ANALYTICAL ELECTRON MICROSCOPY

AND

CREEP BEHAVIOUR

OF

SINTERED SILICON NITRIDE

A Thesis

Submitted to the School of Graduate Studies

for the Degree

Doctorate of Philosophy

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ABSTRACT:

Silicon nitride is sintered with the use of additives, such as Y_2O_3 and Al_2O_3 , in order to enhance densification. After sintering, these additives along with SiO₂, present on the starting Si₃N₄ powder, form an intergranular amorphous phase. The presence of a glassy phase is generally thought to be detrimental to the high temperature creep properties. In the material analyzed, Kyocera SN220, this intergranular glassy phase partially devitrifies upon annealing. Thus the effect of a fully amorphous or a partially crystalline intergranular phase on the creep properties could be assessed. The creep resistance of the material is only modestly affected by partial grain boundary devitrification in both flexural and compressive creep. However the creep life is reduced significantly.

Extensive analytical microscopy was done on the amorphous and partially crystalline material in order to determine what changes were occurring due to annealing and due to creep deformation. A quantitative methodology was developed for electron energy loss spectroscopy to analyze the intergranular phase composition. Using this technique concentrations of light elements, such as oxygen and nitrogen, and heavier elements could be determined. Different crystalline grain boundary products were found near the surface of samples annealed in air compared to the centre of these and throughout samples annealed in an inert atmosphere. However the residual amorphous phase composition was the same regardless of annealing atmosphere or location. In addition, phases present after devitrification did not depend on the stress state. Extensive cavitation, a commonly observed effect of creep, did not occur in samples containing the maximum obtainable strain in flexure of 2.7%.

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1 INTRODUCTION

Silicon nitride is a high temperature structural ceramic. It is currently used or being developed for a variety of engine components due to its low density and high temperature capabilities. It has been the aim to use this material at temperatures as high as 1300°C. However two aspects which must be considered are the microstructural stability and the creep resistance of the material.

An understanding of the creep properties of silicon nitride is necessary in order to assess its viability for a high temperature component. Sintered silicon nitride is made using oxide additives to enhance densification. As a result, it may contain up to 15 volume percent residual glass. This amorphous phase softens at high temperatures and has a detrimental effect on the creep resistance. Thus crystallization of this phase is often suggested as a means of improving the creep properties. A crystalline intergranular phase can be produced by choosing the amounts and types of sintering additives carefully. Crystallization can occur either during sintering or by heat treating the material after firing.

Creep of materials containing an amorphous intergranular phase is generally thought to occur by a combination of cavitation, solution/reprecipitation and viscous flow. Models have been developed for the conditions required for cavitation to occur and for solution/reprecipitation. Models have also been developed which describe observed creep rates or behaviour on the basis of empirical creep relationships. This thesis attempts to use creep resistance data and observed microstructural information to provide a basis for modeling the creep behaviour of a particular silicon nitride. On this basis, suggestions will be made concerning the optimum microstructure of silicon nitride for high temperature structural applications.

The material analyzed for this work is a Y_2O_3 -Al₂O₃ doped silicon nitride, SN220, made by Kyocera. Extensive analytical electron microscopy is used to assess the intergranular structure in the sintered material and after annealing. The effect of creep deformation on the microstructure of the material, crept in the as sintered state and after annealing, is also examined.

The creep behaviour of the material is evaluated using four point bend and compression tests. This macroscopic behaviour, along with the microstructural information, provide the basis for the development of a solel to describe the creep process. This model describes creep due to the non-linear viscous flow of an amorphous intergranular phase around an array of hexagonal grains. The creep behaviour observed for samples crept in the as sintered condition and annealed to partially crystallize the grain boundary phase can be explained on this basis.

The thesis is presented in three sections. The analytical electron microscopy methodology developed for electron energy loss spectroscopy is contained in chapter 2. Microstructural evolution due to annealing and creep deformation are dealt with in chapter 3. Chapter 4 contains the creep test results and analysis. The model for creep due to viscous flow is also developed and compared to the observed creep

test data. Chapter 5 presents the overall conclusions derived from this

study.

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2 ANALYTICAL ELECTRON MICROSCOPY - QUANTITATIVE CHEMICAL ANALYSIS OF SINTERED SILICON NITRIDE WITE YTTRIA AND ALUMINA ADDITIONS

2.1 Introduction

The need for careful analytical electron microscopy (AEM) is particularly true for complex microstructures where significant amounts of light elements (Z < 11) are present. This is the case for structural ceramics such as sintered Si₃N₄, where sintering aids like yttria and alumina lead to complex intergranular glass pockets and films that can crystallize into a variety of phases after heat treatment. As this grain boundary phase is only of the order of 10% by volume, it is difficult to characterize the devitrification process and its products by bulk X-ray diffraction. However, these boundary phases can strongly influence mechanical properties, particularly high temperature creep and damage processes. Without a prior knowledge of microstructural evolution, interpretation of mechanical test data is very difficult (Wilkinson, 1988).

The basic principle behind energy dispersive spectroscopy (EDS) is that primary electrons excite the atom of interest ejecting an electron from an inner shell. The atom can return to its ground state by an electron falling from an outer shell to the vacant position and at the same time emitting an x-ray of a characteristic energy. A spectrum of x-ray counts versus x-ray energy is then collected (figure 2.1). This enables one to obtain chemical information of all elements in the area of interest. However as the detector window absorbs low

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energy x-rays, it is not possible obtain quantitative information on elements with atomic numbers less than or equal to 10 (Na). Lighter elements can be detected with a thin window or windowless detector as these do not absorb all the low energy x-rays produced by the light elements. Quantification is performed using a proportionality constant (k factor) to relate the intensities of x-ray peaks (I_A and I_B) to the relative concentrations (C_A and C_B):

where k_{AB} is an experimentally determined proportionality constant. This equation assumes absorption and fluorescence of x-rays as they pass through the sample are negligible (i.e. the sample is thin). These and additional details of EDS analysis and artefacts can be found in Williams (1984).

 $\frac{C_A}{C_A} = \frac{I_A}{k_{AB}}$

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The smallest area for elemental analysis is approximately 10nm using a LaB₆ filament, and 20 to 30nm for a tungsten filament. The lowest concentration of elements detectable depends on the system of interest. This is due to absorption, fluorescence yield, peak overlap and sample damage rate. However for Al or Y in a Si matrix, a reasonable figure is approximately 0.5 weight percent.

The basic principles behind electron energy loss spectroscopy (EELS) can also be found in Williams (1984) and in greater detail in Egerton (1986). Briefly, in passing through the sample the primary beam loses energy. The beam is then collected and a spectrum of intensity as a function of energy loss is obtained. The elements in the sample require a minimum energy of a characteristic amount in order to move an electron from a lower to a higher energy shell. By looking at the EEL spectrum, it is possible to know which elements have been excited (figure 2.2). Quantification is done similarly to the EDS case.

However either an experimentally or theoretically determined proportionality constant can be used. In EELS, this constant is the ratio of the elemental partial ionization cross sections for the appropriate shell excitation (ex. σ_{A-K} is the cross section of element A for a K shell excitation):

$$\frac{\mathbf{C}_{\mathbf{A}}}{\mathbf{C}_{\mathbf{B}}} = \frac{\mathbf{I}_{\mathbf{A}-\mathbf{K}} (\mathbf{B}, \boldsymbol{\Delta}) \sigma_{\mathbf{B}-\mathbf{K}} (\mathbf{B}, \boldsymbol{\Delta})}{\mathbf{I}_{\mathbf{B}-\mathbf{K}} (\mathbf{B}, \boldsymbol{\Delta}) \sigma_{\mathbf{A}-\mathbf{K}} (\mathbf{B}, \boldsymbol{\Delta})}$$

Here I is the intensity of the edge (called as such due to its shape as seen in figure 2.2). The B indicates the spectrometer entrance angle. The Δ is the energy range over which the intensity is calculated. Δ , determined by the user, is chosen to be large enough to contain a sufficient number of counts in the edge and small enough so information from following peaks is not collected. Ranges of 40, 60, 80 or 100 eV In order to obtain the edge intensity, the are commonly used. background spectrum must first be subtracted. This is done by fitting empirical equations of the form either AE^{-r} (where E is the channel energy loss, A and r are constants) or a log polynomial, to the pre-edge region. A good background fit is one that converges with the spectrum at large energy losses. A value of B is generally chosen in order to collect scattered electrons through a larger angle. However after a certain size the peak signal saturates and the background continues to rise (Williams 1984).

Detection limits are, as in EDS, difficult to quantify as a result of numerous sample dependent factors. The minimum area analyzed is limited by size of the probe on the sample and the minimum spectrum intensity from which an edge is discernable from the background noise. Other factors include background fitting, thickness effects on background shape, proximity of other peaks and peak shape. However a few examples given in Williams (1984) provide an approximate range.

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Using BN, it is reasonably straight forward to obtain an elemental ratio of 1 within ± 5 %. As B and N are easy edges to fit a background to, we may postulate that for more difficult edges a reasonable accuracy is ± 10 %. The minimum detectible quantities also depend on the element and matrix being examined. Williams mentions some experimental work in this area where 3 atomic% C was found in 30nm of Fe and 6 at% O in 37nm of Fe.

Theoretically determined cross sections assume the sample is thin enough that primary electrons do not experience multiple interactions with the sample. This assumption is valid when the sample thickness (t), divided by the mean free path of the electron (lambda), is less than 1 (Malis et al, 1988). Using EELS:

$\frac{t}{1} = \frac{I_0}{1}$ lambda I

where I_0 is the integrated intensity of the zero loss peak and I is the integrated intensity of the complete spectrum (Malis et al 1988).

Energy dispersive X-ray spectroscopy (EDS) has been used by a number of workers to analyze various Si_3N_4 materials. Concentration gradients have been determined across both grain interiors (Bonnell et al, 1986) and grain boundaries (Goto et al, 1986). The overall composition of amorphous phases has been determined by assuming Si to be present as a nitride and Y and Al to be present as oxides (Ahn and Thomas, 1983). Concentrations of O and N in crystals having a significant level of Al or Si substitutions have been calculated by assuming a 1:1 O:Al or N:Si ratio. For example, Leng-Ward and Lewis (1985) assumed that $Y_3Al_5O_{12}$ (YAG) crystals having about 14% Si substitution for Al had a composition of $Y_3Al_{4,3}Si_{0,7}O_{11,3}N_{0,7}$.

Ultra thin window (UTW) EDS and electron energy loss spectroscopy (EELS) have been used to indicate qualitatively the presence of O or N

in amorphous pockets, with the amount of each being estimated from the quantitative cation determination (Bando et al, 1986). UTW-EDS has been used also in conjunction with microdiffraction to characterize boundary phases (Kuroda et al 1986).

Clarke et al. (1981) used both EELS and EDS to determine the composition of amorphous grain boundary phases in MgO-doped Si_3N_4 . In addition, they compared the measured composition of crystalline phases with their stoichiometric compositions, with reasonable agreement for Si_3N_4 and some deviations for Mg_SiO₄ and Si_2N_2O . More recently, Thorel et al. (1987) have used EELS and EDS to analyze SiAlON amorphous phases and determine N/O, Al/Si and Y/Si atomic ratios. The latter two ratios were consistently higher with EELS than with EDS. Similarly, Bischoff and Ruhle (1986) analyzed both crystalline and amorphous SiAlON phases using EELS and EDS and, in comparing data from the two methods, found the Y content as determined by EELS to be less than that measured by EDS. In all of the above cases, details of EELS methodologies were rarely given.

Thus, while AEM has been used to study structural ceramics, there are some discrepancies in quantitative data. Therefore it was decided to develop a detailed EEL methodology for structural ceramics, using Si_3N_4 as an example, which would take into account all available EEL edges and current EEL partial cross-sections (Egerton, 1986). This could then be compared to quantitative EDS analysis considering factors such as specimen artefacts, ease of spectral processing and overall "accuracy of analysis.

2.2 Experimental

A variety of standards were used for the purpose of checking calculated EEL cross-sections, determining experimental ones and obtaining EDS k-factors. These included a series of powders on holey-C films obtained from Microanalysis Consultants, Inc., U.K.; Y_2O_3 (yttria), $Y_3Al_5O_{12}$ (YAG), Al_2SiO_5 (kyanite), KAlSi_3O_8 (orthoclase) and FeSi₂. Other standards whose stoichiometry was known to be accurate included an Al_2O_3 ceramic foil, a NiAl intermetallic foil and sputter-deposited silicides of Ti, Co and Ni. The composition of the NiAl and the silicides had been determined using microprobe, Rutherford backscattering analysis and EDS (Van Capellan technique as described by Carpenter et al (1988)). These and the Al_2O_3 composition were confirmed by cross-correlation of EEL cross-sections with those obtained from a number of other standards (Malis 1989).

The Si $_{3}N_{4}$ material studied was Kyocera SN-220, a sintered material doped with approximately 4 wt% each of yttria and alumina. Both as-received material and material annealed to partial devitrification were studied (as detailed in chapter 3). Thin foils were prepared by slicing and grinding the material to a thickness of about 120 micrometers, cutting 3 mm discs with a Gatan ultrasonic drill, dimpling to about 20 micrometers with 15 and 6 micron diamond on a Gatan dimpler, then ion thinning with Argon ions at 4.5 keV, 0.7 mA and an incidence angle of 12 degrees. A thin carbon coating was applied to prevent charging under the electron beam. Specimens were then examined in a Philips EM400T equipped with an EDAX 9100/60 analysis system and a Gatan 607 EEL spectrometer.

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2.2.1 Energy Dispersive X-ray Spectroscopy

Analyses on all specimens were conducted in a standard Philips Be-insert, single tilt, low background holder. The powder standards were on copper grids and care had to be taken that the grid bars did not preferentially absorb X-rays. Most EDS spectra were collected in the focused nanoprobe mode (beam diameter about 25 nm) with care taken to ensure that a eucentric specimen condition existed so as to minimize electron 'tails' that could excite X-rays from regions other than that desired for analysis (Cliff and Kenway, 1982). Where lower beam intensities were desired to minimize electron damage of the glassy phase (Laval et al, 1982), a focused microprobe beam (diameter about 40 nm) was used. The focused beam was positioned carefully within boundary phases so as to avoid any irradiation of the adjacent Si_3N_4 , with extensive tilting often used to clearly define the location of the interface between the intergranular phase and the Si_3N_4 .

Hole count spectra in both nanoprobe and microprobe mode were taken just off the foil edge for the same live time as on the foil to determine the level of instrument-induced spurious X-ray generation. The Si-K peak was at or below the level of the continuum background for the foil analysis, which is generally regarded as an acceptable level (Williams, 1984). EDS spectra were collected for times sufficient to ensure several thousand counts in the smallest of the integrated peaks. Background subtraction and correction for the substantial overlap of Al-K, Si-K and Y-L peaks (illustrated in figure 2.1) were performed using the EDAX THIN/LIST software. The thickness of analyzed regions, as measured in the adjacent Si_3N_4 grains by EELS, was kept below the inelastic scattering length (lambda) of 120 nm that can be estimated for Si_3N_4 (Malis et al, 1988). While this thickness limitation is necessary for EEL quantification, it had the added advantage of minimizing X-ray absorption and beam broadening, both factors which affect the accuracy of quantitative EDS.

2.2.2 Electron Energy Loss Spectroscopy

The EEL edges available for quantification of Si_3N_4 (and related standards) are; Al-L (70 eV), Si-L (100 eV), Y-M (160 eV), N-K (400 eV), O-K (532 eV), Al-K (1560 eV), Si-K (1840 eV) and Y-L (2080 eV). They may be used in combination in either of the following two ways:

Nethod 1. The low energy loss edges of Si and Y can be collected together with the N and O edges at 0.5 eV/ch. At this setting the expanded EEL spectrum furnishes a greater number of channels for background fitting, particularly important for the Si-L edge considering the proximity of the Al-L edge. However, due to the limited number of channels available (1024), it was necessary to offset the zero loss peak from the CRT after initial focusing in order to collect a spectrum from just below the Si-L edge (about 80 eV) to at least 60 eV past the O-K edge onset. The Si-L/Y-M edge proximity and the above channel limitations necessitated the use of an integration window of 60 eV. (A similar procedure can be used for the collection of the low energy loss edges of Y3A15012, except that the spread between A1-L and O-K necessitates collection at 1 eV/ch). Spectra were collected with the TEM image on the screen (diffraction coupling of the spectrometer) and a collection semiangle of 5.6 mrad as defined by a 30 micrometer objective aperture and objective lens focal length of 2.7 mm. The selected area was defined by the image magnification and the 3 mm. spectrometer

entrance aperture. Care was taken to ensure that the area analyzed was at least 50nm in size as chromatic aberrations limit the accuracy of area analyzed Failure to take this into consideration can lead to errors if elements with largely differing energy loss edges are analyzed near the foil or precipitate edge (Titchmarsh and Malis, 1990). The maximum convergence semiangle for normal TEM imaging (microprobe beam mode) was 2.4 mrad, sufficiently smaller than the collection angle so as not to require a convergence correction to the integrated edge intensities (Egerton, 1986).

Method 2. The high energy loss edges (Al-K, Si-K and Y-L) can be collected together with N and O at 2 eV/ch, with the zero loss peak again offset as per Method 1 due to channel limitations (figure 2.2b). Because of the weaker intensity of these edges and their larger characteristic scattering angles, EEL collection was done with a high intensity, focused nanoprobe beam (convergence angle of 12 mrad), in diffraction mode (image coupling of the spectrometer) and with a larger collection angle of 29 mrad as defined by the 2 mm spectrometer entrance aperture and a 34 mm camera length. The area analyzed was simply the area illuminated by the beam (approximately 25nm). An integration window of 100 eV was used. In all EEL collection, the focused beam (or selected area aperture) position was monitored so as to minimize the effects of either specimen or beam drift. The latter, while not common, can often occur as the filament slowly stabilizes, particularly for some ² LaB₄ filaments.

It should be pointed out that multichannel analyzers of different channel capacities (512 or 4096), or spectrometer configurations with additional features not available for this study (e.g.segmented collection) could lead to alternative EEL collection conditions in terms

of edge separation, background fitting regions and time per analysis.

2.3 Results

2.3.1 Cross-Sections and k-Factors

Malis and Titchmarsh have determined EEL k-factors from a large number of experimental standards at 120 keV and 5.6 mrad by cross-correlation of normalized intensity ratios (Malis and Titchmarsh, 1985). Their results suggest that most calculated cross-sections for K-edges which incorporated a relativistic correction are accurate to about 10% for larger integration windows. The majority of L-edge cross-sections are judged to have similar accuracy, in particular both Al-L and Si-L. (The most widespread programs for cross-section calculations, and the ones used for Table 2.1, gare those based on Egerton's hydrogenic approximation, SIGMAK2 and SIGMAL2, both listed in (Egerton, 1986)). A more recent independent study under the same EEL collection conditions but using different standards (Hofer and Golob, 1989) generally supports the findings of Malis and Titchmarsh (1985). " Finally, work involving selected samples from Malis and Titchmarsh (1985) and using different voltages and AEM systems (Malis et al, 1986) also showed a similar accuracy.

