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Tensile creep of whisker-reinforced silicon nitride

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This paper presents a study of the creep and creep rupture behaviour of hot-pressed silicon nitride reinforced with 30 vol% SiC whiskers. The material was tested in both tension and compression at temperatures ranging from 1100 to 1250 °C for periods as long as 1000 h. A comparison was made between the creep behaviour of whisker-reinforced and whisker-free silicon nitride. Principal findings were: (i) transient creep due to devitrification of the intergranular phase dominates high-temperature creep behaviour; (ii) at high temperatures and stresses, cavitation at the whisker–silicon nitride interface enhances the creep rate and reduces the lifetime of the silicon nitride composite; (iii) resistance to creep deformation is greater in compression than in tension; (iv) the time to rupture is a power function of the creep rate, so that the temperature and stress dependence of the failure time is determined solely by the temperature and stress dependence of the creep rate; (v) as a consequence of differences in grain morphology and glass composition between whisker-free and whisker-reinforced material, little effect of whisker additions on the creep rate was observed.

1. Introduction

Applications for high-temperature ceramics lie in the range 1000 to 1500 °C. The low end of this range includes turbochargers in some current models of automobiles; the high end includes gas turbines for cruise missiles and automobile engines. Ceramics for high-temperature structural applications are mainly two-phase materials, in which hard refractory grains are joined by a less refractory matrix, often a vitreous phase. Silicon nitride and Sialon are two such ceramics made for high temperature application, primarily because of their high strength and resistance to thermal shock. Because single-phase silicon nitride does not sinter easily, densification aids such as yttria or a mixture of yttria and alumina are added to the precursor powders. These react with silica normally present in the silicon nitride powders to form a glassy phase that promotes liquid-phase sintering. The retained intergranular glassy phase inherent in this process governs most high-temperature behaviour.

Currently, the best high-temperature silicon nitride ceramics for heat engines have a thermal limit of $\approx$ 1300 °C. Above this temperature the ceramics soften due to the presence of the vitreous phase at grain interfaces. In an effort to increase this thermal limit, a number of approaches have been developed. These increase the resistance of the intergranular phase to deformation, either by post-sintering heat treatment [1], or by chemical modification of the sintering aid [2, 3]. Both approaches have been used to tailor silicon nitride ceramics for high-temperature applications.

More recently, fibres and whiskers have been added to ceramics to enhance fracture toughness [4–6]. This approach has the potential of not only increasing resistance to fracture at lower temperatures, but of improving creep resistance at elevated temperatures. Thus, SiC whisker additions have been used to improve the high-temperature creep resistance of alumina and mullite [7–9]. By contrast, the addition of SiC whiskers to silicon nitride has yielded contradictory results. In one study, a considerable improvement in flexural creep behaviour was observed when SiC whiskers were added to silicon nitride [10, 11]. In the second set of studies, however, SiC whiskers added to silicon nitride had little effect on compressive creep resistance [7, 8, 12]. As the reason for this conflict is not well understood, further research was deemed necessary to understand the role played by whisker reinforcement in the creep of nitride ceramics. Creep and creep-rupture studies were conducted on both monolithic silicon nitride and silicon nitride reinforced with silicon carbide whiskers. Measurements of creep behaviour were made in both tension and compression, and effects of annealing on the creep rate and microstructure were studied.

2. Experimental procedure

Equipment developed for tensile creep studies on ceramics is described elsewhere [13]. The configuration of the specimens used in this study is shown in Fig. 1. The ends of the specimens contained holes that were centred and tapered, from both sides, to permit

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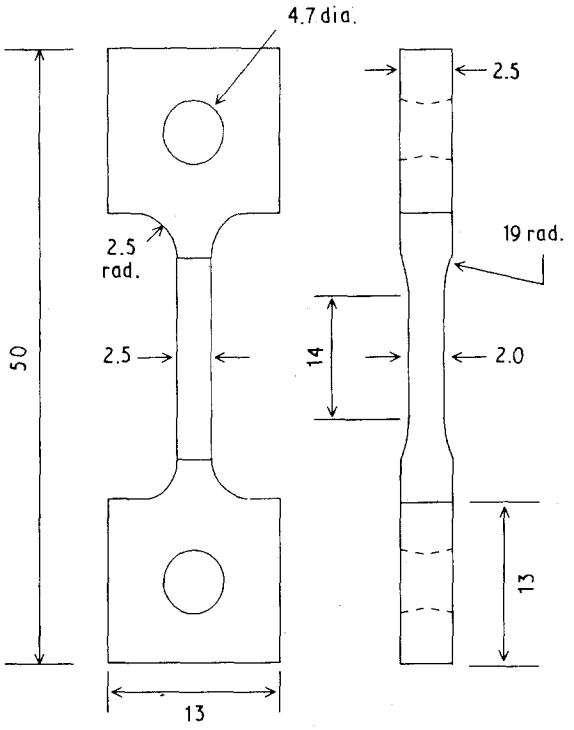


Figure 1 Schematic diagram of dog-bone specimen used in the current study (dimensions in mm). The holes in the specimen are tapered to minimize bending strains.

accurate specimen alignment. Less than 2% of the total strain was attributable to deformation of the specimens in bending. The second reduction in gauge section, i.e. the 19 mm radius, reduced the stress concentration at the gauge section to less than 3% [14]. Displacements were measured with a commercial laser extensometer (Zygo Corp, Model 1102)*. The equipment is stable for test periods in excess of 1000 h. To assure thermal stability, equipment and specimens were heated at the test temperature for approximately 20 h before testing.

Tensile creep studies were conducted on monolithic silicon nitride, AY6 (6.0 wt % Y_2O_3, 1.5 wt % Al_2O_3, balance Si_3N_4) and on a composite made by blending 30 vol % whiskers into milled AY6 powder†. Tests were conducted in the temperature range 1100 to 1250 °C. Creep measurements on the whisker-reinforced materials were made mainly in the as-received state; however, some specimens were tested after annealing for 1000 h at the creep temperature. Annealing appeared to have little effect on the short-term (i.e. high-stress) creep resistance of the whisker-reinforced material. By contrast, the effect of annealing on long-term (low-stress) creep was substantial. Creep studies on the whisker-free material were conducted at 1250 °C; half the specimens were tested after annealing for 500 h at 1250 °C.

