation During Creep in Silicon Nitride, *J. Am. Ceram. Soc.*, **86**, 817-22 (2003).
9. Lofaj, F., Okada, A., Usami, H., Kawamoto, H., Creep Damage in an Advanced Self-Reinforced Silicon Nitride: Part I, Cavitation in the Amorphous Boundary Phase, *J. Am. Ceram. Soc.*, **82**, 1009-1019 (1999).
10. Lofaj, F., Wiederhorn, S.M., Long, G.G., Jemian, P.R., Tensile Creep in the Next Generation Silicon Nitride, *Ceram. Eng. Sci. Proc.*, **22**, 167-174 (2001).
11. The use of commercial names is only for purposes of identification and does not imply endorsement by the National Institute of Standards and Technology.
12. Jemian, P.R., Long, G.G., Lofaj F., Wiederhorn, S.M., Anomalous Ultra-Small-Angle X-ray Scattering from Evolving Microstructures During Creep. In *MRS Symp.* **590**, Applications of Synchrotron Radiation Techniques to Materials Science V, MRS, 131-136 (2000).
13. Lofaj, F., Dorčáková, F., The Effect of Lanthanides on Viscosity of RE-Si-Mg-O-N Glasses, *Metalurgija*, **42**, 229-33 (2003).
14. Lofaj, F., Hvizdoš, P., Dorčáková, F., Satet, R., Hoffmann M.J., Arellano Lopez, A. R., Indentation Moduli and Microhardness of RE-Si-Mg-O-N Glasses (RE = Sc, Y, La, Sm, Yb and Lu) with Different Nitrogen Content, *Mat. Sci. Eng.*, **A357**, 181-187 (2003).
15. Lofaj F., Satet, R., Hoffmann, M.J., Arellano Lopez, A. R., Thermal Expansion and Glass Transition Temperature of the Rare-Earth Doped Oxynitride Glasses, *J. Eur. Ceram. Soc.*, **24** 3377-84 (2004).
16. Lofaj, F., Dorčáková, F., Hoffmann, M.J., The Effect of Nitrogen on Viscosity of La-Si-Mg-O-N Glasses by Compressive Creep and Dilatometry, submitted *J. Mater. Sci.*, (2004).
17. Lofaj, F., Tensile Creep Behavior in the Advanced Silicon Nitride, *Mat. Sci. Eng.*, **A279**, 61-72 (2000).
18. Gu, H., Pan, X., Cannon, R.M., Rühle, M., Dopant Distribution in Grain-Boundary Films in Calcium Doped Silicon Nitride Ceramics, *J. Am. Ceram. Soc.*, **81**, 3125-35 (1998).