

Creep processes in silicon nitride ceramics

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Recent advances in our understanding of creep deformation in silicon nitride ceramics are reviewed and compared to two different models of creep. The classical models adopted from the metals literature are based on the assumption that creep occurs primarily by diffusion of atoms either through the grains, or along grain boundaries. The cavitation model of creep was developed specifically to explain creep in materials that consist of rigid grains with a mobile secondary phase at the grain boundaries, materials having structures similar to that of silicon nitride. Well-known effects such as creep asymmetry and a very wide range of stress exponents in the early commercial grades of silicon nitride can be fully understood within the framework of the cavitation models. The work discussed includes an identification of critical types of creep cavities in silicon nitride, the evolution of cavities with tensile strain, and an analysis of possible mechanisms involved in cavity formation. The analysis amplifies the cavitation creep model of Luecke and Wiederhorn and assumes that creep occurs via a combination of grain boundary sliding, viscous flow and solution-precipitation of the crystalline secondary phase, resulting in a redistribution of this phase among the multigrain junctions of the solid. The increase in creep resistance in the latest generation of silicon nitride materials was found to be related to the suppression of cavitation and a shift toward non-cavitation creep mechanisms. Differences between volume conservative mechanisms in tension and compression depend on the existence of different driving forces for creep: local tensile/compressive stresses and/or dilatational stresses. Increasing the viscosity of residual glassy films at the grain boundaries is believed to be an effective way to suppress cavitation and increase creep resistance. The addition of Lu^{+3} and N^{-3} to the bulk oxynitride glasses, similar to those at the grain boundary films, increases their viscosity. Thus, the suppression of cavitation and the higher creep resistance of the Lu-containing silicon nitride can be explained by the combined effect of Lu^{+3} and N^{-3} in the residual glass.

Key words: Silicon nitride, Tensile creep, Dilatational stresses, Cavitation, Solution-precipitation, Crystalline secondary phases, Residual glass.

Introduction

The use of advanced silicon nitride for ceramic rotors in small power gas turbines (300 kW) enabled an increase of the turbine inlet temperature to 1420 °C and concurrently, an increase in thermal efficiency to 42.1% [1], which is twice that of comparable metallic turbines. However, this turbine operated at 1400 °C for only two hundred hours [2], which was insufficient to establish its long term reliability. Additional problems arose as a consequence of the high sensitivity of ceramic blades to foreign object damage and to surface recession due to corrosion by water vapor in exhaust gases [3, 4, 5]. The problems with the corrosion and foreign object impact led to a significant reduction in research and development activities in the late 1990 s. Additional problems include failure due to creep and creep rupture, and the lack of methods for lifetime prediction [2-5]. Nevertheless, progress in the production of high temperature structural ceramics has been impressive because of the significant increase in creep resistance of

the newest grades of silicon nitride [6, 7, 8, 9, 10, 11, 12, 13].

Fig. 1 compares creep resistance of different grades of silicon nitride in the temperature range 1200 °C to 1600 °C under a stress of 150 MPa [13]. The horizontal line at the bottom of the figure indicates 1% strain in

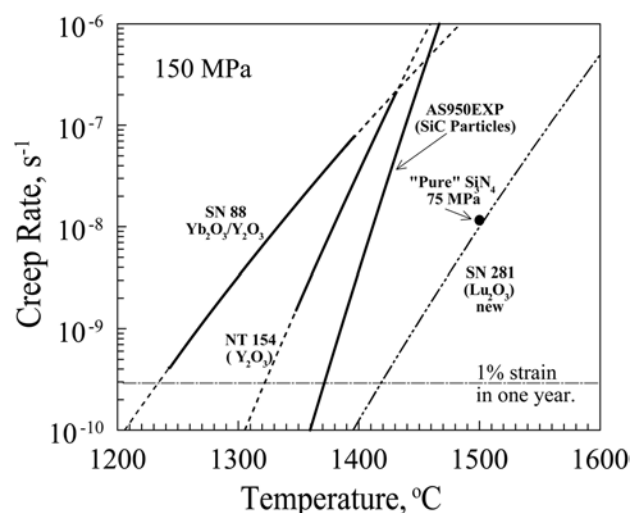


Fig. 1. Comparison of the creep performance in different grades of silicon nitride ceramics at 150 MPa [13].

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the materials under constant load in a period of one-year. This degree of strain can be taken as an indication of specimen failure due to an excessive amount of deformation. The intersection of the creep curves with the 1% line gives the allowable temperature for 1% strain in one-year. The difference between the different grades of silicon nitride is significant at the 1% strain line. The highest temperature allowable for a sustained stress of 150 MPa is approximately 1400 °C for the Lu_2O_3 -doped material, SN281, which is approximately 50 °C better than the AS950EXP the next best creep resistant silicon nitride [11-13]. The AS950EXP has small silicon carbide grains along the grain boundaries to help increase creep resistance.

Understanding physical processes that cause such a remarkable improvement in creep behavior is highly desirable for the development of high temperature structural materials. However, explaining the creep behavior of silicon nitrides and other vitreous bonded ceramics is often not possible using conventional models of creep adopted from metals. Fig. 2 illustrates these problems on a variety of material grades [7]. The tensile and compressive data do not overlay one another, except at the lowest applied stresses, indicating that the sign of the stress makes a real difference in the creep behavior. Obviously, creep in tension is principally different from that in compression. This fact is known as creep asymmetry. At the same time, stress dependence of the minimum creep rates in tension does not follow standard power law behavior, whereas power law behavior is usually observed in compression. The interpretation of such diverse behavior leads to significant confusion despite our understanding of the important role played by cavitation in the creep process.