Comparison of Method 1 and 2 analyses on quite thin regions of a variety of phases produced compositions which were the same within experimental uncertainty. While this confirmed that either diffraction or image coupling EEL collection could be used, potential chromatic aberration errors for the former mode must be kept in mind when near a foil edge or when analyzing small phases if the edges anticipated are well separated (Titchmarsh and Malis, 1989). The calculated Al-K cross-section at 29 mrad was confirmed to have a similar validity as that for 5.6 mrad (Malis and Titchmarsh, 1985) by use of the Al_2O_3 ceramic. However, the four silicide standards produced intensity ratios which, when combined with other data (Malis and Titchmarsh, 1985; Hofer and Golob, 1989; Titchmarsh and Malis, 1989) on Fe, Co, Ni and Ti, suggested a 20-25% difference between the calculated Si-K cross-section and what could be regarded as an 'effective' cross-section. This effective or adjusted cross-section is the one shown in Table 2.1.

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Table 2.1 also lists the experimental cross-sections (and the k-factors from which they were derived) for the Y-M and Y-L edges, as determined by Methods 1 and 2 respectively, using the Y_2O_3 powder standard. (No calculated cross-sections for these edges were available for this study). A 60 eV window value was determined for Y-M because of the Si-L/Y-M overlap, while a 100 eV value was determined for Y-L to maximize the integrated intensity.

EEL analysis of the YAG standard by both Methods 1 and 2 indicated that the composition was near stoichiometry, ie., mean elemental ratios were within 10% of stoichiometric values. The YAG was then used to provide EDS k-factors for Al-K with respect to both Y-L and Y-K (Table 2.1), although the Al-K/Y-L factor was preferred because of lower absorption effects. Both factors differed significantly from the calculated factors generated by the EDS system (Y-L/Al-K - calculated 53% higher, Y-K/Al-K - calculated 35% lower). For an Al-K/Si-K factor, NiSi and NiAl standards had furnished a value of 1.44 in a study (Carpenter et al, 1988) using the Van Capellan extrapolation technique (to minimize absorption effects) on the same AEM system at the same time this study was conducted. This value was significantly higher than a value of 1.23 determined from the kyanite powder, assuming a stoichiometric composition . However, Method 2 EEL analysis indicated

a kyanite composition nearly 20% lower in Si than expected. Since no mass loss was observed during analysis, either visually or by comparing data using different collection times, analysis locations or beam intensities, this EELS-determined composition was regarded as reliable and the resulting Al/Si k-factor of 1.49 was in much better agreement with Carpenter et al. (1988). An attempt to further confirm this factor with the KAlSi₃O₈ powder failed because of large variations in composition from one crystallite to another. The calculated k-factor furnished by the EDS software was 1.15, or 25% lower than the above experimental value.

2.3.2 EEL Methodology

Processing of spectra collected via Methods 1 and 2 showed significant differences regarding reliable background fitting, as illustrated by figure 2.3. In most Method 1 spectra, the normal inverse power law (AE^{-r}) fitting proved very difficult for the Si-L edge. (It is noteworthy that such fits were successful for the Al-L edge in Method 1 YAG analysis despite its being an even lower energy edge). Log-polynomial fitting is recommended for low energy loss edges (Bentley et al, 1982; Malis, 1987), but even this method proved difficult for the Si-L edge (figure 2.3a). The difficulty was not in obtaining a good fit in the pre-edge region, but a fit which extrapolated under the edge so as to reasonably converge with the spectrum at higher losses. In addition, the convergence was not easy to judge because of the proximity of the Y-M edge, a common problem for low loss edges. Figure 2.3a shows that quite different Si/Y ratios (as influenced by the variable Si-L intensity) could be obtained for background fits which differed only

slightly in the pre-edge fitting region. Judging background/spectrum convergence for the Y-M edge was much easier and relatively little difficulty was encountered in consistently obtaining good fits for this edge, although the value used for the onset of the edge (160 eV) should be regarded as somewhat arbitrary. Inverse power law fitting for N-K and O-K edges proved quite straightforward, even for the few atomic percent of N occasionally encountered in the intergranular glass. As a measure of the reproducibility of Method 1 background fitting, several spectra were selected at random and processed independently by the author and by an experienced EELS user (Dr. T. Malis; CANMET, Ottawa). While the majority of Si/L intensities agreed within several percent, a few differed by as much as 30%.

All edges in Method 2 spectra proved amenable to reproducible background fitting, using convergence with the spectrum as a criterion for the O-K edge and exercising some caution in the choice of fitting region for the Si-K and Y-L edges since they are close to preceding edges. The convergence of both inverse power law and log-polynomial fits for the O-K edge is illustrated in figure 2.3b, where three different fits produced intensity differences of only a few percent. A variety of Al, Si and Y edge backgrounds gave much the same intensities provided fitting regions of the order of 100 eV were used (to minimize the effects of the decreased signal/noise ratio). A similar operator comparison of several spectra as described above produced virtually identical results in terms of both mean intensities and their standard deviations, hence Method 2 analysis was used for all subsequent phase identifications.

In certain Method 2 spectra, however, it proved impossible to fit an acceptable background to the lower loss edges (eg., the N-K edge of figure 2.2b). The backgrounds inevitably rose above the spectrum within

a few hundred eV of the edge. The shape of the pre-edge regions in these spectra suggested a non-linear response of the spectrometer, although the single channel intensity in pulse counting mode at these edges was always well within the spectrometer specification of 107 cps/ch for a linear response. Tests on a boron nitride standard revealed, however, that the spectrometer response became non-linear at just over 106 cps/ch (figure 2.4), a value exceeded at the N-K edge of figure 2.2b. Accordingly, spectra where the O-K edge single channel intensity exceeded this amount were not quantified.

2.3.3 Artefacts

Ion thinning can cause amorphous surface layers, and clear evidence for these layers was apparent in all foils. An example is shown in figure 2.5 where a grain boundary disappears close to the foil Log-ratio thickness measurement (Malis et al, 1988) at the edge. transition point between the totally amorphous region at the foil edge and the neighbouring crystal gave a thickness of some 40 nm, i.e. about 20 nm per surface, in reasonable agreement with previous estimations (Simpson et al 1986). If a number of analyses are anticipated in a given region, further measurements can be taken to delineate contours of relative thickness (t/lambda) to determine the extent to which this amorphization and the local foil topography can restrict the useable area for EEL quantification (Malis 1988). A limited number of Method 2 analyses were conducted on the totally amorphous foil edge of both $Si_{x}N_{x}$ matrix and glass phase, then compared to thicker adjacent regions where the crystalline portion was about half of the total thickness. No significant differences in N-Si or Y/O ratios were detected, i.e. the

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ion damage did not appear to cause major chemical changes.

The normal hydrocarbon contamination build up, which can be monitored in a straightforward fashion by combined EELS thickness measurement and quantification (Malis, 1988), showed an effect on background fitting for low loss edges. That is, EEL analyses on the Si_3N_4 matrix in freshly-prepared foils gave the correct concentration ratio using the Si-L and N-K edges. After a certain amount of usage extending over several weeks, when the total contamination layer thickness was of the order of 30 nm, spectra at the same values of t/lambda gave significantly lower Si/N ratios, i.e. the Si-L intensity was underestimated. It was noted as well that no contamination cones were formed, even after several minutes of focused beam analysis.

Slight beam damage of the glass phase occurred after a few minutes with normal viewing conditions, but was not found to alter the composition radically. This artefact has actually been shown to be helpful in delineating the extent of the glass region as shown by Laval et al (1982). A typical example is shown in figure 2.6a. Focused beam (Method 2) analysis accelerated the rate of local damage dramatically (figure 2.6b), but the experimental scatter of glass analyses was not greater than that of crystalline phases which showed no discernible damage. In addition, high resolution secondary electron imaging showed no surface effects from the damage. Thus, mass loss and/or ion rearrangement appeared to be minimal. In one unusual case, however, 'before and after' analyses indicated that Fe had diffused into the glass from a nearby silicide particle (figure 2.6) even though the major damaged region was clearly not in contact with the silicide.

An artefact that occurred for many EDS analyses is illustrated in figure 2.7, which shows both EDS and EEL spectra from a crystalline intergranular pocket. The EDS spectrum (figure 2.7a) shows a clear Si
peak (about 15 at%) whereas the EEL spectrum (figure 2.7b) just as clearly indicates Si to be below the minimum detectable limit (of the order of 5% for Si-K). The EEL analysis and the microdiffraction pattern were consistent with the Si-free YAG phase whereas the EDS analysis was not consistent with any known phase.

2.3.4 Phase Analysis

Figure 2.8 illustrates the nature of the characterization to which the methodology of this study was to be applied, namely the devitrification of the initial glassy phase into various crystalline phases. In figure 2.8, the initial (as-sintered) glass has partially transformed to a crystalline phase with a composition indicative of $Y_2Si_2O_7$, and a remnant glass with composition different from the initial glass. Table 2.2 shows the relative agreement between EEL and EDS analyses for the two major crystalline devitrification products (independently confirmed with convergent beam diffraction) using the Method 2 edges for quantification.

2.4 Discussion

As commented on earlier, an accuracy of about ± 10 % can be attributed to most experimental determinations of EEL k-factors, and a similar figure has been ascribed to calculated cross-sections (Egerton, 1984). The check on the Al-K cross-section with Al₂O₃ was in accordance with this figure. The four experimental values for the Si-K cross-section (from Ti, Fe, Co and Ni silicide) exceeded this range

significantly. One possible explanation is simply a greater influence of plural scattering for the relative positions of the edges involved, and the sign of the 20-25% discrepancy is in the right direction for such an explanation. In other words, the calculated cross-section for Si-K may indeed be the correct value to use in very thin regions of specimens, but signal intensity then becomes a problem, thus the effective cross-section of Table 2.1 is to be regarded as more realistic for regions of reasonable thickness.

The Y-L experimental cross-section would incorporate any such plural scattering effect and thus could be somewhat less accurate in very thin regions, however the low energy Y-M edge would have a much better signal for such regions in any event. The agreement between Methods 1 and 2 for the YAG standard (ie. implying that both Y cross-sections of Table 2.1 are accurate) is also encouraging given the slow-rising nature of the Y-M edge. Indeed, many experimental M-edge cross-sections have been determined (Hofer et al, 1987; Malis 1989) and are summarized here in Table 2.3 because few calculated values are available and these elements are increasingly important in many ceramics. The agreement between comparable cross-sections is striking given the supposed vagaries of EEL background fitting and the radically different standards used; such as oxidized metal films (Hofer et al, 1987) and powders (Malis, 1989).

The difficulty in confirming an EDS k-factor for Al-K/Si-K is perhaps not surprising given the difficulty in obtaining EDS standards of rigorously known composition. The present data would suggest further study of the kyanite is needed before usage as a standard. A further difficulty with the Al/Si factor is the relative ease with which both of these low energy X-rays can be absorbed (in different degrees) at the detector window, a situation which can worsen with time as contamination

builds up on the window. Indeed, a servicing of the detector after completion of the study produced a 10% decrease in the kyanite k-factor, consistent with reduced preferential absorption of the Al-K X-rays. The frequent use of multi-element mineral standards in obtaining EDS k-factors perhaps points to an inherent weakness in EDS analysis, as opposed to the numerous reliable binary standards available for EELS (Malis and Titchmarsh, 1985; Hofer and Golob, 1989; Malis et al, 1986, Hofer et al, 1987; Malis, 1989). Finally, a debate over the general validity of calculated k-factors still exists (Goldstien et al, 1986). While the results in this and a related study using the same EDS system (Carpenter et al, 1988) indicate unacceptably large differences between experimental and EDS system k-factors, such differences could perhaps be reduced by an iterative adjustment of the EDS detector parameters. Indeed, a detailed comparison of theoretical and experimental factors at 200 keV recently found good agreement for K-shell combinations, but not for L-K combinations (Sheridan, 1989).

Background fitting is arguably the single biggest obstacle to EEL quantification becoming an accepted, routine analytical technique (the other major difficulty being the thickness limitations of EELS). Thus, EEL analysis using medium and high energy loss edges (Method 2) is preferable because of its better reproducibility, which in turn is a function of greater edge separation and the reduced effects of plural scattering on pre-edge background fitting and subsequent extrapolation errors. This is despite a much lower signal/noise ratio for the high loss edges, which is a problem compounded by the fact that increasing the EEL signal to improve the ratio can lead to the nonlinear signal

effect (figure 2.4) at the medium loss edges¹.

An additional difficulty with Method 2 spectral collection is that relatively high beam intensities are needed to furnish an adequate signal/noise ratio at the high loss edges while keeping analysis time reasonable in terms of drift. This can cause extensive beam damage in glass phases and, to a lesser degree, in some crystalline phases (figure 2.8). It is fortunate that the compositional changes resulting from such damage were generally minimal in the ceramic examined here, at least in the context of phase identification. Method 1 analysis may be preferable for glasses in other structural ceramics or for other EEL data (near-edge fine structure). The recent development of parallel EEL spectrometers, e.g. (Krivanek et al, 1987), should reduce the disadvantages of Method 2.

Background fitting for low loss edges need not be difficult in all cases, as was found in this study for the Al-L edge in YAG analysis, or in the k-factor determinations for Al-L from Al_2O_3 (Malis and Titchmarsh, 1985) and Si-L from SiC (Malis, 1989). Nonetheless, the sensitivity of Si_3N_4 analysis to contamination layer thickness noted above emphasizes the sensitivity of background fitting for low energy loss edges to subtle changes in the shape of nearby plasmon peaks. Effects of plural scattering on the pre-edge background are greater for low loss edges (Egerton, 1986), hence the thickness constraints are more rigorous for Method 1 analysis than for Method 2. The data in this study suggest an upper limit of about t/lambda = 0.7 for Method 1 and t/lambda = 1.2 for Method 2, a rather significant difference in view of

In theory, insertion of a gain change at an appropriate point in the spectrum should overcome the nonlinearity, but tests on the BN standard showed that a gain change between the B-K and N-K edges reduced the B/N ratio by some 25%. It would appear that some nonlinearity also exists between current and pulse counting in the spectrometer used in this study.

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the specimen topography.

A final point concerning EEL background fitting emerges from a comparison of the various standards used for k-factor determination, such as those of Table 2.3. Examination of the experimental scatter recorded in such studies shows a consistently lower experimental scatter in sputtered or oxidized films (1-5%) than in powder or alloy standards (anywhere from 5-15%, depending on the material). The implication is that compositional inhomogeneities on the scale of the analysis areas contributed the major portion of experimental scatter in the latter materials. Thus, background fitting based on reasonable "good convergence" criteria may have an uncertainty of only a few percent in many EEL applications, particularly if some of the recent developments in background extrapolation (Crozier et al, 1987; Trebbia, 1988) can be incorporated in commercial software.

The possible influence of artefacts, inherent in either the analytical technique itself or in the specimen, is an important consideration for good methodology development. The nonlinearity of EEL signal found in this study (and others such as Cheng et al, 1986) is a good example of the former. An example of the latter would be the Si-rich surface layer found on ion-thinned specimens when silicone diffusion pump oil is used (Simpson et al, 1986). A similar effect can occur if oxygen is entrapped during deposition of the carbon layer to prevent charging, and this excess oxygen was detectable, albeit in small amounts, in analysis of small segments of the carbon film overhanging the foil edges. It is interesting that the process of ion thinning and/or sputtered C coating appears to be beneficial in delaying the formation of focused beam contamination cones which can hinder both EDS and EEL analysis. A similar beneficial effect has been observed for microtomed sections (Malis, 1988).

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The most serious artefacts noted in this study were the beam damage discussed above and the spurious Si effect (figure 2.7). The beam damage did not hamper phase identification but would affect accurate concentration profiles in glass phases. The longer range ion movement noted regarding figure 2.6, however, suggests that beam damage effects should be checked carefully for each ceramic glass system. With regard to the effect of figure 2.7, the EEL analysis is consistent with Si-free YAG phase, therefore the Si X-rays must have originated in the surrounding Si₃N₄ matrix. This spurious effect could result from stray electrons and X-rays generated in the illumination system producing Xrays well away from the area of interest. If this were the problem it would have been detected by doing a hole count. Spurious effects could also result from interactions after the electron beam hits the sample. Here although electrons are scattered in the forward direction, as Williams (1984) states, they may be constrained by the magnetic field of the lower pole piece and strike the bulk material. This will generate X-rays from the bulk metal regions and will backscatter electrons onto the underside of the sample. The specimen can also interact with backscattered electrons which may be following a helical path up the column due to the strong magnetic field of the upper objective pole piece. This is minimized when the sample is at a 0° tilt. An additional source of the spurious peak could be from X-rays emanating from the region of the focused beam (Bentley et al, 1984). The Y-L X-rays have the right energy to efficiently fluoresce the Si in the matrix. A similar effect has been observed in a recent study of an Al-SiC metal matrix composite, producing apparent EDS detection of Al in the SiC due to Si X-rays fluorescing the nearby Al metal (Dignard-Bailey, 1988). The similar sizes of the two phases caused an erroneous Al "diffusion" profile into the SiC. Secondary fluorescence would

explain the EDS-EEL discrepancies for both YAG and $Y_2Si_2O_7$ phases (Table 2.2) since the EDS data show an excess of Si in both cases.

In several instances some of the above factors could have influenced results reported in the literature. For example, most of the attempts at EEL quantification of Si_3N_4 (Clarke et al, 1981; Thorel et al, 1987; Bischoff and Ruhle, 1986) have used cross-sections calculated without relativistic corrections (SIGMAK). This is significant because these studies used Method 2 edges and the relative change in cross-section between SIGMAK and SIGMAK2 increases with edge energy. Thus, at 120 keV, the lower energy N-K and O-K cross-sections increase by about 25%, whereas Al-K and Si-K increase by almost 60%. This differential can be exacerbated in the newer intermediate voltage microscopes, e.g. at 300 keV the respective increases are 30% and 200%. It is imperative that quantitative EELS studies use current calculated cross-sections and, where any doubt exists, to check via use of experimental standards. Similarly, the variability of EDS k-factors is worrisome, since many studies have relied on EDS "fingerprinting" for phase identification. Findings of Y-rich phases by EDS (Ahn and Thomas, 1983; Bonnell et al, 1987) suggest that fluorescence of the matrix may have influenced the Si content. Incorrect calculated cross-sections and/or fluorescence may account for a large portion of the discrepancies between EDS and EELS in those few studies which have used the two techniques in a quantitative fashion (Clarke et al, 1981; Bischoff and Ruhle, 1986).