In addition to tensile creep studies, some compressive creep measurements were made at 1200 °C. The test procedure followed in these studies is outlined elsewhere [13]. Only whisker-reinforced material was used in this compressive creep study. Specimens were taken from the same batch of material as the tensile specimens. In this study, multiple measurements were made on each sample. For some samples, the load was increased sequentially, whereas for others, the load was varied randomly. Regardless of the order of collecting the data, the data on a plot of steady-state creep rate against stress all fell on the same curve, suggesting that the order of collecting the data in compression is unimportant.

The microstructure of the tensile specimens was studied by transmission electron microscopy (TEM). Sections for TEM were taken from the gauge section of the tensile bars after high-temperature creep. These TEM sections were compared with sections from both as-received material and material from the unstressed ends of the tensile specimens. In this way, effects of creep and annealing on the microstructure could be determined. Sections were also taken from tensile specimens that were crept at various strain rates so that the effect of strain rate on microstructure could be studied.

3. Results

3.1. Microstructural analysis

Representative views of the as-received microstructures of both materials are shown in Fig. 2. In the whisker-reinforced material (Fig. 2a) SiC whiskers, whose diameters and length range from ≈ 0.2 to ≈ 1 μm and ≈ 1 to 10 μm, respectively, are randomly dispersed within a matrix of equiaxed, submicrometre sized β-Si_3N_4 grains. The constituent crystalline phases are bonded together by an amorphous intergranular phase, which is present within all multi-grain junctions and two-grain interfaces. In the as-received state, the intergranular phase can be described as an yttria–silicate glass containing minor concentrations of alumina and calcia (the presence of nitrogen could not be determined). Although it extends throughout the microstructure, a significant amount of this glassy phase appears concentrated along the SiC whisker interfaces.

Upon heat treatment, i.e. either static annealing or creep testing, the glassy intergranular phase progressively devitrifies, which results in the formation of crystalline yttrium silicate (Fig. 3a) and residual glass. Within the multi-grain junctions and wider interfacial regions, where crystallization appeared to initiate and be nearly complete, devitrification primarily resulted in the formation of monoclinic y – $Y_2Si_2O_7$ [15], which is invariably twinned about the non-unique axes (Fig. 3a). However, devitrification was never found to be complete in that a residual glassy film was always present between the various crystalline phases, including the y-yttria silicate, regardless of the length of time at temperature (Fig. 3b). Although a definitive comparison of the original and residual glass compositions could not be made, energy-dispersive spectrometry (EDS) showed no detectable concentrations of Al_2O_3 or CaO within the crystalline $Y_2Si_2O_7$, but

*The use of commercial designations does not constitute endorsement by the National Institute of Standards and Technology.
†AY6 is a designation for a grade of Si_3N_4 made by GTE.

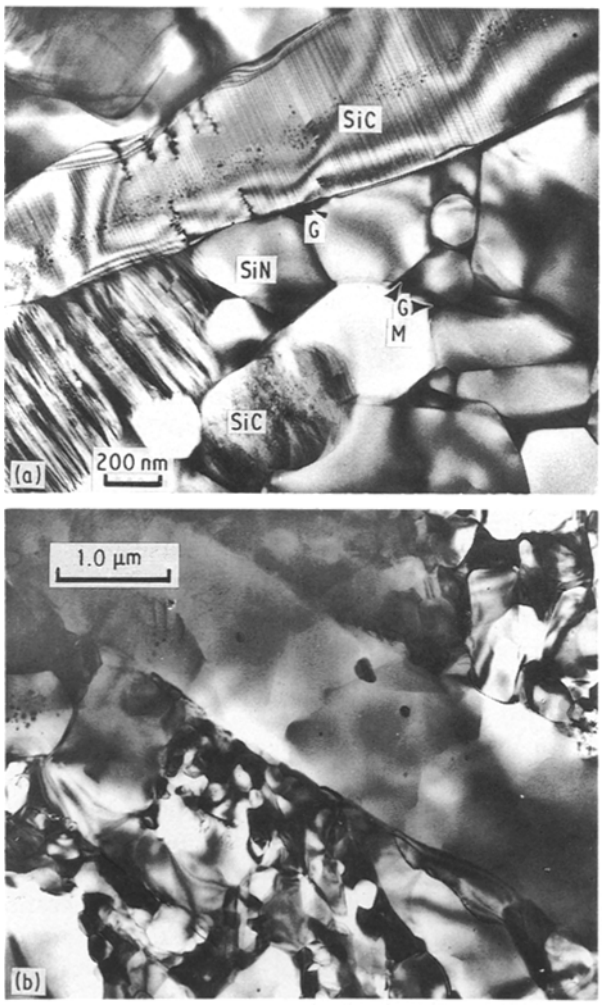


Figure 2 Comparison of (a) SiC whisker-reinforced composite with (b) SiC whisker-free composite. The whisker-free composite contains elongated whisker-like grains of Si_3N_4. The growth of these Si_3N_4 grains seems to be suppressed by the presence of SiC whiskers. Glass is found along the margins of the SiC whiskers.