Several extensive review papers over the last two decades [14, 15, 16, 17] did not solve these problems. The extensive review of creep in silicon nitride ceramics by Meléndez-Martínez and Domínguez-Rodríguez [7] concluded that it is impossible to determine with accuracy the deformation mechanism under fixed experimental conditions, because

none of the models fully account for all experimental observations. Apparently, creep of silicon nitride has to be explained in terms of several mechanisms occurring simultaneously. They suggested that the main mechanism occurring during compressive creep is grain boundary sliding accommodated by solution-precipitation, whereas tensile creep is greatly influenced by cavitation.

The latest review by Fox and Hellmann [17] summarizes recent works on tensile, compressive and even indentation creep. They discuss possible operating mechanisms, equations, activation energies and the effects of microstructure [17]. Based on the analysis of the literature data on density change measurements and other studies [9, 11-13, 18, 19, 20, 21, 22] they concluded that creep of silicon nitride and SiAlONs in tension is typically controlled by cavitation, while compressive creep is controlled by grain boundary sliding. The dilatation creep model of Luecke and Wiederhorn [9] plays an important role in rationalizing the creep behavior of silicon nitride, as it is able to explain the gradual increase in stress dependence of the creep rate and the significant creep asymmetry typical for these materials.

The newest grades of Lu_2O_3 doped silicon nitride, SN281, SN282, [11, 13] do not fit the cavitation model of creep developed to explain creep in the older grades of material, even though the microstructure is similar. Moreover, creep asymmetry is also almost absent. Apparently, the main reason for such behavior and unusually high creep resistance in this material is the suppression of cavitation, which is accomplished by careful engineering of the properties of the residual intergranular films.

The aim of the current work is to review our present understanding of creep mechanisms in silicon nitride ceramics. We focus on the role of cavities and their potential of controlling the creep behavior of this class of materials.

Material characterization

The work is based on the comparison of the behavior of two well-known commercial grades of silicon nitride displaying different kinds of creep behavior. The first grade, SN88, was studied extensively in many laboratories over the last two decades [9, 11-13, 19-22, 23, 24, 25]. SN88 is a gas-pressure-sintered material produced by NGK Insulators, Ltd., Nagoya, Japan, with a bimodal microstructure and secondary phases containing Yb^{3+} and Y^{3+} cations originating from the sintering additives. The major crystalline phases in the as-received materials include $\beta\text{-Si}_3\text{N}_4$, $\text{Yb}_4\text{Si}_2\text{N}_2\text{O}_7$ and/or Y-based isotype, $\text{Y}_4\text{Si}_2\text{N}_2\text{O}_7$, Y-apatite, $[\text{Y}_5(\text{SiO}_4)_3\text{N}]_x$ and SiC nanoparticles [23-25].

The second grade, SN 281, is a gas-pressure-sintered silicon nitride subjected to additional hot isostatic pressing from Kyocera Corp., Kyoto, Japan [10]. It exhibits a similar though less pronounced bimodal microstructure with the crystalline secondary phases of $\text{Lu}_2\text{Si}_2\text{O}_7$ and $\text{Lu}_4\text{Si}_2\text{N}_2\text{O}_7$ [11, 13] located primarily at multigrain junctions.

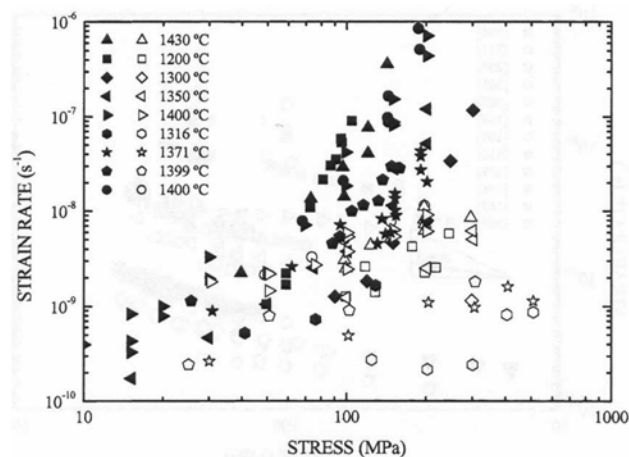


Fig. 2. The comparison of the creep behavior of different grades of silicon nitride in tension (full symbols) and compression (open symbols) [7].

Creep behavior

The difference in creep resistance between the SN 281 and the earlier grades of silicon nitride was attributed to the difference in the cavitation behavior [11-13, 26]. SN281 does not cavitate, whereas the earlier grades do. The same approach is adopted in the current work to facilitate an understanding of various mechanisms that contribute to creep-strain and to the final balance among these mechanisms.

Cavitation creep in SN88

The tensile creep behavior of SN88 at elevated temperatures is illustrated in Figs. 3, 4 and 5. Tensile creep curves obtained in the range of 150 MPa to 180 MPa at 1400 °C are compared with a compressive creep curve at a stress of 160 MPa [19], Fig 3. At the same stress the creep occurs much more rapidly in tension than in compression, illustrating creep asymmetry. Tensile creep curves exhibit all the creep stages-primary, secondary and a slight acceleration of deformation at the later stages of the lifetime (tertiary creep). The maximum failure strain in tension for all of the stresses was almost the same, 3.5%. On the other side, the compressive creep curve may require considerably longer periods to reach steady state.