The plethora of factors that can degrade the accuracy of both EDS and EELS data should not inhibit their usage in certain areas, such as the phase determination exemplified by Table 2.2, providing they are taken into consideration. It is tempting to conclude that the YAG phase has been more positively identified via EELS in this study, but the

overall analytical accuracy of 10% precludes such a conclusion. However, the fact that both of the oxygen ratios for the $Y_2Si_2O_7$ are on the low side, while the Y/Si is not low could suggest any one of a number of factors degrading the analysis for this phase; a larger influence of plural scattering, a greater degree of edge overlap or possible oxygen loss from beam damage (figure 2.8b). If the phase diagram and degree of partitioning for a given system is sufficiently well known, there may be little danger in the use of EDS (providing some thought is given to possible "fingerprinting" fluorescence combinations). On the other hand, the results in this study demonstrate that a more reliable phase confirmation would result by selective application of fully quantitative EEL analysis before EDS fingerprinting. In cases where the expected phases are less certain, or where similar compositions may be present, our conclusion is that EEL analysis is the more generally reliable technique because it can detect and quantify all elements, and do so with quantification factors based on more reliable standards. Unfortunately, thickness limitations remain a major weakness of EEL quantification, although the use of higher keV (increased lambda) and high loss edges may ease this restriction somewhat.

While this study has focused on Si_3N_4 as a useful example, the basic EEL methodology and accuracy have relevance to most other structural ceramics. For example, ZrO_2 , Al_2O_3 and MgO would be eminently suited for Method 2 analysis, as would most transition metal aluminides and silicides. On the other hand, Al or Si carbide or nitride would require Method 1 analysis on EEL systems with nonlinear signal problems (because of the very large separations between the K-edges involved). Many ceramics have only intermediate energy loss edges, and some will be very amenable to rapid EEL analysis due to the edge locations (TiC,

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TiB₂, EN) while others will be difficult due to severe edge overlap (TiN, $2rB_2$, NbC). The recent progress in either confirming or adjusting calculated cross-sections and in determining experimental ones (Table 2.3) make full EEL analysis feasible for even the more complex functional ceramics e.g. $BaTiO_3$, $LiTaO_3$ and the new generation of superconductors.

2.5 Conclusions

In conclusion, EELS can be used to obtain quantitative chemical information in ceramics. There are sufficient reliable standards either for checking calculated EEL partial cross-sections or for determining experimental EEL k-factors pertinent to Si_3N_4 with an overall accuracy of about 10%. Two optimum EEL spectral collection methodologies have been developed and a variety of factors relating to ease and accuracy of quantification have been assessed for each (e.g. edge overlap, background fitting or collection limitations of the microscope). It was also found that a realistic study of ceramic phase compositions requires knowledge of the influence of a variety of artefacts. These include spectrometer non-linearities, mass loss or diffusion under the electron beam, contamination layers and spurious X-rays from fluorescence or electron backscattering.

Unlike EDS, EELS is able to quantify light elements and does not have the problem of secondary fluorescence producing misleading results. For this reason initial quantification of amorphous or crystalline phases is best done with EELS. However as routine quantitative EEL analysis is time consuming, subsequent surveys of phase distribution is

more efficiently done by EDS fingerprinting. Thus EELS and EDS are complimentary techniques, which should be applicable to most structural or functional ceramics.

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2.6 TABLES AND FIGURES

Table 2.1

EEL CROSS-SECTIONS AND EDS k-FACTORS

Technique	Collection Conditions	Cross-Section(x10 ²² cm2/atom) or k-Factor		
EELS	5.6 mrad/60 eV window	Si-L = 579 N-K = 14.6 O-K = 6.82 Y-M = 177°°		
EELS	29 mrad/100eV window	N-K = 47.1 O-K = 26.1 ≈		

EDS

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Y-L/Al-K = 1.69Y-K/Al-K = 3.13Al-K/Si-K = 1.44

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Al-K = 1.97 Si-K = 1.51° Y-L = 2.31°°

- increased by 20% due to Ti, Fe, Co and Ni silicide standards suggesting an effective Si-K cross-section 20-25% lower than the SIGMAK2 value
- ** from Y₂O₃, scatter typically +/- 10%; (O-K/Y-M k-factor = 25.9; Y-L/O-K k-factor = 11.3)
- NiAl and NiSi standards (Carpenter et al, 1988)

Table 2.2

MAJOR DEVITRIFICATION PHASES IN ANNEALED KYOCERA SN-220

Phase 🧠	<u>Technique</u>	atomic	<u>ratio</u>		
Y3A12012		O/Al	0/1	Al/Y	Si/Al
and the second	EELS (11)	2.4	4.0	1.67	no Si
	EDS (9)			1.67	0.33
·	stoich.	2.4	- 4.0	1.7	0.0
2251207		0/Si	0/Y	Y/Si	
н Настан	EELS (13)	3.28	3.14	0.96	
	EDS (18)			0.72	
	stoich.	3.5	3.5 je	1.0	

EEL analysis using O-K, Al-K, Si-K and Y-L edges
 number of spectra analyzed in brackets
 EDS scatter typically +/- 5%, EEL scatter typically +/- 10%

Table 2.3

EXPERIMENTAL EEL CROSS-SECTIONS (X 10²² CM2/ATOM)

Element	Hofer et al (1987)	Malis (1989)
Sr	308 (SrO)	
Y	327 (Y-0-)	363 (Y-0-)
Zr	259 (270)	245 (2r0)
Nb ···	186 (Nb-0-)	180 (LINE O)
Mo	199 (MoO-)	(11110206)
Ba	29.5 (BaCO,)	31.3 (BaSO,)
La	$27.5 (La_0, 0)$	
Ce	23.5 (Ceo.)	22.0 (CeAl_)
Nd	13.5 (Nd.6.)	
Sm	$10.6 (Sm_2^2O_2)$	· • • • •
Gđ	8.0 (Gd.6.)	
Dy	4.8 $(Dy_{0}^{2}O_{7})$	· • • • · · · · · · · · · · · · · · · ·
HO	3.7 (HO_O_)	
Tm	2.0 $(Tm_{2}^{2}O_{2})$	
Lu	$1.0 (Lu_0^{-0})$	
Ta	$0.87(Ta_{0})$	
W	0.75 (WO3)	

standard used in brackets
120 keV, 5.9 mrad, 100 eV window
scatter in Hofer et al (1987) 2-10%, in (Malis, 1989) typically +/- 10%

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Figure 2.1 EDS spectrum from an intergranular glass phase in Si_3N_4 illustrating the overlap between Al-K, Si-K and Y-L peaks.





(a) Si-L to O-K at 0.5 ev/ch (Method 1),

(b) N-K to Y-L at 2.0 ev/ch (Method 2).

Arrows indicate edge onset. C-K edge arises from a layer deposited to prevent specimen charging. Small N-K edge verified by background extrapolation. Note the charge in intensity scales at 240 and 1280 eV.

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Figure 2.3 Extrapolated background fits for: (a) Si-L edge (Method 1) with log-polynomial fitting regions as: A - 93 to 100 eV, B - 86 to 97 eV, and C - 88 to 97 eV, producing Si/Y ratios of 2.7, 2.2 and 1.1, respectively. c (EDS ratio = 1.0). (b) O-K edge (Method 2) with inverse power law fitting regions as: A -475 to 520 eV and B - 490 to 520 eV, plus a log-polynomial fit of C -450 to 520 eV. All 3 integrated intensities for a 100 eV window are within 3% of each other.







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Figure 2.5 Edge of foil showing disappearance of grain boundary as a result of damage induced by ion thinning.

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Figure 2.6 Beam damage in glass phase (a) after a few minutes with the defocused beam and (b) after 100 sec of focused nanoprobe beam (Method 2 analysis) .

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Figure 2.7 Crystalline intergranular phase in annealed Si_3N_4 : (a) EDS spectrum with apparent 15 at% Si, (b) EEL spectrum with no significant Si.

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Figure 2.8 Partially transformed glass phase in annealed Si3N4. Arrows indicate locations of focused beam analysis which showed no detectable Al in the crystalline phase near the interface.

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2.7 References

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3 MICROSTRUCTURE OF SN220

3.1 INTRODUCTION

Silicon nitride is generally sintered with the use of additives such as MgO, Al₂O₃, Y₂O₃ or AlN. These, along with the surface SiO₂ on the starting alpha-silicon nitride, form a liquid at sintering temperatures. The alpha-Si₃N₄ transforms to B-Si₃N₄ through a solutionreprecipitation process (Hampshire and Jack 1983). The type and amount additives used determine the grain morphology and strength of characteristics (Wotting and Ziegler 1983). Large amounts of a low viscosity glass lead to equiaxed grains. Small amounts of a high viscosity glass lead to silicon nitride grains with a high aspect ratio. This also leads to a higher room temperature fracture toughness (Wotting and Ziegler, 1983). The amount and composition of the residual glass after sintering is also expected to affect the high temperature strength and creep properties. Materials sintered with Y203 have a more refractory grain boundary phase than those sintered with MgO. As a result they exhibit improved high temperature strength. Al₂O₃ is generally added along with Y203 to enhance sinterability (Quackenbush et al, 1983). Nitrides may also be added as these form a solid solution with the silicon intride. Thus it may be possible to fabricate a material without an amorphous intergranular phase as suggested by Ziegler et al (1987). In addition, any residual glass having a higher nitrogen content is expected to have a higher viscosity (Hampshire et The stability of the residual amorphous phase is also al 1984).

important. Devitrification or oxidation can produce either beneficial or catastrophic results (Lange et al 1980, Jack 1982).

Some work has been done to understand and predict the behaviour of the intergranular phase. O'Meara et al (1987), Drummond et al (1988), Lange et al (1977), and Quackenbush et al (1980) have fabricated glasses from the Y_2O_3 -SiO₂-Al₂O₃ system and studied their crystallization behaviour. However an understanding of the system is far from complete, as is understanding how the amorphous phase and its crystalline products affect the strength and creep properties of the material.

Material strength is affected not only by sintering additives, but also by flaws. Internal flaws which result from processing are often found in the form of agglomerates or low density regions (Quinn and Braue 1989). Surface flaws, in the form of pits, can result from high temperature oxidation (Tighe and Wiederhorn 1983). Identification of strength limiting defects helps in understanding material properties.

The purpose of this section is to obtain an understanding of the microstructure of Kyocera SN220 in the as sintered condition, after annealing, and after creep deformation. This information is necessary in order to interpret and model creep behaviour.

3.2 EXPERIMENTAL

Sintered silicon nitride doped with Y_2O_3 and Al_2O_3 was obtained from Kyocera in the form of $4 \times 5 \times 60$ mm bars. The amount of additives used were determined through neutron activation analysis (see table 3.1). Assuming the Y and Al were added in their oxide forms (as will be discussed in the discussion section) the material had been sintered

with 4.2 wt% Al_2O_3 and 3.8 wt% Y_2O_3 . These values are close to the 5.1 wt% Al_2O_3 and 4.1 wt% Y_2O_3 as determined by Quinn (1986) on a batch of Kyocera SN220 received from Japan in February 1985. The material for this study was received in February 1986.

A comparison was made between the microstructure of the material in the as sintered condition, after annealing and after creep testing (details of creep testing can be found in chapter 4). The heat treated samples were annealed either in an air or an inert (argon) atmosphere at 1200 and 1250°C as detailed in table 3.2. Most air annealed samples were placed in an Al_2O_3 tube furnace while seated on a SiC boat. In one case a sample was annealed at 1250°C for 200 hours while seated on an Al_2O_3 boat. Samples annealed in flowing argon were placed in a covered graphite crucible packed with Y_2O_3 , Al_2O_3 , SiO_2 and 50% EN. The oxides were added in ratios similar to the glass composition, assuming 3% SiO_2 is on the surface of starting alpha-silicon nitride powder - a reasonable value based on work done on other silicon nitride material (Quackenbush et al 1980). The EN was used to prevent the powders from sintering together. Packing was changed after 100 hours as packing and sample surface turned white after extended annealing times.

SEM was used to qualitatively assess the Si_3N_4 grain morphology. Sample preparation involved polishing the material using the following schedule on a Struers Planopol automatic polishing rig:

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POLISHING SCHEDULE:

step	diamond grain size	cloth	lubricant
1 2 3	600mesh 6 micron 3 micron	resin bonded disk Struers TP-PLAN	water (lots) Struers bluelub.**
4	1 micron	N .	

SPEED: 150rpm

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FORCE: Lowest force was used to check that samples were flat in the sample holder (misalignment could be easily heard when load applied provided no other heavy equipment was operating in the polishing room). Force increased incrementally to force = 4 for step 1 (force = 2 for steps 2 and 3) and then decreased after a few minutes at each load. TIME: A few minutes at each load. Longer times for last steps if needed. Progress was checked by removing sample holder from rig and viewing polished surface under an optical microscope. This could be done without removing samples from holder, thus misalignment during this step could be avoided.

NOTE: Sample holder and samples were cleaned thoroughly between steps with methanol and water to avoid contaminating the next clean cloth. All samples were mounted on a steel plug with 'Crystalbond' and an epoxy collar put on prevent the ceramic sample edges from catching and ripping the polishing cloth.

*TP-PLAN was preferred over Struers PAN-W as it is a harder cloth and produced fewer pullouts.

Only enough Blue Lubricant to ensure the cloth surface is wet.

An alternative, more successful polishing procedure was done at the Mineralogy Section at CANMET, Ottawa using lead laps and diamond polishing media. This procedure is detailed in LaFlamme et al (1979).

Two etching procedures were tried. In the first, silicon nitride samples were left to soak in HF for 5 or 16 hours. The 5 hours etch period provided better results as the 16 hours soak left an uneven finish, over-etched in some areas. An alternative etch involved immersing samples in a melt of a 95 to 12 weight ratio of $K(CO_3)_2$ and NaF for 3 minutes. The first procedure was preferred however, for safety reasons.

The effect of heat treatment and creep deformation on internal microstructural evolution (i.e. crystallization of the amorphous intergranular grain boundary phase) and the effect of heat treatment on

surface oxide formation were examined using TEM and X-ray diffraction. Heat treated and crept samples analyzed are listed in table 3.3. Details regarding TEM sample preparation and quantitative chemical analysis can be found in chapter 2. XRD was done on a Nicolet I2 using a copper source at 40keV and 30mA, and a graphite monochrometer. Analysis was done by comparing spectra with those found in the JCPDS standard file library (see appendix 3a for clarification of JCPDS files). Samples from the centre of heat treated bars were prepared for XRD by dry crushing in a small shatter box using a tungsten carbide container with a spherical tungsten carbide ball to minimize contamination. The fraction of surface oxide included in the powder was minimized by crushing a slice of the oxidized bar away from the bar ends. The oxide surfaces were not analyzed in the powder form. The crystalline phases formed here, as determined by XRD and TEM, were then compared to the phases found at the centre of the heat treated samples.

The effects of oxidation were also assessed through weight gain and relative density measurements. Densities of samples, which were annealed in either an air and an inert atmosphere at 1200 and 1250°C, were determined by weighing them in both air and suspended in liquid. Relative densities were calculated using the following equation (Ratcliffe 1965):

$$\frac{\Delta p}{p} = \frac{S_{ai}(d_{ai}-d_{li})}{D_{ai}(S_{ai}-S_{li})} \frac{S_{af}(d_{af}-d_{lf})}{D_{af}(S_{af}-S_{lf})}$$

where p is the density, S and D are the weights of the sample and dummy sample, the subscripts a_i and l_i refer to the initial weights in air and liquid, and a_f and l_f are the final weights in air and liquid. To obtain the weight in liquid the sample was placed in a holey plastic cup which was suspended on a .001" Nichrome wire. The liquid used was

diethyl phthalate, chosen due to its low coefficient of thermal expansion and good wetting properties (Pratten, 1981). Changes in liquid temperature which occurred while making a series of measurements, were taken into account by weighing the dummy sample at the beginning and end of the series and correcting the intermediate values accordingly.

Crept samples were examined by light microscopy and/or scanning electron microscopy to look for cracks and oxide features on the outer surfaces and to examine fracture surfaces. SEM was not used to characterize creep damage due to the difficulty in distinguishing between true porosity and polishing artefacts such as particle pullouts. Interior damage was characterized using transmission electron microscopy.

Glasses of compositions similar to those found in the triple points of the silicon nitride material before and after heat treatment were made. A low silica glass of composition 33.5 w/o SiO₂, 45.5% Y₂O₃, 21.0% Al_2O_3 and a high silica composition of 46.5 w/o SiO₂, 26.4% Y_2O_3 , 27.9% Al203 were made. Fabrication involved manually dry mixing powders of 99.998% Al₂O₃, 99.999% Y₂O₃ and 99.999% SiO₂ (all powders purchased from Johnson Matthey Ltd.), tamping the mixtures into molybdenum crucibles and heating until melted in an RF induction coil furnace in a static argon atmosphere. After the glass appeared to be melted the furnace was turned off, essentially quenching the glass to approximately 800°C in 3 minutes. The Mo crucible was cut away from the glass to allow optical examination of the slug. If colour gradients existed the glass was remeited. Small pieces of the slug were then placed on a platinum foil and annealed for half an hour at 1600°C in air and quenched by removing from the furnace. Chemical analysis by AEM was done to confirm the glass composition. Pieces were then annealed at

1200 and 1250°C for 2 hours to determine if the glass crystallized in the same manner as that found in the silicon nitride material. Crystal products were examined by powder XRD.

3.3 RESULTS

3.3.1 MICROSTRUCTURE OF AS-SINTERED, ANNEALED AND CREPT SN220:

The microstructure of Kyocera SN220 was investigated using both SEM and TEM. A typical micrograph of a polished and etched as sintered SEM specimen (figure 3.1) shows the silicon nitride grain size distribution. The microstructure consists of hexagonal $B-Si_3N_4$ grains, ranging in size from 0.25 to 1.5 microns, with some elongated grains as large as 3 to 8 microns. Porosity information could not be obtained using SEM samples as it was difficult to distinguish between true porosity and polishing artefacts such as particle pullouts.

Additional microstructural information was obtained using thin foils in the TEM. A typical TEM micrograph of the as sintered material is shown in figure 3.2. The hexagonal $B-Si_3N_4$ grains are surrounded by an amorphous intergranular phase. Amorphous inclusions of the same Al/Y ratio as in the grain boundary phase are found in the silicon nitride grains (the Si ratios were not determined as these amorphous bubbles are imbedded in silicon nitride grains). Numerous WSi₂ particles are also found to be present. In addition, some silicon nitride grains contain extensive dislocation tangles as shown in figure 3.2. Very little porosity is seen.

TEM micrographs of annealed material show all of the above

features in addition to a partially crystalline grain boundary phase. The extent of a single crystalline phase is shown in figure 3.3. Here a single YAG crystal surrounds several Si₃N₄ grains. Both YAG and Y₂Si₂O₇ are observed to grow in the same manner. In some cases the Y₂Si₂O₇ phase appeared faulted as shown in figure 3.4. Dislocations are not found in any of these phases. The frequency of dislocations appears similar to the case of the unannealed material although this was not quantified. In addition, there does not appear to be any correlation between the WSi2 particles and their adjacent crystalline or amorphous phase. Amorphous bubbles are also found in the annealed silicon nitride grains. In some cases they appear to be crystalline however the small size of these particles and their location within the grains limited the amount of the analytical work done on them. Again, cavitation was minimal.