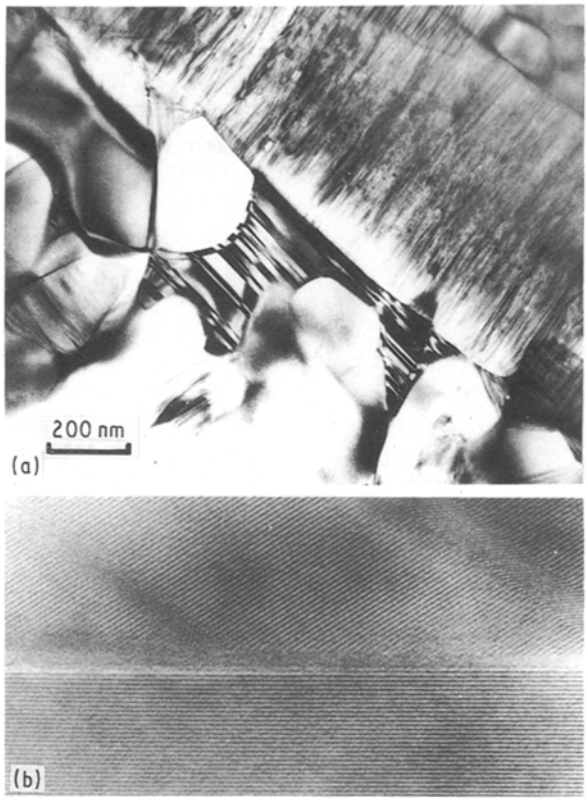


Figure 3 (a) Devitrification of the bonding phase to form crystalline yttrium silicate increases the resistance of the material to creep deformation, resulting in work-hardening creep curves, such that even after hundreds of hours of exposure, devitrification is incomplete. (b) Despite extensive devitrification of the intergranular glass during creep, the crystal phases are separated by residual glassy layers of variable thickness; residual glass ≈ 3 nm thick, separates an Si_3N_4 matrix grain (bottom) from crystalline yttria silicate (top) that forms during creep. Lattice fringe spacing ≈ 0.66 nm.

did indicate a relative increase in Al_2O_3/Y_2O_3 ratio in regions containing residual glass after densification. Accordingly, it is concluded that devitrification results in significant structural and compositional changes within the intergranular phase which can affect creep behaviour.

The microstructure of the whisker-free material contained a higher percentage of high aspect ratio, elongated grains of β-silicon nitride than the matrix phase of the composite. These elongated grains appeared to grow in the silicon nitride as a consequence of exaggerated grain growth during the processing. As these grains are rarely observed in material with SiC whisker additions, it was concluded that the growth of elongated silicon nitride grains was prevented either by differences in chemical composition of the composite resulting from the exsolution of SiO_2 and other impurities from the SiC whiskers, or by physical constraints arising from the SiC whiskers in the composite. Retardation of grain growth as a consequence of whiskers has also been reported for SiC whisker-reinforced aluminium oxide [9, 16].

As in the case of the whisker-reinforced material, examination of multi-grain junctions and two-grain interfaces revealed the presence of a completely interconnected, intergranular glassy phase. Although similar in composition to the intergranular glass present in the whisker-reinforced material, no detectable trace of CaO was found in the non-reinforced material. Considering the known effect of calcia on reducing glass viscosity in silicate glasses, this minor compositional difference is likely to have significant effects on mechanical behaviour [2]. In addition, the distribution of glass within the whisker-free material differs from that in the composite containing the SiC whiskers. In the latter, glass is concentrated along whisker boundaries. By contrast, glass appears to be located primarily in the fine-grain areas of the monolith. Areas containing clusters of the elongated and plate-like grains are relatively free of glass.

Upon heat treatment, progressive, but incomplete devitrification of the intergranular glass phase occurs in the non-reinforced material much in the manner described for the reinforced material. The primary crystalline products of devitrification are different for the two materials, presumably as a consequence of small but significant differences in initial glass composition. Whereas monoclinic y-$Y_2Si_2O_7$ (a low-temperature variant) forms in the reinforced material, orthorhombic δ-$Y_2Si_2O_7$ (the high-temperature variant) forms primarily in the non-reinforced material.

Moreover, while no other yttrium silicates were found in the reinforced material, limited formation of monoclinic x_2-Y_2SiO_5 was found to occur within the interior of non-reinforced samples. Again, a residual glassy film separating the various crystalline phases was retained even after prolonged ($\approx$ 2000 h) heat treatments. In comparison with the initial glass, the retained glass after heat treatment exhibited an enhanced alumina content.

3.2. Mechanical behaviour

At low applied stresses, an important characteristic of the deformation of the silicon nitride is the long period of transient creep that occurs when testing unannealed materials. This behaviour is illustrated in Fig. 4a for a whisker-free specimen. The entire curve in Fig. 4a indicates a process in which the creep rate decreases steadily with time, analogous to work-hardening in metals. By preannealing the test specimens, much of this work-hardening is eliminated. Similar transient creep is observed in the whisker-reinforced silicon nitride. These transient effects are a consequence of devitrification of the intergranular phase during creep. "Steady-state" creep is achieved only when devitrification nears completion and the microstructure has been stabilized.