Fig. 4 summarizes tensile strain rates as a function of applied stress, for stresses ranging from about 10 MPa

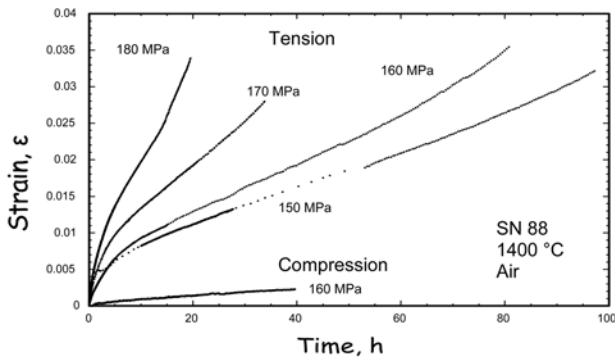


Fig. 3. Tensile and compressive creep curves in SN 88 at 1400 °C under different stresses [19].

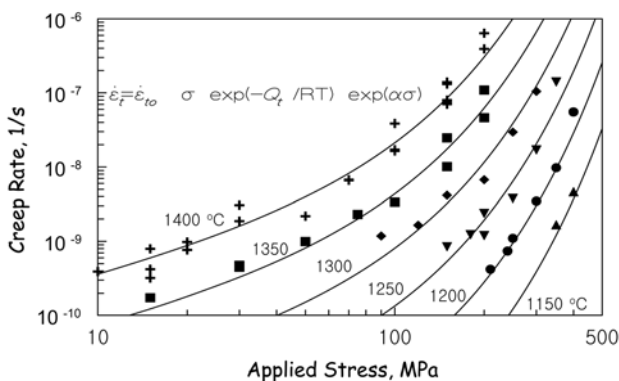


Fig. 4. Strain rates as a function of stress in a wide range of stresses and temperatures in SN 88. The data fits correspond to the exponential equation (2) [22].

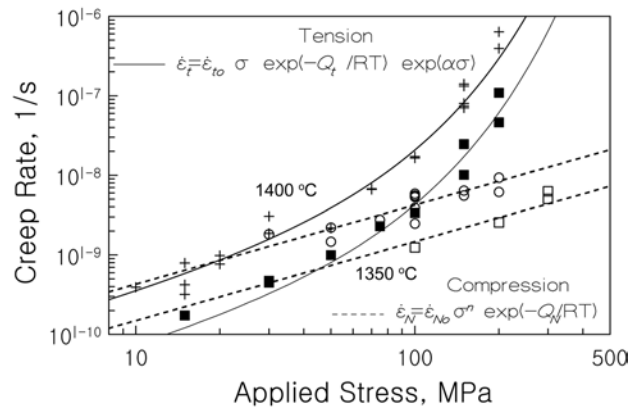


Fig. 5. The amount of creep asymmetry in SN 88 silicon nitride at 1350 °C and 1400 °C and stress dependence as a function of stress state. Tensile creep rates follow an exponential dependence on stress while compression creep follows the power law [22].

to 400 MPa [22]. Over this stress range, stress exponents ranged from approximately 1 at 1400 °C and 10 MPa to approximately 12 at 1150 °C and 400 MPa. These data clearly do not fit a conventional power law, but do fit an exponential function shown by the solid curves in Fig. 4.

A special investigation of creep behavior under very low tensile stresses, Fig. 5, revealed that creep cavities form even at these conditions and the observed behavior follows the exponential behavior over the whole stress range. On the other side, no cavitation was found at low stresses in compression and the behavior follows conventional power-law dependence on stress, with n equal to about 1 [22]. This explains the variations of the stress exponents obtained by different authors when testing their materials in different stress ranges. The comparison with the behavior of the earlier grades of silicon nitride, e.g. NT154 [8], suggests that these conclusions are also valid for other materials from the same family.

The apparent activation energy for tensile deformation of SN88 ranged from 680 kJ/mol to 830 kJ/mol, with the mean value of about 780 kJ/mol [27]. This agrees well with 715 ± 23 kJ/mol obtained for SN 88 in Fig. 5 [22]. In the case of creep in compression, the conventional power law fit resulted in the stress exponent $n = 0.997 \pm 0.128$ and an apparent activation energy $Q_{n0} = 489 \pm 62$ kJ/mol [22].

Transmission electron microscopy observations on samples made from specimens before and after tensile creep testing revealed the presence of extensive cavitation in tension. Cavities exist in the boundary phase, forming numerous and relatively large multi-grain and two-grain junction cavities (Fig. 6(a), (b)); they also penetrate into the silicon nitride grains [9, 23, 24, 27]. Multi-grain junction cavities are very common while two-grain junction cavities are relatively rare. The microcracks and cracks are formed by means of the linkage of multigrain and two-grain cavities at a later stage of the creep process. The defects penetrating into the silicon nitride grains, such as lenticular cavities or intragranular cavities were found only after long-term creep tests [23, 24, 27].