The microstructure of samples crept in bending is very similar to that of the annealed material. An additional feature is the large number of bend contours, indicating larger elastic strains in the material. This is not an artefact due to sample preparation as the annealed material (which also contains a crystalline grain boundary phase) does not have the same feature. Contact stresses can also be seen by tilting the sample. An example is shown in figure 3.5. These features are found in both the tensile and compressive sides of bend bars which were crept at 1200°C either to a maximum strain of 1.3% before fracture at 28hrs, or a maximum strain of 1.79% or 0.89% until the test was terminated and samples cooled under load after 218 and 286 hours respectively. The last sample had been preannealed for 200 hours at 1200°C before creep testing in order to partially crystallize the grain boundary phase. Some additional cavitation is found to be present in the foils taken from the tensile side of the bend bar. However even

when the maximum outer fibre strain was 2% the extent of cavitation appears to be still too low to quantify. As the elastic strain in the material is not homogeneous throughout a thin foil and the amount of cavitation was low, no correlation can be seen between cavitation and strain in the surrounding grains.

3.3.2 COMPOSITION OF AS RECEIVED, ANNEALED AND CREPT SN220:

Information regarding the composition of Kyocera SN220 was obtained by bulk powder XRD. The expected XRD patterns for Si6-2Al,N8-2O, with Z=1, 2 and 4.2 (the latter two being the limiting values at 1400 and 1700°C - Jack 1976, 1982) were calculated using the commercially available PULVERIX program and the structure for Si_3N_4 as determined by Hardie and Jack (1957). The maximum Z expected given the amount of Al found in the material is 0.24. As Jack shows, the change in unit cell dimensions of silicon nitride do not vary linearly with Z. As a result the difference in interplanar spacings for low Z (from 0 to 1) is within the experimental error of the X-ray diffractometer (.005-.008A for small Since analysis of the material in the as received d-spacings). condition and after annealing for 600 hours at 1250°C shows no peak splitting (which would indicate a combination of B and B'), all silicon nitride is said to be in the beta form (within experimental error). The presence of a second phase was identified as WSi2. Analysis of samples which had been annealed for various lengths of time in either an air or an inert atmosphere contained additional peaks. The intensities of these peaks relative to the Si₃N₄ peaks do not vary appreciably between the samples annealed for 25 and 500 hrs in air and for 50 and 300 hrs in an inert atmosphere.

Analytical electron microscopy was used to clarify the identification of the crystalline grain boundary phases found in the annealed material. The analysis was done using both EDS and EELS (as discussed in chapter 2) and electron diffraction. Table 3.4 indicates the phases found near the surface and in the centre of samples annealed in both air and inert atmosphere. At 1250°C residual glass and $Y_2Si_2O_7$ are found at all locations. However mullite is found only near the surface of samples annealed in air. YAG is found in the centre of these air annealed materials as well as throughout samples annealed in an inert atmosphere. Samples annealed at 1200°C contain Al_2O_3 at all locations in addition to the phases distributed as found at 1250°C. Electron diffraction of a few crystals of $Y_2Si_2O_7$ in the material annealed at 1200°C has shown it to be in the delta form (see figure 3.6).

EEL analysis was done on the glass phase in the as received and 1250°C annealed condition. The sampling size was large as indicated in table 3.5a by the number of analyses done on samples of different heat treatments. The average compositions of the glasses following different annealing treatments are listed in table 3.5b in both atomic and weight percent: Since compositions from EELS analysis generally underestimate the oxygen content due to a high background fit for the oxygen edge (as explained in chapter 2), the oxygen compositions given here are calculated by assuming the Al, Si and Y content is correct and the glass is of a neutral charge. The difference between these and the uncorrected compositions is small as shown in table 3.5b. The scatter in glass compositions is clearly shown by plotting the individual glass analyses on the Al_2O_3 -SiO₂-Y₂O₃ phase diagram in figure 3.7a. The standard deviations listed in table 3.5b are within the expected experimental uncertainty of \pm 10 a/o as noted in chapter 2.

The same procedure was carried out for samples annealed or crept at 1200°C. Figure 3.7b shows that the glass composition from the tensile side of a bend bar crept for 28 hours is identical to that formed on the compressive side of the bar. This composition is the same as that found in the centre of a sample annealed without stress at the same temperature for 200 hours. A glass with a higher SiO_2 content is found after almost 700 hours at 1200°C (figure 3.7c). This composition is identical to that found after annealing at 1250°C for over 200 hours.

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It should be noted that nitrogen in the glass is at or below the minimum detectibility limit (a few atomic percent). In addition, in all samples analyzed the amorphous phase were homogeneous throughout the TEM foil. The composition did not depend on the identity of the adjacent crystalline grain boundary phase.

The calculated relative weight percentages of the phases found after annealing at 1250°C are shown in table 3.6. These values were determined by solving an elemental balance equation as detailed in appendix 3b. Note that approximately 60 w/o of the glass remains uncrystallized in the centre of samples after annealing at 1250°C, while 30 w/o remains near the surface. It was not possible to do the same analysis for material annealed at 1200°C because of the presence of an additional crystalline phase. This led to 3 equations (for Y, Al and Si) with 4 unknowns (the amount of YAG, $Y_2Si_2O_7$, Al_2O_3 and residual glass).

The rate at which the grain boundary phase crystallizes was determined by plotting the atomic percentage of yttrium in the amorphous phase as determined by EDS against the preannealing time for samples annealed at 1250°C in both air and an inert atmosphere. This relationship, shown in figure 3.8, indicates that the extent of

crystallization is essentially complete within 200 hours at this temperature.

3.3.3. OXIDE AND FRACTURE SURFACE MORPHOLOGY

Surfaces of samples annealed in air at 1200 and 1250°C were characterized in the SEM. The topography of the surfaces annealed in a clean Al₂O₃ tube furnace, on a SiC support plate is similar after annealing for 25, 50, 100, 200 and 400 hours. Samples annealed at 1250°C appear to contain more glass than those annealed at 1200°C (figure 3.9). Bulk XRD of the surface of material annealed in air at either 1200 or 1250°C for 600 hours shows the presence of B-Si3N4, SiO2 (cristobalite) and two sets 'A' and 'B' of unknown peaks. An inert atmosphere anneal at 1200 and 1250°C for 200 and 300 hrs respectively results in B-Si $_{3}N_{4}$, YAG and unknown phase 'B'. These phases are summarized in table 3.4. Unknown peaks 'A' were at a 20 of 16.8, 30.5, 33.3 and 50.8. Unknown peaks 'B' were at 19.2, 27.8, 28.0 and 29.8. Identification of these phases is not possible using XRD due to the numerous overlapping peaks, crystallographic orientational effects and similarities between various combinations of spectra from possible phases. Possibilities for these phases include α , β , γ , and γ polytypes of Y2Si2O7, x1 and x2 polytypes of Y2SiO5.

The surface topography found above differs from that found in a sample annealed at 1250°C for 200 hours, in the same furnace, while sitting on an Al_2O_3 boat. The resulting crystals are much larger and more sharply defined as shown in figure 3.10. EDS has shown these crystals to have a high yttrium content. XRD has shown ß Si₃N₄ and unknown peaks 'A' to be present.
These oxide layers can be contrasted with the same material which has been crept at 1200°C in the bend furnace lined with refractory XRD from the surface shows the same crystal phases to be bricks. present as in the samples which were annealed in air in a clean Al₂O₃ tube furnace on a SiC support. However, large glass regions and pits up to 50 microns in size are also found after annealing for more than 20 hours. Figure 3.11 shows the surfaces of bars from outside of the inner load pins where the effect of the applied stresses are minimal. EDS analysis shows the glass here to be high in calcium content and to contain some iron. The presence of these flaws do not depend on the initial grain boundary structure of the material as evidenced by the similarity of the bars shown in figure 3.11. The sample in figure 3.11a crept for 218 hours. That in figure 3.11b was preannealed for 400hrs to partially crystallize the grain boundary phase, polished to remove any oxide layer, and then crept for 286 hours. Both contain oxide pits. These pits extend into the bulk of the material as shown on the fracture surface (figure 3.12) of a bar polished, preoxidized for 25 hours at 1200°C and then crept at the same temperature for 4.25 hours before failure.

Although these oxide pits would appear to be prime sites for crack nucleation, in most fractured bend bars which were polished immediately prior to creep testing (ie. after any preannealing treatment) it is very difficult to detect any flaw origins. Thus oxides or glassy pits which form during the bend test do not appear to embrittle the material. Difficulty in detecting flaw origins is partly due to the presence of an amorphous film which coats the fracture surfaces and obscures fracture details. As a result, surface relief (shown in figure 3.13), as opposed to transgranular or intergranular fracture, is used to distinguish slow crack growth from fast fracture

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regions. In many cases the presence of a larger damage zone is indicated by the surface cracks found behind the fractured surface (see figure 3.14).

An additional feature of the fracture surfaces is a white border near the outer edges of the bars. The width of this border does not vary with annealing temperature or time. It is often found to be of a different widths on different sides of a bar including sides parallel to the stress axis (ie. not the tensile or compressive faces). Higher magnification of the border (figure 3.15) shows a higher concentration of bubbles here than in the centre of the fracture surface. Auger analysis was performed on this area with a 10kV, 1 uA electron beam on a 0.06mm² area while sputtering the surface with 4kV, 3uA argon ions. Figure 3.16 shows a large increase in nitrogen concentration after approximately half an hour. This indicates that the bubbles are filled with a nitrogen containing gas. The nitrogen content in the intergranular glass was not quantified for the surface versus the centre of samples as the level of nitrogen in the amorphous material was close to the minimum detectibility limit for EEL analysis (a few atomic percent). A faint but similar feature can be seen visually on polished cross-sections of the material both in the as received condition and after heat treatment or annealing in either air or an inert atmosphere. Unfortunately very poor optical contrast made this feature difficult to photograph.

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3.3.4 ANNEALING- DENSITY AND WEIGHT GAIN RESULTS:

The rate of oxidation was determined from the rate of change in weight of the samples which had been annealed at 1200 and 1250°C. The weight gain results are plotted in figure 3.17a in units of mass gain per unit surface area. The data is replotted in figure 3.17b assuming a parabolic relationship. Parabolic rate constants derived from this are 3.8×10^{-12} and $6.12 \times 10^{-11} \text{kg/m}^2 \text{s}$ for 1200 and 1250°C respectively. These values were used to determine an activation energy for oxidation of 1046kJ/mol. Care must be taken in interpreting this value due to the narrow temperature range examined and the different crystal products which form in the material at each of the temperatures (as shown in table 3.4).

Relative density measurements are shown in figure 3.18a. The wide spread in density values in the unannealed material occurs in all four SSN220 bars examined and varies systematically from one end of a sintered silicon nitride bar to the other. When densities are normalized to their initial density, as is shown in figure 3.18b, there is little effect of initial density on the rate of change.

The density change has been determined to be a surface effect since grinding 50 microns off the 600 hour annealed samples increases the relative densities to within 0.05% of the unannealed values. Removal of another 50 microns leads to much smaller increases. The density of the annealed samples relative to (the unannealed condition before and after partial removal of the oxide scale are plotted in figure 3.19.

3.3.5 AMORPHOUS PHASE FABRICATION AND ANALYSIS

Bulk glass samples of similar compositions to those found in the triple points of the sintered silicon nitride material were fabricated. This was done in order to compare bulk crystallization behaviour with that found in the silicon nitride. Glass compositions chosen were that found in the as received material and that found in material annealed at 1250°C. Initially, glasses were fabricated in an inert atmosphere. However they appeared brown in colour. They were then annealed in air at 1600°C for half an hour and then quenched. This resulted in transparent glasses. All glass samples contained small bubbles. Analysis by EELS showed that each glass has the desired composition (ie. no appreciable mass loss occurred during fabrication). XRD analysis of each glass after annealing for 2 hours at 1200 and 1250°C shows the high silica composition, annealed at both temperatures, contains a lot of 'Y'-Y₂Si₂O₇, some B-Y₂Si₂O₇ and Al6Si2O13. The low silica glass annealed at 1200 and 1250°C contain mainly B-Y2Si207, some Al6Si2O13 and small amounts of 'y'-Y2Si2O7 peaks (see figure 3.20) . These results are summarized in table 3.7.

3.4 DISCUSSION

3.4.1 MICROSTRUCTURE OF AS-SINTERED AND ANNEALED MATERIAL:

The microstructure of Kyocera SN220 is typical of that found in sintered silicon nitrides. The distribution of a thin amorphous layer between the grains and the remainder in the triple points, as seen in SN220, is common in silicon nitride materials regardless of the amount of additives used (Krivanek et al 1979, Greil and Weiss, 1982). Impurities such as WSi₂ and iron silicides up to 0.5 microns in size are often found (Tighe et al 1983; Krivanek et al 1979). Small amorphous inclusions in silicon nitride grains have also been found. In SN220 some of these inclusions appeared to crystallize after heat treatments at 1200 and 1250°C. Again these features are typical of silicon nitride material (Evans and Sharpe 1971; Lee et al 1988; Lewis et al 1988). The density of dislocations in SN220 appears to be independent of heat treatment or creep at 1200°C in the time frames examined here. This is contrary to the results of Lee and Hilmas (1989) who found the dislocation density to increase after approximately 5 hours at 1500°C as the intergranular δ -Y₂Si₂O₇ phase transformed to B-Y₂Si₂O₇. These dislocations were easily annealed out after heating for 10-20 hours at this temperature.

The morphology of the crystalline grain boundary phase found in Kyocera SN220 after annealing at 1200 and 1250°C is commonly seen in Y_2O_3 containing materials (Bonnell et al 1987; Lee et al 1988). The formation of large intergranular crystals surrounding several silicon nitride grains is thought to be due to a nucleation controlled process. Since the crystalline grain boundary phase extends in 3 dimensions and TEM foils allow one to see through only a small slice of that, the intergranular nucleation sites can not be didentified. However, in a study of bulk Y_2O_3 -Al₂O₃-SiO₂ glasses, Dinger et al (1988) found iron silicide impurities to act as the nucleation sites for $y-Y_2Si_2O_7$. As no correlation was found between WSi_2 particles and their adjacent phases (crystalline or amorphous), it does not appear that these particles are nucleation sites in SN220.

The amorphous intergranular phase in the as sintered material surrounds the Si_3N_4 grains. The space it occupies includes pockets between four or more grains, channels between three grains and films

between two grains. The grain boundary crystalline network extends around several Si_3N_4 grains as shown in figure 3.3. This crystalline area may be interconnected by crystalline material in the 3-grain channels, with the boundary between two grains remaining amorphous. According to Raj (1981a), this remaining film would be expected to be a monolayer thick (based on minimizing the interfacial energy contribution) assuming the solid-glass interfacial energy term were independent of glass thickness. A larger equilibrium layer is predicted by Clarke's (1987) model based on a force balance including steric effects in the amorphous film. These forces are discussed in detail in chapter 4.

The thickness of the glass film between grains has not been addressed in the current work. It should be noted that using high resolution electron microscopy to determine whether or not an amorphous grain boundary film is present and how thick it is, is not a simple task (Krivanek et al 1979; Clarke 1979a,b; Lou et al 1978). However this problem has been examined extensively by Clarke (1988), Ahn and Thomas (1983), and Lou et al (1978). A thin amorphous phase was found between silicon nitride grain with and without a partially crystalline grain boundary phase, and between the crystalline intergranular phase and adjacent silicon nitride grain (Krivanek et al 1979).

3.4.2 INTERGRANULAR PHASE COMPOSITIONAL ANALYSIS

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Compositional and phase information on the initially amorphous intergranular regions have been determined with the use of analytical electron microscopy (AEM) and x-ray diffraction (XRD). The composition of the amorphous phase as determined by AEM is plotted on a $Y_2O_3-SiO_2-$

 Al_2O_3 diagram in figure 3.7. A nitrogen containing phase diagram was not used for several reasons. First, EELS has shown that nitrogen is at or below the minimum detectibility limit (approximately 5%) in the amorphous phase. Moreover, neither AEM nor powder XRD indicate the presence of any nitrogen containing crystalline phase. Also, the powder XRD results indicate that $B-Si_3N_4$, not B-sialon, is present after sintering and annealing. Finally, there is no significant change in silicon nitride grain size or grain shape during annealing or creep, which suggests that the silicon nitride does not react with the amorphous phase. Thus the phase diagram of interest is the $Al_2O_3-Y_2O_3-$ SiO₂ diagram.

It is useful to analyze crystallization data for SN220 and the fabricated glasses, in the light of related work by other researchers. Figure 3.21 shows the experimental behaviour diagram as determined by O'Meara et al (1987) for glass compositions fired in air at 1500°C for 1hr and then annealed for up to 24hrs at 1250°C. The crystallization products found by O'Meara et al are indicated by the compatibility triangles. Additional glass compositions which were annealed at 1100°C (presumably in air) for 6hrs by Hyatt and Day (1987) are also shown on this diagram. They found slightly different results as shown in figure 3.21. Neither found the products observed by Bondar and Galakhov (1964) as shown by the compatibility triangles in figure 3.22 along with the relevant binary phase diagrams (from O'Meara et al, 1987). It is worth noting again that the presence of the 2Y203.3SiO2 phase is currently being questioned (Drummond et al 1988, Liddell and Thompson 1986). Clearly the crystallization behaviour of this system is not well characterized.

In the current study the crystalline products found in the centre of SN220 samples annealed in air and throughout the samples

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annealed in an inert atmosphere are $Y_2Si_2O_7$ and YAG $(Y_3Al_5O_{12})$. After annealing at 1200°C, Al_2O_3 was found in addition to $\delta-Y_2Si_2O_7$ phase and YAG. Given O'Meara's compatibility triangles $Y_2Si_2O_7$, mullite, Al_2O_3 and/or SiO₂ would be expected. This discrepancy is not thought to be due to inaccurate determination of the glass composition as the composition determined by EELS of well characterized compounds shows the accuracy of the technique to be within 10% (as shown in chapter 2). In addition the fact that Al_2O_3 is found after annealing at 1200°C and SiO₂ is never found indicates that this discrepancy is not due solely to inaccurate compositional results.

The crystal phases found on the surface of SN220 after heat treatment in air depend on the environment of the anneal. The phases found by XRD after air exposure at 1200 and 1250°C include unknown phases A and B, mullite and cristobalite as determined by bulk XRD. Specifically, more SiO₂ was formed when the sample was contained in the refractory brick lined creep furnace or if the sample was in a clean furnace on a SiC boat. It did not form to the same extent if an Al₂O₃ boat was used. This suggests there is some reaction between the silicon nitride and the SiC or refractory furnace. Since TEM foil preparation of the immediate surface a unsuccessful, the identification of phases A and B could not be determined. TEM analysis did show that at 10-200 microns below the surface mullite forms along with $Y_2Si_2O_7$ after annealing at 1250°C (Al₂O₃ forms in addition to mullite and δ - $Y_2Si_2O_7$ at 1200°C). It is possible that the oxidation of the surface Si₃N₄ and/or the glass promotes the growth of mullite, a SiO₂ rich phase.