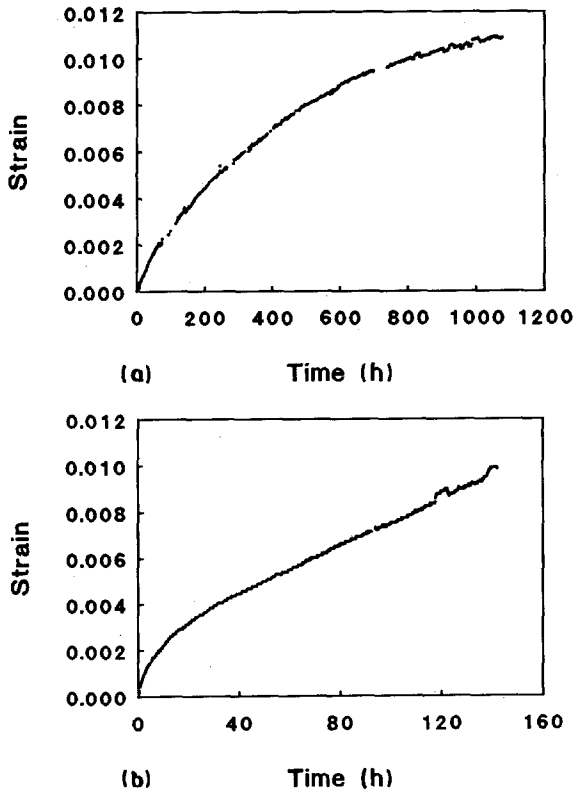


Figure 4 Sample creep curves: (a) SiC whisker-free specimen tested in the as-received state. Test conditions were: temperature 1250 °C; applied tensile stress 48 MPa. Extended deformation, > 1000 h, gives no indication of steady-state deformation. The minimum creep rate, $1.16 \times 10^{-9}\,s^{-1}$, was determined from the last $\approx$ 200 h of creep. (b) Apparent steady-state creep for whisker-reinforced material. The creep rate was $1.4 \times 10^{-8}\,s^{-1}$; the time to failure was 142.4 h. Test conditions were: temperature 1250 °C; applied tensile stress 60 MPa. The apparent steady-state creep represents a balance between work-softening and work-hardening processes that occur during creep. Cavitation and crack growth are believed to be responsible for the softening.

At high stresses, both annealed and unannealed materials give the appearance of "steady-state" creep after only a short transient creep stage (Fig. 4b). This "steady-state" creep is not a true steady-state process, but represents a balance between "hardening" and "softening" processes that occur during creep. Cavitation and crack growth in specimens that creep at rates above $10^{-8}\,s^{-1}$ increase the rate of creep and counter the work-hardening that occurs as a consequence of devitrification. Cavitation and crack growth eventually result in sample failure. In none of the specimens that failed was extended tertiary creep observed. At failure, creep strains were of the order of 1%, indicating essentially brittle behaviour.

The creep behaviour of the whisker-reinforced composite is summarized in Fig. 5, where the minimum creep rate is plotted as a function of applied stress and temperature. Only data exhibiting apparent steady-state creep were plotted. Long annealing periods were used to eliminate transient creep behaviour for data collected at low rates of strain, below $5 \times 10^{-9}\,s^{-1}$. For high strain rates, annealing did not influence the creep curves. The power-law stress exponent of the data shown in Fig. 5 ranged from approximately 4 to 6. This variation in the stress exponent as a function of temperature is believed to be a consequence of random error, and hence has no fundamental significance *vis-à-vis* the creep behaviour. The apparent activation energy for the creep process is 596 kJ mol^{-1}. Activation energies of this magnitude (546–630 kJ mol^{-1}) were reported earlier by Kossowsky *et al.* [17] for magnesia-doped hot-pressed silicon nitride. Based on TEM studies of the deformed microstructure, Kossowsky *et al.* attributed creep in their material to grain-boundary sliding accommodated by the formation of cracks at grain interfaces. In a later paper by Raj and Morgan [18] it was suggested that the rate-limiting step for the sliding process was solution precipitation at interlocking ledges on grain interfaces. Considering the similarities in the value of the activation energy (in the present study and in the study by

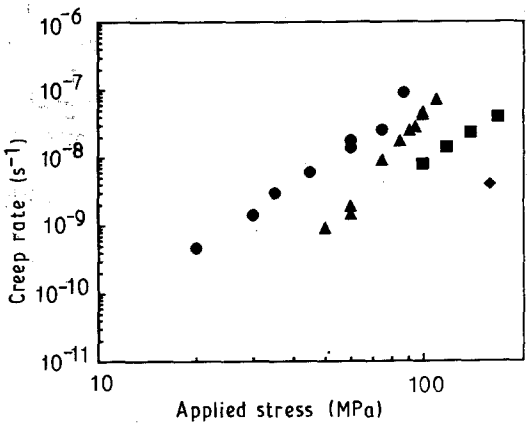


Figure 5 Dependence of creep rate on temperature and applied stress. Only data that appeared to have reached steady-state creep were included in this graph. Data taken at and above $\approx 1 \times 10^{-8}\,s^{-1}$ resulted in failure, as did the point taken at 1100 °C. (◆) 1100 °C, (■) 1150 °C, (▲) 1200 °C, (●) 1250 °C.

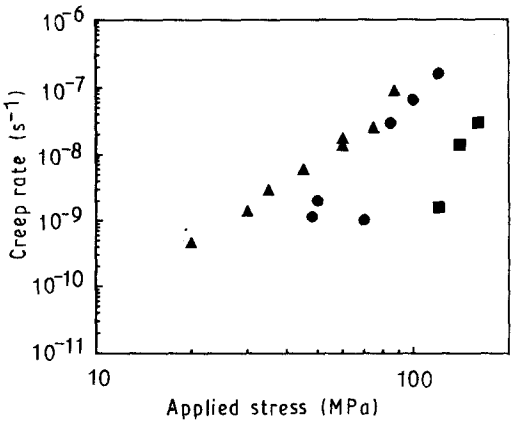


Figure 6 Comparison in behaviour between (●) whisker-free unannealed, (■) whisker-free annealed and (▲) whisker-reinforced material, suggesting that whisker reinforcement is not effective in improving the creep resistance of silicon nitride. It is believed that the elongated Si_3N_4 grains found in the whisker-free material enhance the creep resistance of this material. When internally grown elongated Si_3N_4 grains are not present in the SiC whisker-free silicon nitride, creep is much faster than that obtained from the SiC whisker-reinforced material [20].

Kossowsky *et al.*), the fact that glass was present at all grain interfaces, and the fact that cavitation and crack formation occurred at grain and whisker interfaces, it is probable that the mechanism of deformation described above [17, 18] is active in the present case.