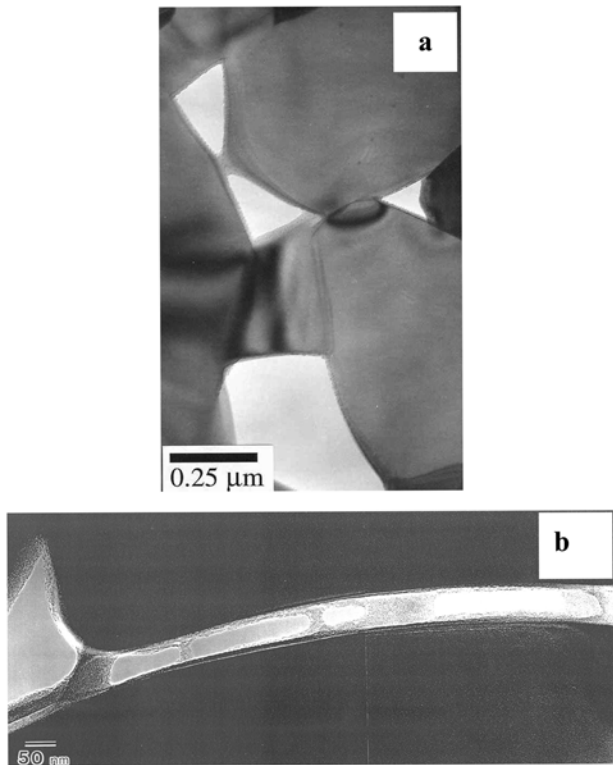


Fig. 6. a-multigrain junction cavities of different shapes in SN 88 after creep for 1693 h at 1300 °C under a stress of 155 MPa; b-two-grain junction cavities observed in SN 88 after creep at 1250 °C under a stress of 180 MPa after 868 h [23-24].

Cavitation can be quantified by using precision density measurements to calculate the volume fraction of cavities [8-9]. The correlation between the volume fraction of cavities and axial strain after tensile and compressive creep is shown in Fig. 7. The creep asymmetry observed in creep rates is almost duplicated by the volume fraction cavity measurements. Considerably fewer cavities form in compression than in tension at the same axial strain. Both dependencies follow linear fits, but the slope (and reliability due to the limited number of data) of the fit in compression is much smaller than in tension. The fit in tension intersects the strain axis at a very small strain which suggests that the onset of cavitation in tension is within the primary creep region. The slope of the fit in SN 88 was in the range from 0.75 to 0.85 [9, 19, 21, 27]. This indicates that 75% to 85% of the axial tensile strain results from the volume of cavities. The remaining 15% to 25% of the total tensile strain is due to processes other than cavitation, i.e., volume conservative processes. The slopes for NT154 silicon nitride were found to be 0.93 ± 0.04 [8], indicating an even greater contribution of cavitation to the creep rate.

High contributions of cavitation to tensile strain have also been demonstrated by the measurements of ultrasonic velocities [20-21, 27, 28], determination of elastic moduli by instrumented indentation [20] and anomalous ultra-small angle X-ray scattering (A-USAXS) [8, 13, 29]. Fig. 8

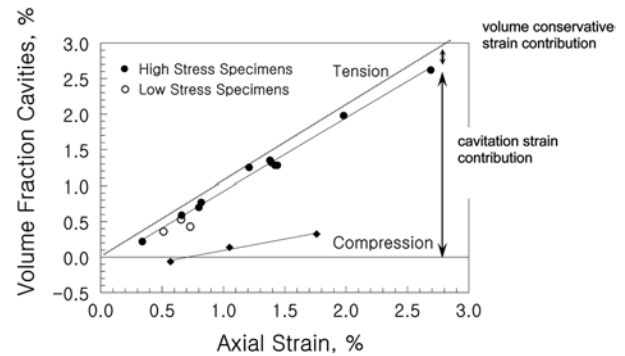


Fig. 7. The contribution of cavities to the axial tensile and compressive strains determined by precise density measurements [22].

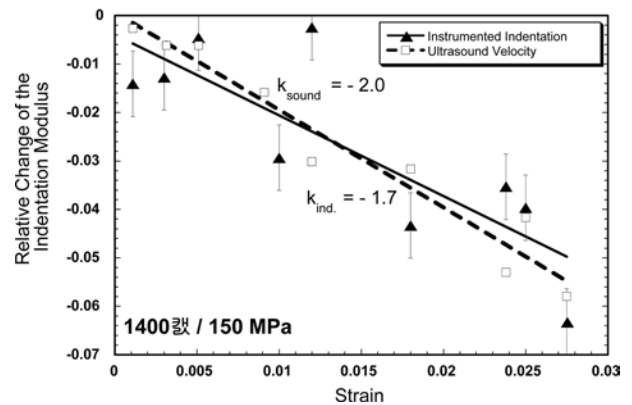


Fig. 8. The relative change in the elastic modulus of the SN 88 silicon nitride due to creep cavitation by ultrasonic velocity measurements and instrumented indentation [20-21].

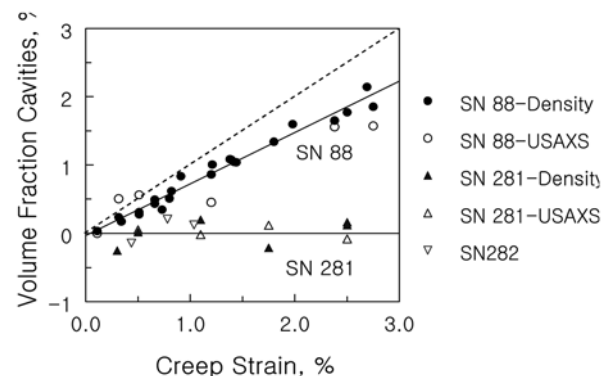


Fig. 9. Volume fraction of cavities as a function of tensile strain in SN 88 (full circle symbols) and SN 281 (full triangles); open symbols correspond to the volume fraction of cavities determined by USAXS [8, 13]. Note that the modified version of SN281, which is called SN282, exhibits identical behavior [S.M. Wiederhorn, R.F. Krause, Jr. W.E. Luecke, unpublished work].

compares the changes of the elastic modulus due to creep cavitation obtained by the ultrasonic and indentation methods. They fully agree with the density change measurements in Fig. 7 as well as with the data from the ultra small-angle scattering (USAXS) in Fig. 9. USAXS is useful not only to determine the total volume of cavities, but to determine their size distribution.