TEM analysis using EELS was used to provide quantitative chemical information on the amorphous intergranular phase as well as on the crystalline phases. Figure 3.7a shows the intergranular compositions for samples in the as sintered condition and after

annealing at 1250°C in both an air or an inert atmosphere. The composition of the residual glass was the same regardless of annealing atmosphere, the location of the TEM foil with respect to the surface of the annealed sample, and the identity of adjacent crystals. This implies sufficient diffusion occurs over the order of a few microns but that no gross ion diffusion occurs towards or away from the surface (as will be dealt with shortly). Knowing the composition of the amorphous phase both before and after annealing, as well as the phases which crystallize, it was possible to do an elemental mass balance to determine to weight percentages of each phase present. Using an estimate of 3.8g/cm³ for the density of the amorphous phase (measured by Loehman (1979) for a glass of composition 16.6a/o Y, 15% Si, 3.2% Al, 65.1% O, similar to the measured residual glass composition of 6a/o Y, 25%Si, 12% Al, 57% O), the volume fraction of each phase could also be calculated. For the cases of an inert atmosphere anneal and in the centre of air annealed samples, the three unknowns are the quantities. of Y₂Si₂O₇, YAG and residual glass. These can be written in terms of the compositions of each phase as follows:

с.	2.0 0.0 2.0	3.0 5.0 0.0	0.0576 0.1106 0.1934	XY2Si207 XY3Al5012 Xresid.glass		P	0.0933 0.1145 0.1602] 。
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Solutions of these expressions lead to the following relative fractions of each phase:

61	±.	7	w/o	- 8	÷	65	±	9	v/ 0	residual	glas
19	±.	4	w/o		Ħ	15	±	3	v/o	Y3A15012	
20	£	3	w/o		=	20	±	3	v/o	Y2Si2O7	

For the material near the surface of samples annealed in air at 1250°C, the same procedure produced:

50	±	8	w/o	•	=	52	±	10) v/0	o Y ₂ S	1207	
22	±	5	w/o		=	18	±	5	v/o	Al ₆ s	12 ⁰ 13	3
27	±	2	w/o		=	30	±	4	v/ o	resid	lual	glass

This assumes that the change in composition of the amorphous phase due to oxidation of the Si_3N_4 grains is below the error in the composition determined using EELS. As the composition of the amorphous phase in the as received material lies on the tie line between the $Y_2Si_2O_7 - YAG Al_2O_3$ and the $Y_2Si_2O_7 -$ mullite - Al_2O_3 compatibility triangles (figure 3.21), slight increases in the Si and O content would increase the likelihood of forming mullite over YAG. The above calculations indicate that the near surface regions of air annealed samples contain considerably less residual glass.

One might expect the difference in the amount of intergranular phase present in the two cases to the obvious when analyzing TEM samples. However estimating the amount of residual glassy phase is difficult since the amorphous phase in SN220 shows a similar contrast to that of silicon nitride and mullite crystals when they are not in a strongly diffracting condition. The glass is of course differentiated from the crystals by its lack of diffraction contrast on tilting. However, visual identification of a phase which does not change contrast and is surrounded by many crystals of different orientations requires careful work. For this reason an estimate of the volume fraction glass from TEM images could not be obtained, although it was found that amorphous regions were slightly easier to find in samples which has been annealed in either an inert atmosphere or were taken from the centre of material a annealed in air. As the contrast of Y containing compounds was different from the silicon nitride grains, qualitatively assessing this difference was easier. The fraction of crystalline Y compounds appeared similar in each. The above calculations indicate that this should be

the case.

3.4.3 RATE OF CRYSTALLIZATION AND ION MIGRATION:

An analysis of the composition of the amorphous phase in all heat treated samples (including areas near both the surface and centre, in samples annealed in either air or an inert atmosphere), gives some indication of the rate of crystallization. Figure 3.8 shows the fraction yttrium in the amorphous phase as determined by EDS analysis as a function of annealing time at 1250°C. Clearly a relatively stable yttrium content is obtained between 50 and 200 hours. This composition remains unchanged up to at least 600 hours, the longest annealed composition analyzed. The same trend is seen for samples heat treated or crept at 1200°C. However, the same final compositions are not reached within 200 hours, but are found after 700 hours (figures 3.7a,b,c). Although additional samples heat treated for intermediate lengths of time were not analyzed, it is clear that the intergranular phase in samples heat treated at 1200°C for 0, 50, 100 and 400 hours have crystallized to differing degrees.

Surface oxidation does lead to the formation of mullite, a silica rich crystalline phase not found in the interior, in addition to $Y_2Si_2O_7$. This is similar to the findings of Quinn and Braue (1989) where a silica rich pyrosilicate ($Y_2Si_2O_7$) is found at the surface rather than Y_2SiO_5 as found in the bulk. The glass composition near the surface of the SN220 air annealed samples is the same as that found in the interior where different crystal products ($Y_2Si_2O_7$ and YAG) occur. It appears that the effect of the oxidation of surface material does not significantly effect the composition of the underlying glass, indicating

that no gross inward diffusion of oxygen or outward diffusion of cations occurs through the glass. This is supported by density measurements taken before and after annealing with 0, 50 and 100 microns of the surface material removed show that any change in density is a surface phenomenon. As the relative change in density of material annealed in air, after removal of the surface 100 microns is 0.005, which corresponds to a less than 2% relative change in Y and Al concentration, there appears to be very little long range ion diffusion. There is however diffusion in the amorphous phase as all the glass analyzed is of a uniform composition regardless of the adjacent crystalline phase.

The lack of evidence for long range diffusion can be compared to results found by other researchers (Babini et al, 1984; Bouarroudj et al, 1985; Falk et al, 1985; and Sato et al, 1987) where yttrium, aluminum and impurities have been found to migrate to the surface. The first three groups used EDS line scans in the SEM to detect yttrium concentration profiles¹. The concentration profile given by Babini shows the Y and Al to be concentrated in the top 25 microns and depleted in the underlying 40 microns. Sato et al. infer grain boundary migration since XRD peak intensity increases with annealing time. A subsequent paper by Falk and Dunlop (1987) attribute the occurrence of yttrium rich crystalline products near the surface and yttrium poor products in the interior of samples annealed in air to yttrium ion migration and subsequent glass crystallization. In none of the above cases is the concentration profile of the as received material given. The gradient is assumed to result solely from annealing, not sintering.

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¹ Our attempts to determine ion concentrations by either elemental mapping in the SEM or by microprobe analysis proved to be irreproducible. This was due in part to the low levels being detected (as approximately 4w/o each of Y_2O_3 and Al_2O_3 are present in the silicon nitride material, as opposed to $Bw/O Y_2O_3$ in Babini's material), the partial overlap of adjacent Si-K and Y-L peaks, and the problem of fluorescence of Si-K peaks by the Y-L energies.

Oxidation activation energies determined for this process range from 260 to 800 kJ/mol. These are lower that the 1046 kJ/mol value measured for SN220. However the validity and usefulness of this value is questionable as different crystal products are found near the surface of the material by TEM at 1200 and 1250°C and the oxide products are environment dependent (as evidenced by figures 3.9, 3.10 and 3.11). In none of the cases from the literature have these effects been taken into account.

Ion migration has also been used to account for the presence of a light coloured border at the edge of the material (Bouarroudj et al 1985). A similar border is also seen in Kyocera SN220. This border is most clearly seen on the fracture surfaces of the crept bars where bubbles are found in the glass. The width of the border does not depend on the bend test temperature or time and it may or may not be of equal width on all sides of the bar (which were machined from a slightly larger bar). As the colour difference is also seen on polished crosssections of the material in the as sintered condition and after annealing in both air and an inert atmosphere, it can be concluded that this colour difference is not a ⁽⁾function of grain boundary Instead, it is most likely to result from the crystallization. fabrication process. This coloured border is commonly seen in sintered material and is thought to be due to lower dopant concentrations at the surface of the material when a sintering bed with low dopant levels are used (Liu and Li, 1989; Pugh 1989). Any differences in dopant or impurity concentrations in SN220 were too small to detect by AEM. However, the difference in bubble formation at the creep temperatures indicate that either the border region has a lower viscosity than the centre of the bar, or that the rate of reaction (possibly oxidation of Si_3N_4 as Auger analysis indicates bubbles in the border contain

nitrogen) occurs at a different rate in the two regions.

The oxide scale was not investigated further as it was found to be a function of annealing environment and, as explained in chapter 4, it was removed prior to creep testing to eliminate surface pits. Any new oxide layer formation did not appear to affect the creep lifetime of the material in bending or compression.

3.4.6 AMORPHOUS PHASE FABRICATION AND CRYSTALLIZATION PRODUCTS:

The amorphous phase compositions determined by EELS and EDS are shown in figure 3.7. The composition of the glass has been found to be homogeneous throughout the material. As it is independent of the adjacent crystalline grain boundary phase, diffusion through the glass must be occurring readily on a scale at least that of the silicon nitride grains and of the intergranular grains (0.25 to 8 microns as shown in figure 3.1). This suggests that the amorphous phase is interconnected (consistent with the calculation by Clarke (1988) for a stable intergranular film). Moreover, the uniformity of the final amorphous phase composition, regardless of location or annealing atmosphere, suggests the presence of a stable glass. This was investigated experimentally instead of theoretically for several reasons. First, the available thermodynamic data for the Y-Al-Si-O system are incomplete. In addition, some of the expected phases are currently being questioned (e.g. Lee et al (1988) [and Liddell and Thompson (1986) question the presence of 2Y203.3SiO2). Finally, kinetic factors would not be taken into account. Therefore, glasses of the same compositions as those found in the silicon nitride material were

fabricated. Compositions were confirmed by EELS to check that elemental losses had not occurred during fabrication. Annealing the glass with the low silica composition (the same as found in the as sintered material) resulted in mainly β -, some 'y'-Y₂Si₂O₇ and mullite being formed. By way of comparison, δ -Y₂Si₂O₇ and mullite were found in the surface region of air annealed SN220 samples. The high silica glass contained 'y'-Y₂Si₂O₇, some β -Y₂Si₂O₇, and mullite after annealing. This glass was the same composition as the residual glass found in the SN220 after annealing. There are several reasons which may explain why the bulk glass crystallized, and the difference in crystallization products between the glass in the silicon nitride material and in the bulk. These will now be examined.

A factor not taken into consideration in assessing the residual glass stability is the effect of a negative hydrostatic pressure. This pressure may develop due to a decrease in volume of the intergranular phase during crystallization. It is unlikely that this occurs as residual glass can flow inwards to accommodate the volume change. The ability of the glass to flow is supported by observations of a very homogenous residual glass composition.

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Another possibility is that the remaining amorphous triple points are smaller than required for nucleation of the crystalline boundary phase (Raj, 1981; Raj and Lange, 1981; Falk and Dunlop, 1987). However growth of adjacent crystals through large interconnected channels would then be expected. These channels exist as crystalline boundary phases are observed to surround several Si_3N_4 grains. This would lead to a SiO_2 -rich glass. As this does not occur, it appears that the residual glass may be stable.

The δ -Y₂Si₂O₇ polymorph found in the interior of SN220 differs \simeq from the polymorphs found in the annealed glasses (B and 'y'-Y₂Si₂O₇).

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The conditions under which one phase forms preferentially over another is not currently understood. The different polymorphs have been found in other silicon nitride work as well. For example Falk and Dunlop (1987) found the $B-Y_2Si_2O_7$ polytype on the surface and the α polytype at depths greater than 200 microns from the surface of Y_2O_3 -Al₂O₃ doped samples (produced by nitridation and pressureless sintering followed by heat treatment in air at 1400°C). Researchers in the same group (O'Meara et al., unpublished work) made a series of glasses with a fixed $Y_2O_3-Al_2O_3-SiO_2$ ratio and varying amounts of Si_3N_4 in order to study crystallization behaviour of glasses of similar composition as the grain boundary phase in the silicon nitride material. They found that on crystallization, the compositions with lower Si_3N_4 levels contained the α as well as the ß phase. Drummond and Lee (1988) have also done extensive work on Y_2O_3 -SiO₂ glasses for comparison with a Y_2O_3 doped silicon nitride (Lee et al 1988). They find the B Y2Si2O7 phase forms in Y_2O_3 doped silicon nitride when either no SiO₂ or 3.6 w/o SiO₂ has been added. This can be compared with work by Kumar and Drummond (1989) who find predominantly the γ form when a glass of approximately the same composition as the second silicon nitride made by Lee et al (above) and mainly the B form in lower silica glasses. These results do not agree with previous work by the same group (Drummond et al. 1988) where a variety of phases are found for glasses of the same composition.

The fact that the 'y'-Y₂Si₂O₇ polymorph was found in the fabricated glasses after annealing leads one to question the importance of impurities. $y-Y_2Si_2O_7$ is an impurity stabilized form with the general formula $RY_5Si_6O_{21}$ where $R=H_+$, Na_+ , Mg_{2+} , Mn_{2+} , Fe_{2+} , Fe_{3+} , Al_{3+} , Th_{4+} , or $2r_{4+}$. The 'y' phase has also been known to transform to $\alpha-Y_2Si_2O_7$ on heating to 1200°C (Liddell and Thompson 1986). The α phase, according to Ito and Johnson (1968), should transform to B at 1225°C. Clearly if

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the 'y' phase is present in the fabricated glass and neither the 'y', α or B phases are present in SN220, the difference in the impurity content of the two glasses may be significant. This may have a large effect of the overall stability of the glass.

An impurity found in the SN220 glass at concentrations of a few atomic percent (as determined by EDS), but not considered in the fabricated glass, is calcium. Previous work of Thorel et al (1986) has shown decreasing the level of calcium impurities in sialon ceramics promotes the formation of YAG instead of a glassy phase. Thus had calcium been present in the fabricated glass, the effect of heat treatment may have been different.

3.4.7 MICROSTRUCTURE OF CREPT SAMPLES

The microstructure of the crept material appears identical to that of the annealed material with the added contributions of cavitation and internal strain. Care was taken to ensure that the cavitation damage or internal strain, identified by TEM, was due to creep deformation and not initial sintering porosity or sample preparation artefacts. Cavities are found in the triple points and occupy the complete grain junction, a feature also found by Tighe et al (1983). Unlike Clarke (1985) and Marion et al (1983), no cases were found in which amorphous material still surrounded the cavity. However as the cavity density was low it is possible that this feature was simply not observed (Clarke, and Marion et al state that only a few of these cavities were found). Additional effects of stress were found by Tighe (1978 and 1983). Bubbles were found in the silicon nitride grains on the compressive side of a bend bar. Tighe also states that some

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thickening and distortion of the $Y_2Si_2O_7$ phase was found on the compressive side of bend bars crept at 1400°C to 0.27% outer fibre strain. These effects are the result of stress accommodation. These features were not seen in the current work on SN220, possibly because tests were run at a lower temperature (1200°C).

Contact stresses, as found in crept SN220, appear similar to 'stain whorls' found by Quinn and Braue (1989) and Lange et al (1980) in silicon nitride materials. "Quinn and Braue found this feature near the tensile surface of a Y_2O_3 -Al₂O₃ doped Si₃N₄ crept in bending, indicative of grain boundary sliding. Lange et al saw this feature in a MgO doped silicon nitride material which was crept in compression and cooled under load. They did not see it when the material was relieved of applied loads before cooling. This corresponds well to their observation of strain recovery at high temperatures. In the current study the presence of internal strain, as observed by TEM regardless of cooling conditions, indicates that little or no strain recovery occurs between the time a bend bar fractures and it is cooled (the time for the temperature to drop form 1200°C to 800°C is approximately 10-15min.). Residual stresses have also been detected in some materials after annealing. This is expected due to grain boundary crystallization and differences in thermal expansion (Bonnell et al 1987).

The density of dislocations in the silicon nitride grains does not appear to be affected by creep. Dislocations are inhomogeneously distributed, existing mainly in large tangles inside grains. This is similar in both the as received and annealed materials. Thus the dislocation density was not assessed quantitatively. As cavitation density was low, no correlation could be made between dislocations and cavities as seen by Din and Nicholson (1975) on the tensile side of bend bars crept at 1200°C. Similarly, as TEM foils did not contain any creep

cracks, dislocation activity at crack tips could not be assessed. Thus dislocation formation could not be compared to that found by Tighe (1978) where dislocations were generated at the crack tip in double torsion specimens. Tighe also found dislocations associated with grain boundaries in the compressive side of bend bars crept at 1400°C. Since they were not present in the as received material they must have occurred as a result of bending.

An additional stress-induced microstructural change is the deformation of the intergranular grain boundary phase. Quinn and Braue (1989) found that the intergranular phase $\delta Y_2 Si_2 O_7$ contains more faults after deformation at temperatures 1200°C than 1000°C. As this phase is known to be highly faulted and is often twinned (Dinger et al 1988), it is thought that it can accommodate deformation by diffusional rearrangement or twinning (Quinn and Braue 1989). The $Y_2 Si_2 O_7$ phase found in SN220 often appeared faulted, or more specifically to contain grains which were slightly misoriented (figure 3.4). Additional faults or twinning in the crept material was not noticed, however the material was not analyzed with this in mind.

No other stress induced microstructural changes were found in Kyocera SN220 or have been reported in silicon nitride materials.

3.4.8 OXIDE AND FRACTURE SURFACE MORPHOLOGY:

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SEM analysis of the annealed surfaces indicate the formation of surface crystals and glass. The surfaces of samples crept for comparable lengths of time also contain large amorphous pits. As these pits occur on all areas of the bend bar, they are not due to the effect

of surface stress. The difference is due to the atmosphere. The annealed samples were heated in a clean alumina tube furnace and the bend bars in a refractory brick lined furnace. Impurities given off from the furnace lining react with the silicon nitride material forming large pits. These pits have not been found to be flaw origins in any of the fracture surfaces of as sintered material. For materials annealed before creep testing, provided the material is polished prior to creep testing, the surface flaws do not appear to be strength limiting.

Analysis of the fracture surfaces of crept SN220 did not provide much information due to the presence of an amorphous film which formed over the fracture surface. This film may be the result of surface oxidation and survivion of the intergranular phase. The latter has been seen by Clarke (1985) on the oxide surface of a hot pressed alumina containing an intergranular amorphous phase. This effect may not be as pronounced in SN220 as it was sintered under atmospheric pressure. In addition, partial crystallization of the intergranular film has two effects on glass extrusion. It decreases the amount of glass available to be extruded and, through a decrease in volume as a result of crystallization, causes a decrease in pressure of the intergranular Thus less glass would be expected to flow to the surface. phase. Observations of an amorphous film on both annealed and fracture surfaces for samples with a totally amorphous and partially crystalline grain boundary phase indicate that intergranular extrusion is not the predominent source of amorphous film. A light etch to remove the amorphous film was not effective in distinguishing between intergranular and transgranular fracture, or in helping to detect flaw origins. Determining the size of the slow crack growth region was easily done by looking at the surface topography at lower magnification (figure 3.13).

Additional cracks were sometimes seen on the fracture surface, indicating a larger damage zone existed (figure 3.14).