Whisker reinforcement of the grade of silicon nitride studied here does not improve its creep resistance. As shown in Fig. 6, the unannealed, whisker-free specimens tested at high creep rates fall along the same curve as the whisker-reinforced specimens. Strains to failure of the unannealed whisker-free specimens, however, are approximately twice those of the whisker-reinforced specimens, $\approx 2\%$, indicating a greater tolerance to deformation in the former. Annealing at the test temperature for extended periods improves the creep resistance of both materials, but the creep resistance of the whisker-free material is improved more than that of the whisker-reinforced material (Fig. 6). This is seen in both the preannealed specimens and the specimens that were tested at low creep rates, in which case annealing occurred during creep. Strains to failure of the annealed whisker-free specimens are approximately the same as those of the whisker-reinforced material. As will be discussed, these differences in creep behaviour depend on the composition and volume fraction of the intergranular phase in the two materials. In particular the presence of calcium and other impurities in the retained glass of whisker-reinforced material probably reduces its resistance to creep.

3.3. Creep cavitation

Both the whisker-reinforced and the whisker-free material failed by the nucleation and growth of cavities from the interfaces of large grains or whiskers. In the whisker-reinforced material, the whiskers act as nucleating sites for cavities that grow along the whisker interface to form micrometre-size cracks. These develop further into macroscopic-size creep crack segments that eventually link together to cause failure. A typical microcrack is shown at the interface of an SiC whisker in Fig. 7a. In this example, the microcrack grew along the whisker interface and then branched into the material. Adjacent microcracks linked to form larger creep-crack segments.

At the highest creep rates, very few creep cracks are observed distributed within the samples. Apparently, once the first few cavities are nucleated at favourably oriented whisker interfaces, they grow unstably, leading to rapid failure in a nearly brittle manner. At somewhat lower strain rates, however, cavity nucleation is followed by slow crack growth. Under these conditions, failure occurs in a more ductile fashion by the eventual linking-up of crack segments that are distributed within the sample (Fig. 7b).

At still lower creep rates (below approximately $5 \times 10^{-8} s^{-1}$), the rate of cavity nucleation and crack growth appear to decrease dramatically with decreasing strain rate. For strain rates below $\approx 5 \times 10^{-8} s^{-1}$ creep deformation occurs in a fully accommodated manner; failures were not observed for test durations of up to 2000 h. Cavities that did form had a blunt

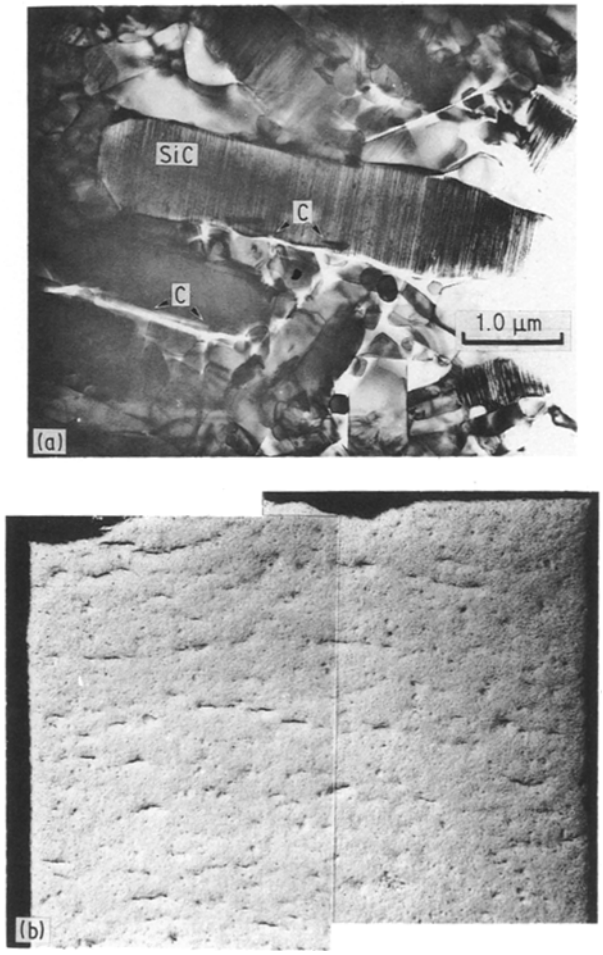


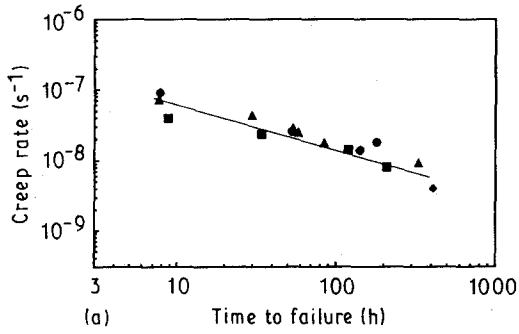
Figure 7 (a) Cavity nucleation in whisker-reinforced materials occurs at the vitreous interfaces bordering the SiC whiskers. Cavities grow from the whisker interfaces into the bulk of the material, where they link up with other cavities eventually forming life-limiting cracks. (b) Polished gauge section of whisker-reinforced Si_3N_4 specimen, showing that cavities form uniformly throughout the gauge section. The gauge section width is ≈ 2.5 mm.

morphology and appeared to be confined to the interface on which they nucleated. This observation suggests a stress threshold for the propagation of cavities along the whisker interface.

In the whisker-free material, a similar description of the initial stages of cavity nucleation and growth applies. However, now cavitation occurs primarily at interfaces bounding elongated, β-Si_3N_4 grains. At strain rates greater than $\approx 5 \times 10^{-8} s^{-1}$, the density of cavities appears to increase with increasing strain rate. Unlike the behaviour of whisker-reinforced material, however, the growth of these cavities into stable, creep-crack segments is not observed prior to rupture. Instead, rupture probably occurs rapidly once a critical density of isolated cavities is developed. For strain rates below $5 \times 10^{-8} s^{-1}$ only low densities of blunted, isolated interfacial cavities were observed in the whisker-free material. Both the density of these cavities, and their tendency to grow to full-facet dimensions, appear to diminish with decreasing strain rate.