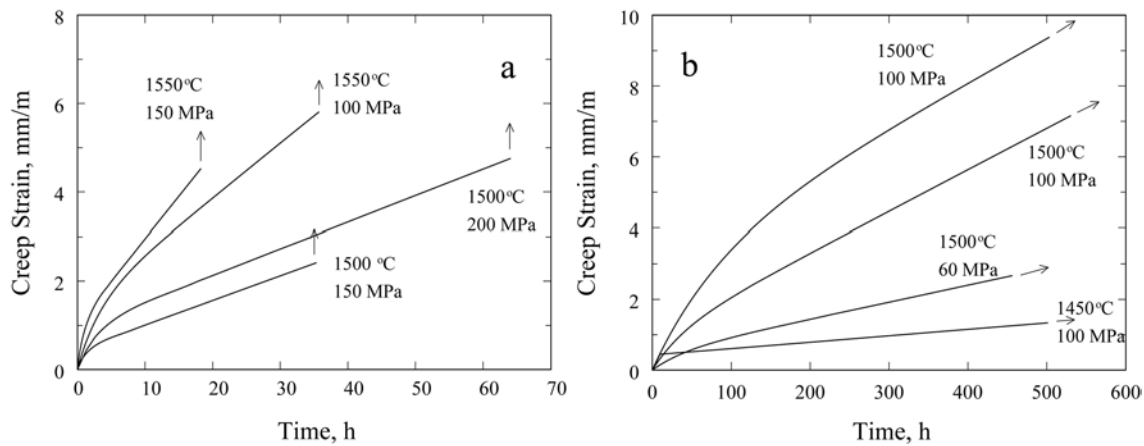


Fig. 10. Creep curves of SN 281 in the temperature range 1450 °C–1550 °C and various stresses: a—at relatively high stresses and short lifetime and b—at lower stresses (the tests were terminated after 500 h) [26].

Non-cavitation creep in SN281

SN281 exhibits a distinctly different tensile creep behavior, Fig. 10. Primary creep is often extended when compared to creep in SN88. At 1400 °C and a stress of 200 MPa, the primary creep stage exceeded 4,000 h and the lifetime exceeded 10,000 h [11, 13]. The testing temperature reached up to 1550 °C, which is considerably higher than those used for any other grade of silicon nitride [7]. Depending on the stress, creep rates at 1400 °C are more than four orders of magnitude lower than those for SN 88.

The dependence of creep rate on stress and temperature in SN 281 is also different from other materials. A log-log plot of the creep rate as a function of applied stress indicates no curvature in the creep plots over the range studied (Fig. 11) [30]. The slope of the curves, $n = 1.87 \pm 0.48$ (95 % confidence limits), is much lower than that obtained for the SN 88 over most of its stress range and certainly at the higher stresses. The activation energy for the SN 281 was approximately 1079 ± 142 kJ/mol. Although high, this value is not atypical of activation energies obtained for the creep of silicon nitrides.

Unlike earlier grades of silicon nitride, the creep rate of this grade of material is almost the same in tension and compression, Fig. 11 [30]. The absence of creep asymmetry suggests that the mechanism of creep for the SN 281 differs from that of other grades of silicon nitride. Except for its low strain to failure, the creep behavior of SN 281 is more like that of the high-temperature metals than it is of silicon nitride. The principal idea to explain such behavior follows from Fig. 9. The dependence of the volume fraction of cavities on strain in SN281 is zero for tensile creep tests. Note that the same behavior was observed also in the gas pressure sintered version of SN281, which is called SN282 (see Fig. 9). This is in sharp contrast to SN88, where cavitation comprises the main creep strain contribution [9, 19, 21, 27–29]. Thus, the suppression of cavitation in SN281 and SN282 is probably the reason for its increased creep resistance.

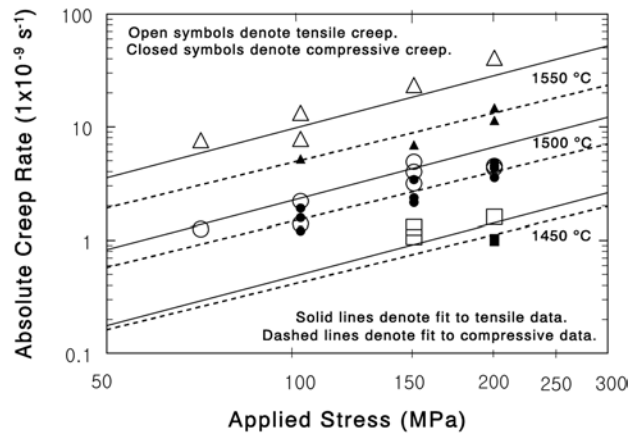


Fig. 11. Stress-strain rate dependence in SN 281 [26] indicates the power-law behavior of this material over the entire range of applied stresses regardless of the stress state. Tensile and compressive creep rates overlap which indicates the absence of creep asymmetry.