3.5 CONCLUSIONS:

SN220 contains an amorphous intergranular phase which partially devitrifies upon annealing. The composition of the initial and residual glass was determined with the use of EELS and found to be very homogeneous, indicating diffusion occurs readily in the glass. Unfortunately, even knowing the amorphous phase composition, the crystallization products could not be predicted using existing phase Although the residual glass was of the same composition diagrams. throughout samples annealed in either an inert or air atmosphere, a silica rich phase (mullite) is found near the surface of samples annealed in air in place of YAG. The possibility of the residual glass being a thermodynamically stable phase was investigated experimentally instead of theoretically as thermodynamic data are not available for all It was found that the residual glass was not phases of interest. However, as a glass of the same composition as the initial stable. amorphous phase in SN220 was also fabricated and heat treated, and found to produce different crystallization products, the effect of impurities (particularly calcium) and pressure constraints on the crystallization process could be an additional influencing factor. Impurities may also affect the viscosity of the intergranular phase or rate of oxidation as shown by the extent of 'bubble' formation in the amorphous film on the fracture surfaces. The intergranular glass Y-Al-Si-O composition in both regions was identical. However, N content was at or below the

detectibility limit, impurity levels of Ca were not quantified and other impurities may have been present but not detected.

The fraction of residual glass in SN220 was calculated using an elemental mass balance of the intergranular phases. It is approximately 60v/o in samples annealed in an inert atmosphere and in the centre of samples annealed in air at 1250°C. This is twice as much residual glass as found near the surface of samples annealed in air (assuming the composition of the intergranular phase is not changed due to oxidation of the Si₃N₄}. Crystallization in both cases approached completion in between 50 and 200 hours.

The evolution of the intergranular phase was the same in crept samples as in annealed material (as regards to the crystalline products formed and the residual glass composition). Additional features in crept material include a significant amount of internal strain, evidence of contact stresses and some cavitation. As cavitation was limited, no correlation was found between cavities and intergranular phases.

Fracture surfaces of bars crept in bending were analyzed. Fracture origins were rarely found, although the thin glass film which coated the surfaces may have obscured small flaws. It should be noted that oxide pits which formed during the bend tests were not fracture origins. Oxide pits which resulted from preannealing and which were not removed prior to creep testing did cause fracture. For this reason all samples which were preannealed to partially crystallize the grain boundary phase were polished prior to creep testing. The oxide scale was not investigated further as it was found to be a function of annealing environment and, provided samples were polished prior to creep testing, it did not effect creep behaviour. Cracks behind the bend bar fracture surface were often found in addition to large slow crack growth regions, indicating a diffuse damage region.

3.6 Tables and Figures

Table 3.1

SN220 Chemical Analysis

Element	Amount
Al	$2.2 \pm 0.1 $ w/o
Ca	$0.13 \pm 0.02 \text{ w/o}$
Fe	$0.124 \pm 0.001 \text{ w/o}$
K	<20 ppm
Na	<50 ppm
W	$1.30 \pm 0.01 \text{ w/o}$
Y 1	$3.00 \pm 0.01 \text{ w/o}$
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Heat Treatment Conditions Used to Study the Effect of Annealing on Microstructural Evolution.

1200°C Ai r	25hr 50 100 200 400 600 [*]	1200°C	Argon	25hr 50 100 200 400
1250°C Air	25hr 50	1250°C	Argon	25hr 50 100
	200 400 500 ^{**} 600	\$ e	, 	200 300 400

* 4 samples with weight gain and density measurements done at 25, 50, 100, 200, 300, 400 and 600 hours.
** 4 samples with weight gain and density

** 4 samples with weight gain and density measurements done at 25, 50, 100, 200, 400 and 500 hours. $\mathbb{P}^{\mathbb{P}^{n}} \to \mathbb{P}^{n} \in G$

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Heat Treatment Conditions for Samples Analyzed in TEM and by IRD.

TEM:	•	•		
TEMPERATURE	ATM	TIME	LOCATION IN	ANNEALED SAMPLE
(°C)		(hr)	CENTRE	SURFACE
as sintered	n/a	0	centre	near surface+
1200	air	200	centre	
1200	air	28		near tensile and
				compressive [*]
1200	air	700		near tensile and
	-		C	compressive**
1250	air	50	centre	near surface
1250	air	400	1	near surface
1250	air	500	centre	
1250	argon	25	centre	near surface
1250	argon	200	centre	near surface
1250	argon	300	centre	near surface
		1 C C		

XRD:			
TEMPERATURE	ATM	TIME	LOCATION IN ANNEALED SAMPLE
(°C) ≦		(hr)	
as sintered	n/ã	0	surface and interior (powder)
1200	air	24*	surface
	air j	200	surface
·	air	600	surface
1200	argon	200	surface
	argon	400	surface
1250	air	200°	surface
А	air	260 ⁰⁰	near surface (powder)
	air	500	interior (powder)
	air	600	surface
1250	argon	200	surface
	argon	300	surface
2	-		

All samples annealed on a SiC boat in alumina tube furnace except where noted.

"sample crept in bending

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**sample annealed 400hrs prior to creep testing in bending (it was very difficult to obtain thin areas in TEM foils at the surface, near surface is 10 to 200 microns form the surface. Oannealed on an Al₂O₃ boat ⁰⁰crent in bending 45WPa material taken near tensile and compressive

 $^{\rm oo}{\rm crept}$ in bending, 45MPa, material taken near tensile and compressive faces and crushed.

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Phase Identification by TEM and IRD of SN220 in as sintered condition and after annealing in air and inert atmospheres at 1250°C and 1200°C (in addition to B-Si₃N₄ and WSi₂).

samples	XRD surface	TEM near surface	TEM centre
As Sintered	none	glass	glass 🍣
Air Anneal 1250°C	SiO ₂ phase 'A' phase 'B'	Y ₂ Si ₂ O7 mullite residual glass	Y ₂ Si ₂ O ₇ YAG residual glass
Inert Anneal 1250°C	YAG phase 'B'	Y ₂ Si ₂ O ₇ YAG residual glass	Y ₂ Si ₂ O ₇ YAG residual glass
Air Anneal 1200°C	SiO ₂ phase 'A' phase 'B'	Y ₂ Si ₂ O7 mullite Al ₂ O3 residual glass	Y ₂ Si ₂ O7 YAG Al ₂ O3 residual glass

YAG Inert Anneal phase 'B' 1200°C 0

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*SiO₂ = crystobalite, YAG = $Y_3Al_5O_{12}$, mullite = $Al_6Si_2O_{13}$

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Table 3.5a: Number of amorphous pockets analyzed from samples of different annealing conditions.

anneal	near surface	ŧ	centre	ŧ
as sintered	as sintered	2	as sintered	2
1250°C	air 500hr	2	air 200hr	1
anneal			air 400hr	- 8
	inert 25hr		4	
i a cara da car	inert 200hr	3	inert 200hr	1
	inert 300hr	3	inert 300hr	3
1200°C	air 200hr	5	air 28hr	1
anneal	· · · · · · · · · · · · · · · · · · ·	<i>1</i>	air 686hr	3

⁹composition identical to as sintered condition *samples crept in bending at 1200°C **sample annealed 400hr, crept 286hr at 1200°C

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Table 3.5b: Average compositions of glass in as sintered condition and (after annealing. As compositions from EELS analysis generally underestimated the oxygen content due to a high background fit for the oxygen edge, the compositions given here are calculated by assuming the Al, Si, and Y content are correct and the glass is of a neutral charge. The unadjusted composition of the as sintered glass is $Al_{12+2}Si_{17+2}Y_{11+1}O_{60+3}$, the 1250°C annealed glass is $Al_{12+1}Si_{22+2}Y_{6+1}O_{60+2}$.

samples	composition atomic %	composition weight %	
As Sintered (avg of 8)	^{Al} 11±2 ^{Si} 16±2 ^Y 9±1 ^O 63±7	21±4 Al ₂ 03.36±5	sio ₂ ·43±4 ¥203
1250°C (avg of 21)	Al _{11±2} Si _{19±2} Y _{6±1} 0 _{64±4}	24±2 Al ₂ 0 ₃ ·49±6	SiO ₂ ·27±6 Y ₂ O ₃
1200°C 28 and 200hrs (avg of 16)	Al _{14±1} Si _{15±1} Y _{8±1} 0 _{62±8}	28±2 Al ₂ 0 ₃ ·37±2	SiO ₂ ·34±3 ¥203
1200°C 686hr ° (avg of 3)	Al _{13±2} Si _{19±1} Y _{5±1} O _{62±1}	28±3 Al ₂ 0 ₃ ·47±1	SiO ₂ ·25±4 Y ₂ O ₃

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Calculated Weight Percentages of Phases Present After Annealing at 1250°C:

air-centre and inert-centre and near surface air-near surface

20±3 Y₂Si₂O₇ 19±4 Y₃Al₅O₁₂ 61±7 residual glass 50±8 Y₂Si₂O₇ 22±5 Al₆Si₂O₁₃ 27±2 residual glass

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Figure 3.1. Polished and etched SN220 surface. Bar is 10 microns.



Figure 3.2. (a) Bright field micrograph of as sintered SN220. Si_3N_4 grains surrounded by an amorphous intergranular phase. Some grains contain impurities. Si_3N_4 grains at upper left contain dislocations. Centre dark grain is WSi₂. (b) Dark field micrograph clearly showing distribution of amorphous phase.



Figure 3.3. Bright and dark field micrographs of a single YAG crystal surrounding several Si_3N_4 grains.



Figure 3.4. Faulted Y₂Si₂O₇ crystal in SN220 intergranular pocket.

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Figure 3.5. TEM micrograph from near compressive surface of a bend bar crept at 1200°C for 28 hours. Fracture strain was 1.3%. Bend contours indicate presence of internal strain despite amorphous pockets seen in centre.

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Figure 3.6. CBED (convergent beam electron diffraction) pattern of $\delta Y_2 Si_2 O_7$ from sample annealed at 1200°C for 300 hours. The presence of two mirror planes (labeled m) as seen in the HOLZ, indicate the phase has a whole patern symmetry of 2mm. Therefore there are at least two orthogonal axis (i.e. it is not monoclinic like gamma or $Y Y_2 Si_2 O_7$, X_1 or $X_2 Y_2 SiO_5$ or triclinic like $\alpha Y_2 Si_2 O_7$). Zone axis [010]. e e

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Figure 3.7a. Amorphous phase compositions as determined by EELS. Samples are SN220 in the as sintered condition and after annealing at 1250°C from 200 to 500 hours. Annealed data includes material near the surface of samples annealed in an inert atmosphere and material in the centre of samples annealed either air or an inert atmosphere.

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Figure 3.7b. Amorphous phase compositions in SN220 after creep testing at 1200°C for 28 hours. Samples taken from tensile and compressive sides are indicated.


Figure 3.7c. Amorphous phase compositions in SN220 from centre of samples annealed at 1200°C for 200 hours and from centre of sample crept at 1200°C for 286 hours after a 400 hour anneal.

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Figure 3.8. Fraction yttrium in amorphous phase as determined by EDX as a function of annealing time at 1250°C.



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Figure 3.9. Surface of SN220 after annealing in an alumina tube furnace for 400 hours at (a) 1200°C and (b) 1250°C. Bar is 10 microns in both cases. Samples annealed while sitting on a SiC support.



Figure 3.10. Surface of SN220 after annealing in an alumina tube furnace for 200 hours at 1250°C. Sample annealed while sitting on an Al_2O_3 boat.



Figure 3.11. Surface of bend bar after 1200°C (a) 218 hour creep test (b) 400 hour anneal, surface polished, followed by a 286 hours creep test.



Figure 3.11 c. Higher magnification of pit shown in 11b.



Figure 3.12. Fracture surface of sample polished, annealed at 1200°C for 25 hours, following by a creep test at 1200°C. Sample fractured in 4.25 hours.



Figure 3.13. Fracture surface of bend bar showing extent of slow crack growth region.



Figure 3.14. Crack below the fracture surface.



Figure 3.15. (a) White 'bubble' border as seen on fracture surface. (b) Higher magnification of edge of border.





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Figure 3.17a. Weight gain of samples annealed in an alumina tube furnace (while sitting on a SiC plate), in air at 1200 and 1250°C as a function of annealing time.

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Figure 3.17b. Data of fig. 17a. plotted as weight gain squared as a function of annealing time.

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Figure 3.18a. Change in density with annealing time at 1200 and 1250°C. Density measurements are relative to a dummy, unannealed sample.

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Figure 3.18b. Change in density (normalized to density of sample before annealing) with annealing time.

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Figure 3.19. Density change measured after removal of 0, 50 and 100 microns of surface oxide for samples annealed 600 hours at 1200 and 1250°C.





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Figure 3.21. Experimental behaviour diagram from O'Meara et al, 1987. All compositions indicated formed all the products expected from the compatibility triangles. Also shown are two compositions investigated by Hyatt and Day (1987). YAS-7 crystallized forming mullite $(3Al_2O_3 \cdot 2SiO_2)$ and $Y_2O_3 \cdot 2SiO_2$; YAS-2 forming $Y_2O_3 \cdot SiO_2$ and $3Y_2O_3 \cdot 5Al_2O_3$.



Concentrations in wt1

Figure 3.22. Phase diagram from Bondar and Galakhov (1964) and binary phase diagrams from O'Meara et al 1987.

3.7 APPENDICES

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APPENDIX 38: CLARIFICATION OF Y-Si-O CRYSTALLOGRAPHIC DATA:

In order to interpret either electron or X-ray diffraction data it is necessary to be able to compare acquired spectra with those from standards. Reference data files are available through the JCPDS catalogue. These files contain the reference from which the data was obtained, a brief fabrication description, the interplanar spacings which give rise to diffraction peaks and the relative intensities of the peaks. In some cases these interplanar spacings may be indexed and unit cell dimensions given. The space group and (where applicable) the polytype may or may not be given.

In the case of $Y_2Si_2O_7$, the X-ray data in the JCPDS files is incomplete and confusing. Although Liddell and Thompson (1985) have made some progress in clarifying the matter, ambiguities and contradictions still exist. The following is a summary of the JCPDS files for various polymorphs of $Y_2Si_2O_7$.

Ito and Johnson (1968) established the following transformation temperatures for $Y_2Si_2O_7$:

 α 1225°C β 1445°C γ (gamma) 1535°C δ

They also discuss a 'y' form of the naturally occurring mineral yttrialite of the general formula $M_2Si_2O_7$ where M is predominantly yttrium.

The X-ray powder data for the α and β phases from Ito and Johnson's study are found in JCPDS cards 21-1457 and 22-1103 respectively. The β phase is indexed in 22-1103 and the α phase from 21-1457 is indexed in Liddell and Thompson's work.

Ito and Johnson state that the unlabelled phase indexed by Batalieva et al. in 20-1416 is $\gamma-Y_2Si_2O_7$ (Liddel and Thompson's statement that the original indexing as done by Batalieva et al can be found in 20-1436 appears to be typographical error). An additional phase is labelled as γ in the file 32-1448. However reference to the original paper by Nakrasov and Kashirtseva (1976) shows that they find that the published diffraction peaks of their γ phase compares well to one published by Ito and Johnson (1968). As the phase described by Ito and Johnson has actually been labelled a 'y' phase it leads one to believe that in going from English to Russian a 'y' has been interpreted as a 'Y'. This 'y' phase is almost identical to 'y' phase data published by four other groups as shown in Liddell and Thompson's work. The problem of distinguishing between 'y' and ' γ ' recurs in another XRD standard file system called ICSD (Bergerhoff et al, 1983) where the phase from the english translation of Balatieva and Pyatenko's paper (1972) entitled 'Artificial Yttrialite ("y-Phase") -A Representative of a New Structure Type in Rare Earth Diorthosilicate Series' is labelled 'qamma'.

The 'y' phase has been thought to be stabilized by impurity atoms, giving it a general formula of RY5Si6O21 where R= H+, Na+, Mg+2, Mn+2, Fe+2, Fe+3, Al+3, Th+4, or Zr+4 (Ito and Johnson). This phase has been found during low temperature oxidation of silicon nitride densified with yttria (Smith, 1977). It has also been reported in crystallized glasses from the AlN-Y₂O₃-SiO₂ system (Dinger and Thomas, 1986). It appears that it has also been found in the Y₂O₃-SiO₂ system (Drummond et al, 1988) although called 'y-prime' as a result of comparison with the JCPDS file 32-1448 (mentioned above).

The documented δ phases are compared in Liddell and Thompson's paper. Additional work however has been done by Rai et al (1986) who,

in crystallizing glass find a δ -1 and a δ -2 phase which are directly related by an a/2 translation. The unit cell parameters given for the δ -2 phase match those mentioned in Liddell and Thompson's review.

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The 'z' phase found in JCPDS file 21-1459 is referred to in Liddell and Thompson's work as a possible hydrated disilicate.

Additional points worth noting in Liddel and Thompson's work are the existence of Y_2SiO_5 polymorphs and discrepancies regarding the existence of $Y_4Si_3O_{12}$ found by Bondar and Galakhov (1964). The existence of the latter phase has also been questioned by Drummond et al (1988).