3.4. Creep rupture

Creep rupture data collected on the whisker-reinforced material fit a Monkman–Grant [19] type of plot, in which the logarithm of the time to failure, t_f, is plotted as a function of the logarithm of the minimum creep rate, $\dot{\varepsilon}$. When represented in this way (Fig. 8a) the data for the whisker-reinforced material fall on a curve that can be approximated by a straight line with a slope of -1.69. This slope differs substantially from the value of -1 proposed by Monkman and Grant, indicating that the strain to failure is not a constant for this material. Indeed, measurements of failure strain as a function of rupture time indicate that as the stress is increased, the failure strain decreases for this material (Fig. 8b).



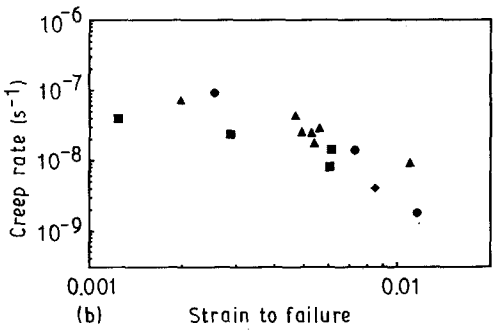


Figure 8 (a) Monkman–Grant type of curve shows an inverse relation between the minimum creep rate and the rupture time. These data fit the relationship $t_f = A\dot{\varepsilon}^m$, where m is the strain-rate exponent. The value of this parameter, -1.69, differs from the value of -1 for the normal Monkman–Grant curve, indicating that the strain to failure is not constant. (b) Plot showing that, in fact, the failure strain is greater for slower creep rates. (◆) 1100 °C, (■) 1150 °C, (▲) 1200 °C, (●) 1250 °C.

3.5. Compressive creep

In compressive creep, work-hardening was also observed during the initial stages of creep (Fig. 9). Beyond this initial transient creep period, the creep data could be approximated by a straight line, and a minimum creep rate could be determined. A summary of data prepared in this manner is presented in Fig. 10, where compressive creep data are compared with the tensile creep data obtained at the same temperature. In compression, a higher stress is necessary to achieve the same rate of creep as in tension. Thus, it is more

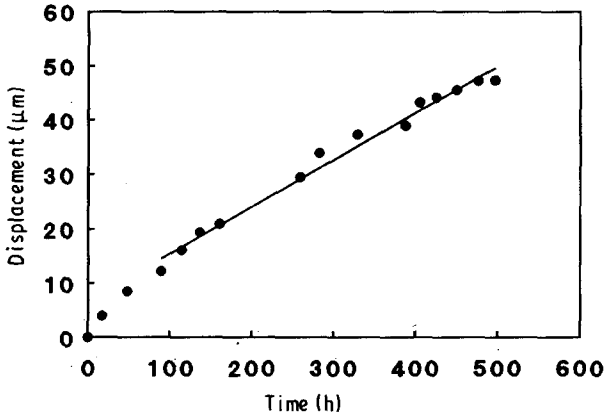


Figure 9 Compressive creep curve for whisker-reinforced, hot-pressed silicon nitride. Test temperature 1200 °C; applied compressive stress 180 MPa. Transient creep is observed during the initial stages of creep. Excluding the initial curved portion of the creep curve, the data could be approximated by the straight line $\dot{\varepsilon}(s^{-1}) = 2.98 \times 10^{-9}$.

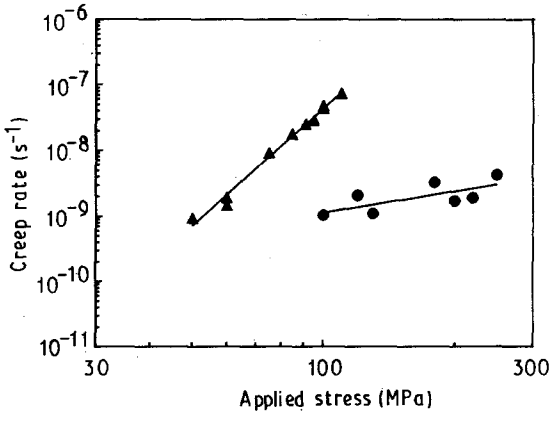


Figure 10 Differences in creep behaviour in (▲) tension (slope = 5.9) and (●) compression (slope = 1.1). This type of creep asymmetry has been reported for other multi-phase ceramics [21–24]. In the current study, cavitation and crack growth in tension contribute to the creep rate, reducing the stress required to achieve a given creep rate. In this material, cavitation is not observed in compression [1]. The stress exponent of ≈ 1 in compression is consistent with a number of different creep mechanisms.

difficult to deform this composite in compression than in tension. Representing the creep data as a power-law function, the stress exponent in compression, ≈ 1, is considerably less than that obtained in tension, 4 to 6, suggesting a significant difference in the creep mechanism.

4. Discussion

4.1. Role of whiskers

In this study, the creep of monolithic Si_3N_4 and an Si_3N_4–SiC whisker composite were compared. Earlier compressive creep studies by Koester and co-workers [7, 8] on whisker-reinforced composites that were similar to that used in this study indicated little effect of whisker addition on the creep rate of their material. Moreover, the creep rate was independent of the amount of SiC whiskers added to the material. In the present study, the compressive creep data obtained on the whisker-reinforced material fell close to the data obtained by Koester and co-workers [7, 8], suggesting that the two studies effectively gave the same results. The compressive creep of whisker-free material was not studied in this paper, so that a comparison between whisker-free and whisker-reinforced material in compression is not possible.

From the present studies, it is concluded that the creep resistance of hot-pressed silicon nitride in tension is not improved by the addition of SiC whiskers. Creep data on the as-received, whisker-free material were virtually identical to those on the whisker-reinforced material. However, creep data from pre-annealed samples, and from samples tested for long periods at slow creep rates, suggest a superior performance for the whisker-free material. The primary reason that the creep resistance of silicon nitride is not improved by reinforcement rests in the fact that the non-reinforced material contained an appreciable concentration of elongated grains of β-Si_3N_4, which increased both the fracture resistance and the creep resistance of the material [20]. The addition of SiC whiskers to the silicon nitride powder effectively replaced the elongated β-Si_3N_4 grains with the SiC whiskers. If the whiskers and elongated grains act in a similar manner during creep, then little change in creep resistance is expected by replacing elongated silicon nitride grains with SiC whiskers.