Creep mechanisms in silicon nitride

The results of the previous section suggest principally different creep behavior in various silicon nitrides. Earlier materials represented by SN88 exhibit creep asymmetry and an exponential dependence on stress with a dominant role of cavitation, whereas SN281 is characterized by volume conserving creep behavior and conventional power-law behavior without creep asymmetry. These differences can be rationalized in terms of principally different mechanisms controlling creep deformation.

Cavitation creep model

Classical creep theories often applied to silicon nitride; assume that the creep rate, $\dot{\epsilon}$, is a power law function of the applied stress [14]

$$\dot{\epsilon} = \dot{\epsilon}_0 \cdot \left(\frac{g}{g_0}\right)^m \cdot \left(\frac{\sigma}{\sigma_0}\right)^n \cdot \exp\left(-\frac{Q}{RT}\right), \quad (1)$$

where g is the grain size, T is temperature, m , n and

Q are constants of the fit of equation 1 to the data. The constants m , n and Q are the grain size exponent, the stress exponent and the activation energy, respectively. The parameters g_0 and σ_0 are normalization constants. Although Eq. (1) is widely acceptable in metals, its use is inappropriate to describe creep of SN88 in tension. The exponential law based on continuous cavity formation is preferable to describe tensile creep Fig. 4 and Fig. 5. Luecke and Wiederhorn adapted ideas of the dilatational stresses from soil mechanics theory [9], which arise because a network of rigid, elongated and densely packed silicon nitride grains can only expand as a whole after any grain boundary sliding [31]. Dilatation generates local hydrostatic tensile stresses within the secondary phase at grain boundaries and multigrain junctions. Cavities nucleate in the multi-grain junctions where dilatational stresses are highest, provided that the stress exceeds the threshold stress for cavity nucleation [9].

Once a cavity forms within a multi-grain junction, the stress in the junction relaxes to zero resulting in a relatively large stress gradient from the cavity to other multi grain junctions that have no cavities. The stress gradient is the driving force for the redistribution of the secondary phase towards the cavity-free junctions, primarily along the tensile axis because the stress gradient is greatest in that direction. The formation of cavities and redistribution of the secondary phase leads to an expansion of the multigrain junctions, which relaxes the hard contacts between the grains that surround the junctions.

Possible mechanisms involved in cavitation include grain boundary sliding, viscous flow of the glassy phase at the grain boundaries, solution-precipitation of the crystalline secondary phases between pockets, and solution-precipitation of silicon nitride, either between grains or from one grain surface to another. A schematic description of the interactions between these mechanisms during creep is shown in Fig. 12 [27]. The feedback indicated between cavitation and viscous flow relaxes the hard contacts and enables a continuous increase in the number of cavities, which results in a linear dependence of cavitation strain on tensile strain (Fig. 7). Besides continuous nucleation and growth of cavities at multi-grain junctions, the diagram also explains the development of intragranular cavities.

The minimum strain rate of such cavitation creep according to the model of Luecke and Wiederhorn (L-W) is [9]:

$$\dot{\epsilon} = \dot{\epsilon}_0 \cdot (\sigma/\sigma_0) \cdot \exp(\beta_c \cdot \sigma) \cdot \exp(-Q_c/RT), \quad (2)$$

where $\dot{\epsilon}_0$, β_c , and Q_c are constants of the fit of the equation to the creep data. The parameter, σ_0 , is a normalization-constant for the stress. Using the method of least squares, the constants for Eq. (2) were obtained from the data in Fig. 4: $\ln(\dot{\epsilon}_0) = 27.2 \pm 1.6$ ($\dot{\epsilon}$ is in s^{-1}); $Q_c = 715.3 \pm 22.9$ kJ/mol and $\beta_c = 0.0197 \pm 0.001$ [22]. The model also predicts the convergence towards a conventional power law as the stress decreases because the exponent term approaches 1 and the creep rate is

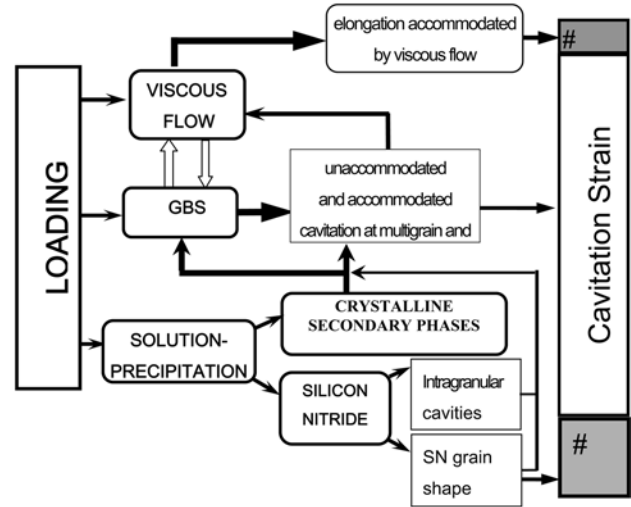


Fig. 12. Schematic model of the cavitation processes during tensile creep deformation in silicon nitride [27].

determined by the linear stress term. However, cavities form even at very low stresses hence the mechanisms in tension and compression are not the same.