As a result of the above discussion the following can be used as a summary of the JCPDS files appropriate for each of the $Y_2Si_2O_7$ and Y_2SiO_5 polymorphs (these have been used in the XRD searches and electron diffraction pattern analysis for the current work):

Y ₂ Si207 polymorph	JCPDS file #	cell information (Liddell and Thompson,1986)		
α .	21-1457	triclinic (PT) $a = 6.59 \alpha = 94.0$ b = 6.64 B = 89.2 $c = 12.25 \gamma = 93.1$		
ß	22-1103	monoclinic $(P2_1/n)$ a = 6.875 b = 8.970 B = 101.74 c = 4.721		
Ŷ	20-1416	monoclinic $(P2_1/a)$ a = 5.579 b = 10.857 $B = 95.99c = 4.696$		
δ	21-1460	orthorhombic (Pna2 ₁) a = 13.66 b = 5.020 c = 8.152		
' Υ'	32-1448	monoclinic $(P2_1/m)$ a = 7.46 b = 8.07 B = 112.0 c = 5.03		
'z'	21-1459			

Y₂SiO₅ polymorph JCPDS file #

X₁

X2

21-1456 monoclinic $(P2_1/c)$ a = 9.012 b = 6.979 B = 106.7 c = 6.63022-992 monoclinic (I2/c)

a = 10.4b = 6.7

c = 12.4

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APPENDIX 3b: CALCULATION OF DISTRIBUTION OF PHASES IN GRAIN BOUNDARY AFTER PARTIAL CRYSTALLIZATION:

The following describes the elemental mass balance used to calculate the relative amounts of crystalline phases and residual glass present in SN220 after annealing. For the cases of an inert atmosphere anneal and in the centre of air annealed samples, the three unknowns are the quantities of $Y_2Si_2O_7$, YAG and residual glass. These can be written in terms of the compositions of each phase as follows:



where matrix B is the concentration of Y, Al, and Si in the as received glass of composition $Al_{11\pm2}Si_{16\pm2}Y_{9\pm1}O_{63\pm7}$ atomic %. Matrix X consists of the unknowns, the quantities of each phase after annealing. Matrix A represents the concentrations of Y, Al, and Si in each of the phases given in X. Solutions of these expressions lead to the following relative fractions of each phase:

> 20 \pm 3 w/o $Y_2Si_2O_7$ 19 \pm 4 w/o $Y_3Al_5O_{12}$ 61 \pm 7 w/o residual glass

For the material near the surface of samples annealed in air at 1250°C, the same procedure produced:

$\begin{bmatrix} 2.0 & 0.0 \\ 0.0 & 6.0 \\ 2.0 & 2.0 \end{bmatrix}$	0.0576 0.1106 0.1934	X _{Y2Si207} Xsi2Al6013 X _{resid.glass}	· · · · · · · · · · · · · · · · · · ·	0.0933 0.1145 0.1602	(A3)
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Solving the expression yields:

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50	±	8	w/o	Y2Si2O7	
22	t	5	w/o	Al2Si2O17	
27	±	2	w/o	residual	glass

The errors in these values are calculated based on the uncertainty in the glass compositions as determined by EELS. These uncertainties are given by the standard deviations of numerous EELS analyses on a variety of samples (as detailed in table 5a). The error calculation is done in two steps:

1) x_1 , x_2 , x_3 are solved for, assuming errors in a_{ij} were zero. 2) The errors in x are obtained by first expressing the errors in b_1 in the form:

$$\Delta b_{1} = \frac{\delta b_{1}}{\delta a_{11}} \Delta a_{11} + \frac{\delta b_{1}}{\delta a_{12}} \Delta a_{12} + \frac{\delta b_{1}}{\delta a_{13}} \Delta a_{13}$$

$$+ \frac{\delta b_{1}}{\delta x_{1}} \Delta x_{1} + \frac{\delta b_{1}}{\delta x_{2}} \Delta x_{2} + \frac{\delta b_{1}}{\delta x_{3}} \Delta x_{3}$$
(A3)

 $\begin{array}{rcl} \Delta b_1 &= x_1 \Delta a_{11} &+ x_2 \Delta a_{12} &+ x_3 \Delta a_{13} \\ &+ a_{11} \Delta x_1 &+ a_{12} \Delta x_2 &+ a_{13} \Delta x_3 \end{array}$

In general:

$$\Delta b_{i} = \text{sum of } (x_{j} \Delta a_{ij} + a_{ij} \Delta x_{j})$$
 (A5)

Since x_1 , x_2 , x_3 ; Δa_{11} , Δa_{12} , Δa_{13} ; a_{11} , a_{12} , a_{13} ; b_1 ; etc are known, we can rearrange eqn (A4):

$$\begin{array}{rcl} \mathbf{a_{11}}\Delta \mathbf{x_{1}} &+ \mathbf{a_{12}}\Delta \mathbf{x_{2}} &+ \mathbf{a_{13}}\Delta \mathbf{x_{3}} &= \Delta \mathbf{b_{1}} &- (\mathbf{x_{1}}\Delta \mathbf{a_{11}} &+ \mathbf{x_{2}}\Delta \mathbf{a_{12}} &+ \mathbf{x_{3}}\Delta \mathbf{a_{13}}) \\ &= \Delta \mathbf{b_{1}} &- (\mathbf{0} &+ \mathbf{0} &+ \mathbf{x_{3}}\Delta \mathbf{a_{13}}) \\ &= \Delta \mathbf{b_{1}} &- \mathbf{x_{3}}\Delta \mathbf{a_{13}} \end{array}$$
(A6)

 Δa_{11} and Δa_{12} are zero as these are stoichiometric values for the crystalline material. We now have three equations (and three unknowns Δx_1 , Δx_2 , Δx_3) of the form:

$$\begin{bmatrix} \mathbf{a}_{ij} \end{bmatrix} \star \begin{bmatrix} \Delta \mathbf{x}_i \end{bmatrix} = \begin{bmatrix} \Delta \mathbf{b}_i - \Delta \mathbf{a}_{ij} \mathbf{x}_j \end{bmatrix}$$
(A7)

Thus we can solve for Δx_i , the error in the relative amounts of phases after partial grain boundary crystallization.

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(A4)

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4 CREEP OF SN220

4.1 INTRODUCTION

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Creep of materials containing an amorphous intergranular phase is generally thought to occur by solution/reprecipitation, viscous flow or cavitation. Cavitation in ceramics has been observed by a number of groups and models describing the required conditions for cavitation have been developed. Solution/reprecipitation creep has been examined using ideal systems and (necking and island) models for this process have been proposed. Models have also been developed which describe observed creep behaviour on the basis of empirical creep relationships. Some of these even give the expected creep curves for bending tests. However results can be misleading in applying these to observed creep behaviour as this assumes the creep characteristics of the material follow the same empirical behaviour.

As SN220 is made with oxide additives to enhance densification, the sintered product contains residual glass. This amorphous phase softens at high temperatures and is expected to have a detrimental effect on the creep resistance. Partial grain boundary crystallization occurs on heat treating the material, enabling the effect of an amorphous versus a crystalline intergranular phase on the creep properties to be determined. The creep properties are assessed through four point bend and compression tests.

The creep resistance data and observed microstructural information (chapter 3) provide a basis for modelling the creep behaviour of a particular silicon nitride. This model describes creep due to the non-linear viscous flow of an amorphous intergranular phase around an array of hexagonal grains. It can be used to describe the observed creep behaviour.

4.2 LITERATURE REVIEW:

4.2.1 Observed Creep and Creep Fracture Behaviour of Si₃N₄: Grathwohl and Quinn

The most extensive high temperature failure studies of sintered silicon nitrides are those done by Quinn (1983, 1984) and by Grathwohl and co-workers (Grathwohl, 1983, 1984; and Ernstberger et al., 1986). Both groups performed four point bend tests under static load to differentiate between the slow crack growth and creep fracture regimes. The Grathwohl group also measured strain in situ, which provided additional information on creep behaviour.

Grathwohl did extensive work on creep of HPSN (Grathwohl 1983, 1984). This involved high temperature bend tests of both as machined and indented materials, in air and in vacuum. As machined samples contain both natural and machining flaws. With these Grathwohl (1983) found that, below a threshold stress, tests done in air exhibit a larger rupture strain and a longer time to failure than tests done in vacuum. Above the threshold stress, rupture strains and failure times are not influenced by the test environment (figure 4.1). In addition, in comparing precracked samples with machined samples, both tested in air, Grathwohl (1984) found that at stresses below the threshold stress, rupture strains of precracked samples approach that of the machined samples (figure 4.2). Both of the above effects are due to oxidation, which induces crack healing of natural flaws, and of machining-induced flaws and precrackes. Grathwohl (1984) also found that below the threshold stress, a strain limited rupture criterion exists (i.e. the Monkman-Grant relationship holds). A plot of log strain rate vs. time (figure 4.3) shows the region of minimum creep rate. For tests done at stresses below the threshold stress the minimum strain rate varies as a function of stress to the power of n = 1.9, and the activation energy is 558-709kJ/mol (Grathwohl, 1983). Grathwohl does not provide an interpretation of these values.

Ernstberger et al. (1986) did additional work on a variety of silicon nitride materials over a larger temperature range. They found the same apparent minimum strain rate as Grathwohl (1983) at high temperatures. However at lower temperatures the creep behaviour could be described by:

 $\epsilon = a t^{-c}$

where $c \approx 1$ (figure 4.4). They suggest that there is an increasing creep resistance of the material with strain due to a rising number of As the temperature is increased, the blocked grain boundaries. parameter c decreases in value to a minimum of 0.5 at a critical temperature. The authors claim that this illustrates that processes occur which reactivate grain boundaries, processes such as stress induced diffusion or solution-reprecipitation. The critical temperature at which this minimum strain rate occurs is independent of applied This critical temperature also corresponds to a transition stress. temperature above which activation energy for oxidation increases. At low temperatures the activation energy corresponds to that for O2 diffusion in a SiO, layer. At higher temperatures the higher activation energy value is thought to result from more than one process, connected to the first occurrence of a liquid intergranular phase. At the transition temperature the structure of the intergranular phase changes

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significantly. Only above it is fracture preceded by extensive cavitation. The minimum creep rates observed are thought to result from an overlapping of the primary and tertiary creep regimes, and do not represent a true steady state. Therefore at temperatures greater than or equal to the transition temperature, the stress dependence is not meaningful. Thus this work casts doubt on the usefulness of the stress exponents previously measured by Grathwohl (1983).

An alternative explanation of the data presented by Ernstberger et al. (1986) is also possible. The decrease in creep rate below the transition temperature may be occurring as the creep rate is approaching a minimum. As the authors state, the minimum is thought to result from an overlap of primary and tertiary creep. As tests below the threshold temperature were stopped after approximately 100 hours, it is not clear that had the tests been run longer, a minimum creep rate would have occurred with failure preceded by extensive cavitation.

Quinn (1986a,b) has produced the most extensive body of stress rupture data on a silicon nitride material. Using several hundred bend bars he characterized the slow crack growth and creep fracture regimes in NC132, a hot pressed MgO doped silicon nitride. The creep fracture regime was assumed to occur whenever the time to failure was the same for both as-machined and pre-cracked bars (figure 4.5). Analysis of the fracture surfaces indicated that creep fracture does not occur from a severe flaw in this regime. In addition, although based on a small amount of data, static fatigue plots (figure 4.6) indicate a change in slope between the slow crack growth regime and the creep fracture regime. Activation energies (calculated from the failure times at various temperatures for indented bars and as machined samples) are the same for both regimes. Quinn (1986a) states that this is "undoubtedly"

slow crack growth and creep. However he provides no evidence which supports this.

Unlike Grathwohl (1983, 1984), Quinn did not find any evidence of a critical strain to failure or a threshold stress below which failure time and strain increased. As Quinn was not able to monitor the strain in situ, no data on either a steady state or minimum strain rate were obtained.

4.2.2 Creep Due to Cavitation: Experimental Observations and Theory.

A commonly observed feature in the microstructure of crept material containing an amorphous intergranular phase is the presence of cavities. Tighe et al (1984) found this in both Y_2O_3 and MgO doped silicon nitride. Cavities are located at triple junctions, and tungsten inclusions in both materials and along grain boundaries in the MgO doped material. These cavities join to form microcracks. Marion et al (1983) and Lange et al (1980) found cavities in crept silicon nitride, generally in clusters or as subcritical cracks. Most are at triple junctions with only a small portion at two-grain interfaces. Clarke (1985) characterized cavitation in compression samples of liquid phase sintered alumina. In this case cavities are inhomogeneously distributed and localized into bands. Crack propagation at high temperatures results in the formation of a cavitational zone around the fracture In liquid phase sintered alumina analyzed by Page et al surface. (1987), the cavity spacing after creep corresponds to that for grain boundary ledges, suggesting the ledges are nucleation sites. The theoretical analysis of creep due to cavity nucleation, growth and coalescence in material containing an amorphous intergranular phase has

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been dealt with extensively by a number of authors (Marion et al, 1983; Tsai and Raj, 1982). They developed expressions describing the nucleation and growth of cavities. Figure 4.7 depicts the process for oblate holes in thin glass films and spherical holes in three grain pockets (Marion et al 1983). The critical stresses predicted by the model for cavity nucleation, although often in excess of the applied far field stress, may be obtained locally as a result of grain boundary sliding. For the case of spherical holes, at stresses less than that required for oblate hole nucleation and greater than that for grain pocket nucleation, the first step in cavity growth is the viscous expansion of the hole within the triple point. This occurs by flow of the amorphous phase into the adjacent two grain channels and is controlled by the stress at the hole surface or by the viscous flow rate. When sufficient material has been removed from the triple point, an increase in curvature near the two grain channel occurs. Provided that the local stresses exceed that due to the surface tension component, the liquid meniscus will be drawn into the two grain channel by viscous flow. As this occurs, it is possible for the flow to become unstable. This is found in liquid phase sintered alumina subjected to creep, frozen under load and fractured at room temperature (Marion et al., 1983). Full facet cavitation may also occur by interface or diffusion controlled solution-reprecipitation of the solid phase from the cavity surface to the grain surfaces within the channel. This is consistent with observations in silicon nitride (Marion et al., 1983) and alumina (Clarke, 1985) where cavities larger in size than the original grain pocket are observed. In alumina the increasing width of the two grain channels near the cavity, rather than the constant thickness channels observed in cases where cavities are still confined to the size of the glass pocket, also indicates that solution-

reprecipitation is occurring.

4.2.3 Creep Due to Solution/Reprecipitation and Dislocations

Solution/reprecipitation has been investigated in a variety of model systems (Pharr and Ashby, 1983; Raj, 1982) and in glass ceramics (Raj and Chyung, 1981). Pharr and Ashby looked at the creep properties of KCl and sugar, both dry and in saturated salt or sugar solutions, and in kerosene. They found that the strain rate has a stress exponent of n=1 and increases exponentially with temperature when the solid is soluble in the solution. A considerably lower strain rate with a higher stress exponent occurs in both the dry state and in the kerosene solutions in which the solids are not soluble. Pharr and Ashby examined the models for creep due to viscous flow and diffusional flow and found them lacking in that they all assume a constant grain boundary thickness. They then presented a model for the liquid enhanced creep behaviour which allows for the squeezing out of the intergranular fluid from between the grains. Here the liquid, which has some solubility for the grains and has a low wetting angle, penetrates the boundary between the grains. This decreases the neck between the particles, causing the local stress to rise. Plastic deformation then occurs here and grain boundary dissolution occurs again. The effect of wetting was also investigated in Al and Cu alloys (Pharr et al 1989). It was concluded that greater than 70% of the grain boundaries have to be wet before any increase in the creep rate is seen.

A similar idea is presented by Raj and Chyung (1981) in which solution/reprecipitation is assumed to occur through an interface modeled by an island structure. The islands represent regions of grains

in contact across a boundary. Surrounding these are channels of the amorphous phase. These islands are supposedly required to support normal tractions and gradients in normal traction so that the amorphous phase would not be squeezed out from between grains, which would eliminate transport of the solid through the amorphous phase. Equations developed for both interface and diffusion controlled creep have a stress exponent of n=1, but different grain size dependencies.

An alternative explanation is the existence of an equilibrium grain boundary thickness which can support stresses and allow for diffusive flow through the grain boundary phase. Numerous high resolution electron microscope measurements of various silicon nitrides show an amorphous intergranular film ranging in thickness from 0.6 to 8nm exists between most silicon nitride grains and between silicon nitride grains and crystalline intergranular phases (Lou et al 1978, Clarke and Thomas 1978, Ahn and Thomas 1983). Clarke (1989) found that a thicker (2-10nm) film exists when the material was quenched, rather than slowly cooled, from 1450°C. It is possible for the intergranular film to exist even under an applied compressive stress (Clarke 1987).

Dislocation creep in silicon nitride is another deformation, mechanism which is generally assumed negligible in silicon nitride materials. The commonly accepted view is that dislocations in Si_3N_4 are immobile at temperatures below 1700C (Evans and Sharp, 1971; Kossowsky, 1973). Recent work of Lee et al (1988) however, has shown that the dislocation density in silicon nitride increases after annealing at 1500C for 5hrs, during which time $B-Y_2Si_2O_7$ crystallizes. These dislocations anneal out after 10-20 hours. Tighe (1978) found dislocations at the crack tip in double torsion specimens and in the compressive side of bend bars crept at 1400°C. Din and Nicholson (1975) also found dislocations near voids on the tensile side of bend bars

crept at the same temperature. Kossowsky found that most grains show no evidence of increased dislocation density after creep deformation at 1000 to 1300C. However dislocation tangles are found only in the deformed material. Kossowsky calculated the total dislocation strain contribution to be less than 10⁻⁵ (although this calculation does not account for dislocations which may have been annihilated during creep) and concludes that deformation (is controlled by grain boundary sliding due to observed grain boundary separation and cavitation. Thus it would appear that while dislocations are active in silicon nitride, there is no evidence that dislocation motion is the dominant creep mechanism.

4.2.4 Stress Redistribution in Bend Tests and Empirical Models

The bend test is a common method for analyzing creep data of ceramic materials because sample preparation and experimental procedure is simple and inexpensive. Unfortunately analysis of the bend data is complicated because stresses redistribute within the bar. This section provides an overview of previous work on the analysis of stress redistribution within a bend bar for creep characterized by an empirical formula. In addition, previous work on stress redistribution and creep due to viscous flow will be discussed.

Steady state creep is generally described by the empirical relationship:

$\epsilon = A \sigma^{n}$

where ϵ is the strain rate, σ is the stress, n is the stress exponent and A is a prestress constant. As plane sections are assumed to remain plane throughout a bend bar, a linear stress distribution occurs whenever n=1. For values of n>1, the stress redistributes from the
initial linear stress state to a new stationary stress distribution

 $\sigma(y) = \sigma_{elastic, maximum} (2y/h)^{1/n}$

where y is the distance from the neutral axis and h is the specimen thickness, as shown in figure 4.8 (Cohrt et al 1981). For the case of n=2 the relaxed outer fiber tensile and compressive stresses decrease to 83% of the initial elastic stresses. This also means a 21% decrease in the outer fiber strain rates (Cohrt et al 1981).

Cohrt et al (1981) have also treated the case in which the resistance to creep is greater in compression than in tension. This is commonly observed in ceramics (Birch et al 1978; Kossowsky et al 1975). They assumed that the stress in tension $\sigma_t(y)$ and compression $\sigma_c(y)$, are related by:

$$\sigma_{c}(\mathbf{y}) = \mathbf{S} \ \sigma_{t}(\mathbf{y})$$

where S = constant. Both the tensile and compressive strain are assumed to occur by the same mechanism (ie. $n_t=n_c$). These assumptions were based on creep work done by Birch et al (1978) on a reaction bonded silicon nitride. The resulting stress redistribution as a function of time is shown in figure 4.9 (Cohrt et al 1984). This model predicts the movement of the neutral axis, a feature commonly found in ceramic bend tests (Wiederhorn et al, 1986).

Chuang (1986) also modelled this problem (i.e. $n_t = n_c$, $\sigma_c(y) = S\sigma_t(y)$) and extended the model to include cases were n_t does not equal n_c . His analysis treats only the steady state. Transient effects are not considered. Chuang produced a series of plots which show the effect of different n_t , n_c and R (where R is the ratio of strain rate-stress proportionality constants, equal to S^n as defined by Cohrt et al. (1981) for the special case where $n_t = n_c$) on the rate of curvature and neutral axis location, as a function of applied moment. For all combinations there exists a range of applied moment, for which curvature

rate and neutral axis location are very insensitive to the n and R values. Chuang also provides an example in characterizing the creep data of a vitreous-bonded alumina. Using a trial and error procedure to find the values of the stress exponents and prestress constants which give the best fit to the experimental data, a profound difference in creep behaviour in tension and in compression is found.

Chuang and Wiederhorn (1988) extended the above analysis to compare creep results of a siliconized silicon carbide obtained in bending with theoretical results based on data obtained in pure tension and compression. As transient creep lasted an order of magnitude longer in bending than in tension, it was necessary to account for stress redistribution within the bend bar. This was done using the same methodology as Cohrt et al (1984). The predicted times to reach steady state in bending were found to agree well with those obtained experimentally.

Although Chuang and Wiederhorn have used tensile and compressive data to obtain bend information, it appears more difficult to use bend data to obtain tensile and compressive information when the constitutive equations for creep are not known. The case of Si-SiC, where a bimodal power-law relationship was found in both tension and compression (Chuang and Wiederhorn, 1988), clearly shows that a simple power-law relationship can not always be assumed as was done for the case of the vitreous-bonded alumina (Chuang 1986).