This interpretation of the role of microstructure on creep is supported by recent studies by Buljan *et al.* [20], in which flexural creep studies were made on a series of silicon nitride specimens, some of them whisker-reinforced, others whisker-free. The microstructure of the whisker-free material depended on the particular silicon nitride powder lot used in the processing. One powder lot gave a monolith that had a low proportion of elongated β-Si_3N_4 grains, while the other produced a monolith that had a high density of elongated β-Si_3N_4 grains. As in the present study, the creep rate of the silicon nitride containing elongated grains was approximately the same as that of the SiC whisker-reinforced silicon nitride. By contrast, the silicon nitride that contained no elongated silicon nitride grains crept at a rate that was ≈ 4 to ≈ 8 times faster than the others; the authors [20] attributed these results to the absence of elongated grains in this silicon nitride. Thus, the findings of the two studies are consistent.

4.2. Effects of annealing

Differences in creep behaviour of whisker-reinforced and whisker-free silicon nitride are more pronounced with increased high-temperature exposure. These differences are believed to be due to differences in initial composition of intergranular glass and to progressive changes in the volume, composition and distribution of retained glass, caused by devitrification. EDS analyses of the intergranular glass in both "as-received" materials showed that, while the glasses in both materials contained similar concentrations of yttria, silica and alumina, the intergranular glass in the whisker reinforced material also contained ≈ 1 wt % CaO. As calcium is a natural impurity in the silicon carbide whiskers, this element undoubtedly leaches from the whiskers during processing. Earlier studies on the creep of silicon nitride have shown calcium ions in the intergranular phase to be detrimental to the creep rate of this material [2]; so much so, that initial steps to improve the creep behaviour of commercial grades of silicon nitride were directed at the removal of calcium from the silicon nitride. Calcium probably plays the same role in the current studies, decreasing the effective viscosity of the intergranular phase, thereby decreasing the resistance of the whisker-reinforced composite to creep. By contrast, the whisker-free material contains no calcium and is not subject to the influence of this element.

The progressive devitrification of the initially glassy intergranular phase during high-temperature exposure changes not only the volume fraction of glass, but also its composition. This occurs because devitrification results in the formation of various crystalline phases of yttria–silicate, which to the detection limits of EDS contain neither Ca nor Al. Thus, with devitrification, the concentrations of both Al and Ca within the remaining glass of the whisker-reinforced material increases, whereas in the whisker-free material, only the concentration of Al increases. As Ca is known to reduce the creep resistance of silicon nitride [2], the increased concentration of Ca in the retained glass partially offsets the enhancement in creep resistance brought about by devitrification of the glass. This role of Ca in the creep behaviour suggests the need for calcium-free whiskers for use in the processing of Si_3N_4.

4.3. Compression versus tension

Differences between compressive and tensile creep of ceramic composites have been reported earlier for other ceramic materials, usually multi-phase materials in which the mechanism of creep differs substantially in tension and in compression [21–24]. In many materials, cavitation occurs in tension, but not in compression. When this happens, the rate of creep in tension is increased over that in compression because

of the requisite increase in volume when cavities form. In the present study, the formation of large crack-like cavities along the interfaces of silicon carbide whiskers probably played a major role in increasing the creep rate of the composite materials in tension. In compression, however, TEM studies on similar whisker-reinforced material by Koester and co-workers [7, 8] gave no evidence of whisker interface cavitation. Hence, cavitation does not affect the creep rate in compression and, as a consequence, the creep rate in tension is expected to be greater than that in compression for a given applied stress.

Direct intergranular contact between grains or whiskers can also lead to a different creep resistance in compression and tension [23]. For creep to occur in two-phase solids of the kind studied in this paper, grains must slide over one another. The density of contact sites between grains is important in establishing the magnitude of internal friction and, hence, the creep resistance of the solid: the higher the density of such sites, the greater the resistance to deformation. In tension the grains are pulled apart, thereby decreasing the number of points of contact. As the density of contact between grains of silicon nitride or whiskers of SiC decreases, the principal resistance to creep within the solid changes from deformation at the sites of contact, to deformation of the intergranular phase. By contrast, grains are pushed together in compression thereby increasing the number of contact sites between silicon nitride grains, which increases the creep resistance of the composite. In the present study, both mechanisms (cavitation and intergranular contact) probably play a role in the deformation process.

4.4. Specimen lifetime

Creep rupture data for the whisker-reinforced material can be represented as a Monkman–Grant curve [19], in which the time to failure is plotted as a function of the creep rate (Fig. 8a). Regardless of stress or temperature, data fell on a single curve. When this happens, the lifetime of a material can be determined solely by the creep behaviour of the solid, and improvements in lifetime can be achieved by modifying the microstructure to improve creep resistance. These structural modifications include increasing the effective viscosity of the intergranular phase, decreasing the amount of intergranular phase, and increasing the grain size of the solid. To date, the first two of these have been shown to be effective in improving the high-temperature creep behaviour of structural ceramics. Thus, improvements in the creep resistance of silicon nitride have been achieved by removing calcia as an impurity [2] and by replacing magnesia with yttria [3] as a sintering aid. Post-sintering heat-treatments have also been used to devitrify the intergranular phase, thus increasing the resistance of this phase to creep [1]. Finally, increasing the size of the grains of two-phase ceramics has been shown by Raj and co-workers [25, 26] to reduce the creep rate in glass ceramics. Despite the above results, the role of microstructure on the deformation and fracture of multiphase ceramics has still to be investigated systematically. Such studies are needed to fully understand the creep and creep rupture behaviour of these materials.