Eq. (2) describes only the cavitation contribution in the total axial strain rate. The contribution of the volume conservative mechanisms, though small, is omitted. The simplest solution would be to assume that the compressive and the volume conservative mechanisms during tensile creep are identical [19]. Another approach used by Wereszczak *et al.* unites Eq. (1) and Eq. (2) based on the assumption that the activation energies in tension and compression are equal [18]:

$$\dot{\epsilon} = [A\sigma^n + B\sigma \cdot \exp(\beta_c \cdot \sigma)] \exp(-Q_c/RT), \quad (3)$$

where A , B , and C are the empirical constants. Although the activation energies are not the same, the differences between the data fits based on Eq. (2) and Eq. (3) were within the standard error and it was not possible to determine which model is more applicable [22], the idea of the coexistence of both mechanisms is reasonable.

The suppression of cavitation in compression leads to the question of the differences between the compressive creep mechanisms and the volume-conservative mechanisms involved in tensile strain. This is discussed in the section devoted to the analysis of non-cavitation creep mechanism in SN281.

Non-cavitation creep

The absence of cavitation in SN281 during tensile creep deformation suggests the presence of only volume-conservative mechanisms. Negligible creep asymmetry, stress exponents and activation energies that are nearly the same in tension and compression, Fig. 11, imply that the mechanisms of deformation are the same or nearly the same in tension or compression. The driving force usually considered in the conventional models results

from the gradient of chemical potential within one grain; creep is controlled by the local tensile or compressive stresses surrounding a single grain, and hence is referred to as a micro-mechanical approach to creep.

In cavitation creep, the gradient of chemical potential is controlled by the differences of the dilatation stresses amongst the grains surrounding the cavity. Because the area surrounding the cavity contains a significant number of grains the creep mechanisms represent a meso-mechanical approach to creep [32]. Both types of driving forces may exist at the same time after applying an external load. Thus, the difference between the volume-conservative mechanisms in tension and compression in S281 is related not only to the suppression of cavitation, but it is also a question about the prevailing driving forces: local stresses within the grain or dilatation stresses.

Thus, two principal possibilities can be considered and a combination of both driving forces can be the third case. If the local stresses are dominant then the creep process is controlled by the conventional viscous flow, grain boundary sliding and solution precipitation mechanisms. In the opposite case, when cavitation is prohibited, the same mechanisms are active but the resulting strain rate is different because of a different driving force. The combined approach would mean a shift of balance towards such mechanisms as viscous flow, grain boundary sliding and solution-precipitation at the expense of cavitation. However, regardless of the approach, the same mechanisms are involved. Obviously, the differences arise not from these mechanisms, but from the driving forces and geometrical considerations.

In the conventional micro-mechanical case, viscous flow controls deformation in both tension and compression. Deformation in both cases occurs in the same manner: silicon nitride grains are rigid and the boundary phase is squeezed out or flows among the grains depending on the sign of the local stress. The thickness of the amorphous phase between grains either decreases or increases depending on the sign of the local stress [15, 16]. As the grains approach one another the difficulty in forcing the amorphous phase from between the grains increases to the point that deformation eventually stops. For grain boundaries that are approximately 1 nm thick [33] and with the grain size of 1 μm , the total strain allowable by such a mechanism is of the order of 0.1%. This strain is not sufficient to account for around 1% compressive strains observed in many grades of silicon nitride and > 0.5% contribution of non-cavitation mechanisms in the tensile strain of SN88 and SN281.

Grain boundary sliding is an integral part of the creep process and cannot be separated from viscous flow. Apparently, the only viable mechanism to rationalize the deformation process is solution-precipitation of the silicon nitride grains. Solution-precipitation of silicon nitride is typically considered to be the main mechanism in compressive creep in SN88 [22] and the same arguments can be applied to SN281.

In the case of dominant dilatation stresses (cavitation prohibited), grain boundary sliding accompanied by viscous flow of the secondary phase has to occur to generate the stresses. The driving force is determined by the distribution of dilatation stresses among the multi-grain junctions, not by the gradients among cavitated and uncavitated junctions as in SN88. Obviously, current gradients and the resulting driving force are smaller than in cavitation. The gradients of dilatation stresses do not apply to silicon nitride grains but to the crystalline secondary phases. Thus, the model based on the dilatation stress controlled driving of the redistribution of secondary phases among the junctions with different dilatation stresses via solution-precipitation is similar to that during cavitation with the exception of a smaller driving force. It would cause the expansion of some junctions at the expense of others, release of the hard contacts between silicon nitride grains and redistribution of the dilatation stresses similarly as during cavitation.

The combined approach summarizes both possibilities. Solution-precipitation of silicon nitride would be concentrated at the hard contacts and would be more important in compression, whereas redistribution of the secondary phases would be more important in tensile creep. The estimation of the ratio between these two mechanisms from the existing experimental data requires a new analytical solution which is not available. Thus, the possible non-cavitation creep mechanisms in SN281 are understood at the qualitative level. The remaining question to be answered is the way to suppress cavitation.

Suppression of cavitation

As mentioned earlier, dilatation stresses necessary for cavitation arise after initial grain boundary sliding. The simplest way to suppress cavitation is therefore to increase the material resistance to grain boundary sliding. Then, the dilatation occurs slowly enough that the stresses that normally build up at multi-grain junctions are relieved either by solution-precipitation or by transport of the secondary phase toward the highly strained multigrain junctions. The most likely cause for the suppression of both grain boundary sliding and deformation of the secondary phase is an increase in the viscosity of the amorphous phase at the grain boundaries, which can be accomplished by changing the composition of the sintering additives used to densify silicon nitride. The history of the development of more creep-resistant silicon nitrides (see Fig. 1) in this case corresponds to an increase of the viscosity of the residual glassy films in different generations of silicon nitride. The suppression of cavitation and significant improvement of creep resistance of SN281 can be explained, if the presence of Lu^{+3} in the residual glass increases its viscosity dramatically over that obtained when Yb^{+3} and Y^{+3} cations are used as sintering aids.

The residual glass at grain boundaries of silicon nitride is an oxynitride glass containing impurities and elements from sintering additives [33]. Its viscosity is controlled

by the type and concentration of additives and impurities. The main difference between SN 281 and earlier grades of silicon nitride is the presence of Lu^{+3} instead of Yb^{+3} or Y^{+3} at the grain boundaries [11]. Lutetium is special among all lanthanides because it has the smallest ionic radius, which affects the way it is incorporated in the glass structure [34].

The investigation of the effects of different lanthanide cations, including Lu^{+3} , on the structure of the intergranular amorphous films in silicon nitride requires special high resolution electron microscopy studies combined with modeling. It was shown that large La ions bond preferentially and with relatively small periodicity to sites at the interface between the intergranular film and prismatic planes of silicon nitride grains [35, 36, 37], whereas the periodicity of these ions increases, as the size of the ionic radius decreases [38]. This means that the Lu concentration at the interfaces is lower compared to larger lanthanide cations.

Lutetium and the viscosity of a bulk glass

As direct measurement of the viscosity of a grain boundary is experimentally very difficult, bulk oxynitride glasses were used instead to quantify the role of rare earth oxides on the viscosity of glass [39, 40, 41, 42, 43]. A direct comparison of the viscosity changes in the bulk RE-Si-Mg-O-N glasses with various N contents revealed that the replacement of Yb^{+3} with Lu^{+3} increases the viscosity by a factor of less than twenty [41, 42]. However, substitution of Lu^{+3} for Yb^{+3} also changed the amount of nitrogen in the glass, and nitrogen is much more effective than the Lu^{+3} in enhancing the viscosity of the glass. Nitrogen can easily make up for approximately 2.5 orders of magnitude in viscosity. Thus, the suppression of cavitation may result from both the presence of the Lu^{+3} and an increase in the concentration of N^{-3} in the glass. Lutetium, with its smaller ionic radius, “tightens” the glass network, while the incorporation of 3-coordinated N^{-3} increases the network “cross-linking”. Both effects increase the glass viscosity [39–44]. This, though indirect, explains the effect of Lu^{+3} additives on the suppression of cavitation and increase of creep resistance in SN281 silicon nitride.

Conclusions

Tensile creep in silicon nitride ceramics are best described by meso-mechanical models based on the dilatation of granular solids. These models are based on the assumption that grains of silicon nitride are rigid during deformation so that displacements between adjacent grains can only occur along the grain boundaries. As a consequence, the network of grains has to move apart giving rise to dilatational stresses, which are responsible for cavitation within the material. Cavitation occurs when the dilatational stress at a multigrain junction exceeds a critical stress for cavity nucleation. Subsequent cavity growth occurs via redistribution of the secondary phases from the cavity

towards the uncavitated material. As the secondary phase flows away from the cavitated junction, the stress required for cavity nucleation relaxes, thus releasing the stressed contacts between silicon nitride grains. Rearrangement of dilatation stresses then results in a new round of cavity formation. The contribution of cavitation to tensile strain in the earlier grades of vitreous bonded silicon nitride exceeds 75% to 95%. Subsequently, cavitation is the main tensile creep mechanism in these materials. Cavitation creep follows an exponential rather than power-law dependence on stress. This dependence, together with the understanding that cavitation only contributes to axial tensile strain, explains creep asymmetry and the unusually high stress exponents measured in tension at high stresses.

However, the newer grades of silicon nitride such as SN281, exhibit non-cavitation behavior. If dilatation stresses are not sufficient to nucleate cavities, creep deformation occurs regardless of the stress state by the solution-precipitation of the individual silicon nitride contacts and secondary phase grains. The driving forces for creep are then determined by the gradients of local stresses around individual grains or gradients of the dilatation stresses among different multigrain junctions. At a given temperature and stress, creep by solution-precipitation occurs much more slowly than creep by cavitation. Thus, the suppression of cavity formation is an effective way to increase the creep resistance of silicon nitride. The non-cavitation creep mechanisms in tension and compression seem to be controlled by solution precipitation and the differences between them can be attributed to the balance between solution-precipitation of silicon nitride and secondary phase depending on stress state.

Increasing the viscosity of the grain boundary phase is one way to suppress cavitation, as it reduces grain boundary sliding, viscous flow and solution-precipitation. Replacement of Yb^{+3} by Lu^{+3} in the bulk oxynitride glass increases the viscosity of the grain boundary glass by about 4 orders of magnitude, partly due to a “tightening” of the glass structure by the smaller rare earth ion and in part by an enhancement of N in the glass due to the presence of Lu. These two effects account for the more than four orders of magnitude increase of creep resistance of SN 281 compared to earlier generations of silicon nitride.

Acknowledgments

The contributions of W.E. Luecke of the National Institute of Standards and Technology to the development of some of the basic ideas used in this paper are gratefully acknowledged. The role of the Science and Technology Agency, the Fulbright Foundation and the A. von Humboldt Foundation are appreciated. The work was also supported by NANOSMART, Centre of Excellence, SAS, and by the Slovak Grant Agency for Science, grant No. 2/0088/08 and APVV grants No. APVV-0034-07 and APVV-COST-0042-06.

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