5. Summary

The role of SiC whisker reinforcement on the creep of silicon nitride in tension was investigated. In agreement with other studies on this type of material, conducted in compression, little effect of whisker addition on the creep rate was observed. A microstructural study comparing whisker-free with whisker-reinforced silicon nitride rationalizes this observation in terms of the elongated silicon nitride grains that were present in the whisker-free material. These elongated grains are believed to enhance the creep resistance of the SiC whisker-free material. As both materials contained whisker-like reinforcement, it is not surprising that the creep behaviour is similar.

The creep behaviour in tension appears to be dominated by the state of devitrification of the intergranular phase. The gradual devitrification of this phase leads to long-term transient creep in both the whisker-free and the whisker-reinforced composites. "Steady-state" creep is not achieved until devitrification of the composite nears completion.

Creep rupture of the whisker-reinforced material can be described by a Monkman–Grant plot; when the rupture time is plotted as a function of the minimum creep rate, all of the data fall along a common curve, regardless of temperature or applied stress. When such a plot is universal for a given material, it can be used as a basis of design, and material improvement can be achieved by increasing the resistance of the material to creep. As creep behaviour is more amenable to theoretical treatment than creep rupture behaviour, modelling of creep behaviour may facilitate the development of materials that are more resistant to creep rupture.

Creep in compression was observed to require about twice as much applied stress to achieve the same deformation rate as creep in tension. This difference in behaviour has been observed in a number of other multi-phase ceramics. In the present study, the difference in creep behaviour is attributed to cavitation that occurs in tension, but not in compression. The difference in creep behaviour may also be attributable to differences in the density of interparticle contact in tension and in compression; enhancement of interparticle contact in compression would necessarily require higher stresses for deformation.

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References

1. M. H. LEWIS, High-Temperature Applications, in "Tailoring Multiphase and Composite Ceramics," Materials Science Research Vol. 20, edited by R. E. Tressler, G. L. Messing, C. G. Pantano and R. E. Newnham (Plenum, New York, 1986) pp. 713–730.
2. F. F. LANGE, *J. Amer. Ceram. Soc.* **57**, (1974) 84.
3. G. E. GAZZA, *ibid.* **56** (1973) 662.
4. P. F. BECHER and G. C. WEI, *ibid.* **67** (1984) C267.
5. P. F. BECHER, C. H. HSUE, P. ANGELINI and T. N. TIEGS, *ibid.* **71** (1988) 1050.
6. P. F. BECHER, T. N. TIEGS, J. C. OGLE and W. H. WARWICK, in "Fracture Mechanics of Ceramics", Vol. 7, edited by R. C. Bradt, A. G. Evans, D. P. H. Hasselman and F. F. Lange (Plenum, New York, 1986) pp. 61–73.
7. D. A. KOESTER, R. D. NIXON, S. CHEVACHAROENKUL and R. R. DAVIS, "High Temperature Creep of SiC Whisker-Reinforced Ceramics," Whisker- and Fiber-Toughened Ceramics, edited by R. A. Bradley, D. E. Clark, D. C. Larsen and J. O. Stiegler (ASM International, Metals Park, Ohio, 1988) pp. 139–145.
8. R. D. NIXON, D. A. KOESTER, S. CHEVACHAROENKUL and R. R. DAVIS, *Compos. Sci. Tech.* **37** (1990) 313.
9. H.-T. LIN and P. F. BECHER, *J. Amer. Ceram. Soc.* **73** (1990) 1378.
10. S. T. BULJAN, J. G. BALDONI, M. L. HUCKABEE, J. T. NEIL and G. ZILBERSTEIN, in Proceedings of 25th Automotive Technology Development Contractors' Coordination Meeting P-209, Dearborn, Michigan, October 1987 (Society of Automotive Engineers, Warrendale, Pennsylvania, 1988) pp. 137–144.
11. J. G. BALDONI and S.-T. BULJAN, "Ceramic Materials and Components for Engines", edited by V. J. Tennery (American Ceramic Society, Columbus, Ohio 1989) pp. 786–795.
12. M. BACKHOUS-RICOULT, J. CASTAING and J. L. ROUTBORT, *Rev. Phys. Appl.* **23** (1988) 239.
13. D. F. CARROLL, S. M. WIEDERHORN and D. E. ROBERTS, *J. Amer. Ceram. Soc.* **72** (1989) 1610.
14. R. E. PETERSON, "Stress Concentration Factors" (Wiley-Interscience, New York, 1974) p. 37.
15. K. LIDDELL and D. P. THOMPSON, *Br. Ceram. Trans. J.* **85** (1986) 17.
16. P. F. BECHER, E. R. FULLER Jr and P. ANGELINI, *J. Amer. Ceram. Soc.* submitted.
17. R. KOSSOWSKY, D. G. MILLER and E. S. DIAZ, *J. Mater. Sci.* **10** (1975) 983.
18. R. RAJ and P. E. D. MORGAN, *J. Amer. Ceram. Soc.* **64** (1981) C143.
19. F. C. MONKMAN and N. J. GRANT, *Proc. Soc. Test. Mater.* **56** (1956) 593.
20. S. T. BULJAN, M. L. HUCKABEE, J. G. BALDONI and J. T. NEIL, "Ceramic Matrix Composites", GTE Laboratories Semiannual Report for Oak Ridge National Laboratories (October 1989).
21. R. MORRELL and K. H. G. ASHBEE, *J. Mater. Sci.* **8** (1973) 1253.
22. M. S. SELTZER, *Amer. Ceram. Soc. Bull.* **56** (1977) 418.
23. S. M. WIEDERHORN, D. ELLIS ROBERTS, T.-J. CHUANG and L. CHUCK, *J. Amer. Ceram. Soc.* **71** (1988) 602.
24. M. K. FERBER, M. G. JENKINS and V. J. TENNERY, *Ceram. Eng. Sci. Proc.* **11** (1990) 1028.
25. R. RAJ and C. K. CHYUNG, *Acta Metall.* **29** (1981) 159.
26. J.-G. WANG and R. RAJ, *J. Amer. Ceram. Soc.* **67** (1984) 381.

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