Other empirically based bend test analyses are those by Fett et al (1988a,b) and Rosenfield et al (1985). Fett et al treated an elastic-creeping solid with a constitutive equation given by :

 $\epsilon(y) = \epsilon elastic(y) + \epsilon creep(y)$

They included both the primary and secondary state creep effects. Thus:

 ϵ creep = ϵ primary + ϵ secondary = $C\sigma^{n}\epsilon_{p}^{p} + DS|\sigma|^{m}$

where C and D are constants, S is different in tension and compression. They solve the limiting cases of very short and very long times such that by plotting experimental bend data in a number of ways, all the unknown creep variables can be determined. Using these parameters the time dependent stress-strain state and the outer fiber strain versus time plots were obtained and compared to the experimental curves obtained for alumina containing a glass phase. This model does predict the movement of the neutral axis after long times. Fett et al (1988a) find that a more complex creep law has to be used in the analysis of a hot pressed silicon nitride.

Rosenfield el al (1985) also provide a useful approach to analyzing bend data. Both deformation and damage are assumed to contribute to the creep strain. The deformation is assumed to be the same in tension and compression and is equal to the constitutive equation for linear viscoelasticity:

$$\epsilon = \sigma/(\sigma_1 t_1)$$

where σ_1 is the viscoelastic modulus and t_1 is the reference time. The above equation also equals:

where $A = 1/(\sigma_1 t_1)$, and n = 1. Damage is assumed only to occur in tension and is proportional only to the stress. It is described by:

$$w = \sigma/\sigma_{\rm c}$$

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where σ_0 is a damage modulus. The damage is related to the creep rate by:

The net result is a higher strain rate in tension than compression and stress exponents which increase as a function of stress in both tension and bending. Rosenfield et al also used their model to characterize the bend data analyzed by Chuang (1986) and find that it fits surprisingly well.

There are a number of shortcomings to the above models. Chuang's model (1986) assumed steady state, thus the transient period to reach this must be small. Most models assumed that creep follows empirical relationships. Chuang and Wiederhorn (1988) assumed the uniaxial constitutive equations are known. When damage is considered (Rosenfield et al, 1985) it is assumed to vary as a function of stress only. Since damage is often found in the form of microcracks and cavitation (as previously discussed), it is probable that damage may also vary as a function of strain as suggested by the Monkman-Grant relationship. In addition, none of the models include any fracture criterion. As a result, all models predict that creep occurs even under very high loads.

4.2.5 Viscous Flow Creep Models

Limited work has been done on creep of materials containing an intergranular amorphous phase. In the simplest model, Lange (1975) considered two cubic grains separated by an intergranular fluid. Lange used a solution for the rate of squeezing of a liquid layer as found in the literature on adhesion (Healey, 1926). More specifically, as described in Bikerman (1965), Healey's solution deals with the squeezing of a drop of liquid between two surfaces. From this the bulk strain rate was found to vary as a function of the boundary height s and the

initial boundary height sat

$$a \begin{bmatrix} s \\ -- \\ s_{\alpha} \end{bmatrix}^{5} \sigma$$

Thus the strain rate under a compressive stress (where $s/s_o < 1$) is much less than under a tensile stress. Therefore a polycrystal is expected to be more resistant to deformation under compressive conditions. Creep of a real material was modeled as a combination of this boundary separation and grain sliding (which accommodates any changes in boundary volume). The separation was shown to be the rate limiting step.

Pharr and Ashby (1983) used the same sort of geometry to model lubricated flow, where the liquid allows the grains to slide over each other more easily. An array of cubes of length d separated by an incompressible fluid of thickness w and viscosity η has a strain rate:

Where $\overline{\sigma}$ is the deviatoric stress and α is a constant. As Pharr and Ashby state, this model has a number of shortcomings. Figure 4.10 shows grains will slide over one another instead of jamming together as they would in a real material with an irregular grain morphology. In a real material, the rate of deformation would then be determined by the grains riding up over each other (causing dilatation) or by the grains undergoing deformation. In addition, due to the simplicity of the model, a linear dependence on the film thickness is predicted. More realistically, w should depend on stress. As a result creep by viscous flow has generally been assumed to be an unrealistic process.

A more complicated model was developed by Lange et al (1980b) to explain the viscoelastic effect seen in crept silicon nitride. They assumed the total stress in the material was the sum of stresses accommodated by grain boundary sliding (which is controlled by the viscosity and the thickness of the intergranular phase) and elastic stress of grain aspirates in the grain boundaries. This viscoelastic response is responsible for primary creep and strain relaxation transients. This mechanism occurs in conjunction with diffusional and cavitational creep processes which are responsible for the unrecoverable creep strain in the material.

Drucker (1964) also modelled creep due to viscous flow. Although this model is old, it treats the most realistic geometry. Using a two dimensional array of hexagons separated by an incompressible fluid, he calculated the average strain rate as a function of stress, viscosity and fraction of intergranular phase. This was done by relating the rate at which the fluid phase flows horizontally between grains to the rate at which the grains are squeezed together:

 $w_{n}h = 2vx^{-1}$

where w is the fluid velocity in the horizontal channel, v is the velocity of the grains, h is the height of fluid, and x is the length of grain boundary as shown in figure 4.11. Knowing that the velocity of the fluid varies parabolically with distance from the grains (Bikerman 1965), the maximum velocity gradient (which is the shear strain rate) could be calculated. Neglecting acceleration, the shear stress T (= $1/\eta \, d\gamma/dt = 12\eta vx/h^2$) is balanced by the pressure gradient across the length of the grains. Thus the pressure profile was determined. As the volume of the fluid is incompressible, squeezing the expanding the inclined boundaries. horizontal boundary means Conservation of mass and force equilibrium allowed Drucker to calculate the pressure at the grain junctions and the average stress. The resulting average strain rate is:

$$\dot{s} = \frac{\sigma_{avg}}{\eta\sqrt{3}} \left[\frac{h}{a} \right]^3$$

where a is the grain facet length.

Vaandrager and Pharr (1989) used some of the same principles to calculate the strain as a function of time due to percolation of the amorphous phase around grains. The flow behaviour of the linear viscous intergranular fluid was described using the equation commonly found in lubrication theory where the pressure gradient within a thin film is proportional to the rate of squeezing of the film. The grain boundary height varies as a function of time:

 $\left[\frac{1}{h}\right]^2 = \left[\frac{1}{h_o}\right]^2 + \frac{4\sigma t}{3\eta a^2}$

for two circular plates of radius a. For a grain size d the strain produced by fluid flow is:

$$(t) = \frac{h(t)-h_o}{d}$$

where h_0 is the initial boundary height and h(t) is the height at time t. Vaandrager and Pharr calculate the strain as a function of time for copper containing different initial fractions of liquid bismuth. They find that the time frame over which the percolation occurs in this material is very fast, less than 10^{-5} sec. In addition, from the theoretical strain-time plots, it is clear that the initial strain rate due to percolation is initially constant and then decreases as the intergranular thickness approaches zero (figure 4.12).

Dryden et al (1989) have provided the most complete model describing linear viscous flow of the grain boundary phase around a hexagonal array of grains. For the special case where all intergranular fluid heights are equal, this model predicts the same strain rate dependence on viscosity as Drucker's model. The model by Dryden et al also describes strain rate as a function of strain (i.e. when all grain boundary heights are not equal) and extends the analysis to a multiaxial stress state. As in the models by Drucker (1964) and Vaandrager and Pharr (1989), the flow of the amorphous phase is assumed to be linear viscous and described by:

$$\gamma = (1/\eta) T$$

where γ = shear strain rate, η is the viscosity and T is the shear stress. It is also assumed that all the strain occurs by the flow of the intergranular phase (i.e. grains are rigid). The rate of change of the grain boundary height is related to the applied force. In the simplest case where there is no constraint at the ends of the grain boundaries, the problem is reduced to one commonly found in lubrication, simply the flow of fluid from between two parallel plates. Given the simplified case shown in figure 4.13a where a force F is applied to two plates of length 2L separated by an intergranular fluid of height 2H, the rate of change of grain boundary height (and the rate of strain) is given by :

$$2H = (1/\eta)(H/L)^3 F$$

However in a polycrystalline material with an intergranular glass phase, there is a constraint at the ends of the plates since the fluid is trapped within the triple points. As a result, a pressure P develops here. Taking this into consideration gives a similar solution (Dryden et al 1989):

$$2H = (1/\eta) (H/L)^3 (F + 2LP)$$

with P unknown at this stage. For a large hexagonal array of grains as shown in figure 4.13b, the pressure is determined by imposing the conditions of strain compatibility and force equilibrium. As shown by

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Dryden et al (1989), this results in the following relationship for the strain rate as a function of strain and the fraction of grain boundary phase f where $f=2H/(\sqrt{3}L)$:

where
$$S(\epsilon_N) = \frac{3 f^3 \sigma S(\epsilon_N)}{(1+2\epsilon_N)^3 (1+2\epsilon_N)^3}$$

and $\epsilon_{\rm N} = \epsilon/f$.

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Figure 4.14 shows a plot of the strain dependent term $S(\epsilon_{u})$ as a function of normalized strain ϵ_{y} . Clearly the model predicts a nearly constant strain rate at low strains followed by a rapid decrease in strain rate as a maximum strain is approached. This maximum value equals the fraction of intergranular phase in tension and half that value in compression. As Dryden et al. (1989) state, this difference can be visualized by considering a cubic array of grains separated by a glass of thickness H. When the cubes are squeezed in compression, the maximum strain occurs when there is no longer any fluid left between faces under compression. For a cube side length L, the maximum compressive strain is -H/L. Similarly in tension the maximum strain occurs when there is no fluid left between adjacent faces. As 2/3 of the faces in the material are feeding fluid to the remaining 1/3, at the maximum strain the grain boundary height is three times its initial value and the strain is 2H/L. Thus the maximum strain in tension is twice that in compression.

The stress redistribution expected in a bend bar as a result of fluid flow was calculated using the following three assumptions: plane sections remain plane, the sum of forces across a bend bar equal zero, and the applied moment is constant. They found that the outer fibre tensile/compressive stresses decrease/increase respectively with time

and the neutral axis moves towards the compressive surface. These results are similar to the stress redistribution found by Cohrt et al (1986) using empirical constitutive equations to describe the creep behaviour of the material.

4.2.6 Effect of Oxidation on Creep Results

An additional factor not considered in any of the above creep models is the effect of oxidation and partial grain boundary crystallization. Although this effect is difficult to model as the creep response of various materials after preoxidation treatments differ, its influence should be considered. The following examples illustrate the importance of analyzing the creep properties of materials with changing structures.

Wiederhorn et al (1986) found that annealing a vitreous-bonded aluminum oxide causes the glass to partially devitrify. Bend tests of as received and preannealed materials show the latter to have lower strain rates and longer failure times by factors of almost 100 (figure 4.15). These differences are attributed to changes in the volume fraction and viscosity at the grain boundaries. It was also found that the unannealed samples do not experience steady state creep although the samples preannealed to a relatively stable microstructure do.

Lange et al (1980c) also found that partial grain boundary crystallization of a vitreous-bonded material has a significant influence on the creep properties. As it was found that the MgO doped Si_3N_4 material does not exhibit steady state creep, the strain rates in the last 4 hours of a 20 hour test were used to characterize the creep behaviour. This short time frame was used so as not to allow for too much oxidation or change in crystal structure during the duration of the

test. Since oxidation increased the creep resistance of the material regardless of preannealing history, it was necessary to use new samples for all tests. In testing a number of materials with different amounts and compositions of amorphous intergranular phase, it was found that compositions with small amounts of glass have a stress exponent of n=1, corresponding to diffusional creep. Samples with large amounts of glass have a stress exponent of n=2, and experience pronounced cavitational creep. Partial devitrification of samples with the larger volume fractions of glass cause the deformation mechanism to change from cavitational to diffusional. Later work done by Lange et al (1983) on a Y_2O_3 doped Si₃N₄ material deformed in compression also showed that preoxidation increases the creep resistance. In this case the stress exponent was not affected.

The influence of grain boundary devitrification on the creep respnose has been treated theoretically by Wilkinson (1988). Creep was assumed to occur by a solution reprecipitation mechanism where the strain rate is proportional to the applied stress and grain boundary thickness layer. The glass thickness was related to the volume fraction of glass which is assumed to decrease only as a function of time due to devitrification (i.e. devitrification does not depend on stress or strain). As a result, if the strain rate exponent is calculated at constant strain, tests at high stresses (which are of short duration and see little effect of devitrification) will have a stress exponent of n=1, the value expected for solution reprecipitation. At low stresses where there is a large effect of devitrification, n will be very large. Wilkinson's model also suggests that the above ambiguity can be avoided by calculating the stress dependence at constant time instead of constant strain. Unfortunately a large stress range between which measurable strain and fracture occur may be difficult to obtain

experimentally.

The above experimental and theoretical examples show that creep properties of vitreous-bonded ceramics may change as the intergranular phase devitrifies. If this process occurs on the same time scale as the creep tests, interpreting creep results can be very frustrating (Lange et al 1980). For this reason it is important to understand the rate of change of microstructure with annealing and to perform creep tests on well characterized samples, preferably materials which have a stable microstructure throughout the creep test.

4.2.7 Effect of Oxidation on Failure Time

Oxidation or preannealing affects not only the intergranular phase but also the surface of the material (as shown in chapter 3.). This in turn has a significant effect on the time to failure and strength of the material. Wiederhorn and co-workers (Wiederhorn, 1983; Wiederhorn and Tighe, 1983) have characterized the effect of high temperature exposure time on the high temperature strength of a MgO containing an amorphous intergranular phase doped Si_zN₄ material (figure 4.16), and a Y_2O_3 doped Si_3N_4 material containing a crystalline intergranular phase. They found the strength of the MgO doped material initially increases as machining flaws heal due to oxidation. After 2 to 4 hours exposure strength decreases, as a result of surface pit It then levels off as subsequent pit formation does not formation. effect the strength. After long exposures, strength decreases due to creep cavitation. However in the Y203 doped material, microcracks do not form and thus the strength is not degraded.

Quinn (1983) studied the effect of preannealing Si_3N_4 samples at 1200°C for 100hrs on the room temperature strength and the stress rupture properties for sample which were tested with the oxide scale intact. He found that the room temperature strength is reduced due to the presence of large surface pits which are fracture origins. The stress rupture lifetimes are also shortened. However, it could not be determined if the slow crack growth zones grew from the surface pits.

Although neither Quinn nor Wiederhorn tested annealed material after removing the oxide scale, it is clear that the surface finish or oxide scale has a marked effect on the failure times of the material. Thus it is important in analyzing the properties of the internal microstructure to prepare all samples to the same uniform surface finish to eliminate premature failure due to pitting.

4.3 EXPERIMENTAL:

4.3.1 Bend Tests

Four point bend samples were approximately 3 x 4 x 60mm in size. Tests were performed in a dead load creep rig with top load pins approximately 28.5mm apart and bottom support pins 54mm apart. Maximum outer fibre stress was calculated using the formula of Hollenberg et al. (1971):

$$\sigma_{\max} = \frac{3(L-a)P'}{bh^2}$$

where h is the height of sample, b is the width of sample, L is the distance between support pins, a is the distance between load pins, P'is the applied load (the weight of load multiplied by the load arm lever ratio) and σ_{max} is the outer fibre tensile stress. Three alumina probe

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extensometers touching the tensile surface at the mid point between load pins and 12.5mm on either side were connected to linear voltage displacement transducers (LVDT) in order to determine the strain during the test. The maximum outer fibre strain was calculated using the formula of Hollenberg et al. (1971):

$$\epsilon_{\rm max} = c^2 / (8y_r)$$

where y_r is the difference between the average height of the outer LVDT probes and that of the centre probe, and c is the separation of the outer probes. The LVDT readings were collected by computer after either maximum time or strain increment intervals. Both of these collection parameters could be changed during a bend test to ensure that sufficient data was collected throughout both low and high strain rate regions of each test.

The bend rig was placed in a furnace lined with refractory bricks and heated with four SiC elements. The heating elements surrounded the bend rig parallel to the bend bar in order to provide an Temperature was monitored with a Pt/Pt-Rh even heat distribution. thermocouple in an alumina shield which was placed a few millimeters aways from the centre of the bend bar. Temperature fluctuations were controlled to within 5°C. The rig was equipped with a microswitch so that the furnace would shut off when the sample fractured. The temperature of the sample decreased by several hundred degrees in approximately 15 minutes following furnace shut down. Additional details of the bend rig can be found elsewhere (Robertson, 1990).

Noise in the LVDT reading occurred as a result of 60Hz interference with the LVDT signal connection from the bend rig to the computer. The effect of this noise was minimized by fitting a flexible curve through the strain data, digitizing and applying a spline fit. Strain rates were calculated by determining the slope over two adjacent strain-time points on the smoothed curve. Several sets of raw data were

also smoothed using an in-house curve fitting routine (FITG developed by E. McCaffery) in which several different types of curves (linear, parabolic, etc.) could be fit to the data in segments of any size. The strains calculated from the raw data smoothed in this manner were the same as those determined using the flexible curve procedure.

Bend tests were performed at temperatures of 1150, 1200, 1250 and 1325 and 1400°C using a variety of applied loads ranging from 20 to 200 MPa as outlined in table 1. Sample preparation involved grinding faces and bevelling tensile edges. Tensile face and edges were polished with 6 micron diamond until the surface between load points were free of surface flaws as seen using a low power optical microscope. Bars that had been pre-annealed at the bend test temperature of 1200°C were generally repolished to eliminate surface pits which formed during heat treatment. A few tests were done on preannealed samples with their oxide scale intact in order to determine the effect of the surface finish. Any fracture origins and microscope and/or the scanning electron microscope (SEM).

The location of the neutral axis in a bend bar was determined as follows. The average length of 7 bars as sintered bars and the tensile and compressive surfaces of 6 crept bars were determined by taping the surfaces, scratching the end edges, removing the tape and measuring the length of tape. The method was checked by measuring the as sintered bars with vernier callipers. The two sets of readings agreed within experimental error, indicating the tape did not stretch during measurement. The neutral axis location was determined using a single geometrical formula:

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 $h_{c} = \frac{\Delta L_{c}}{\Delta L_{t} + \Delta L_{c}}$

where ΔL_c , ΔL_t are the change in lengths of the compressive and tensile surfaces after creep testing, and h_c is the distance of the neutral axis from the compressive surface.

4.3.2 Compression Tests:

Compression test samples were approximately 3x3x7mm in size. This provided a length/width ratio of 2.3, a value in the range suggested for cylindrical samples to minimize the effects of buckling and barrelling (Birch et al 1976). Sample ends were made parallel by mounting samples on their side so that both ends extended beyond the width of the support plate. The support plate was attached to a Struers disk cutter grinding chuck by vacuum such that the overhanging silicon nitride samples did not interfere with the vacuum. In this manner the support plate could be turned over to grind the other end of the sample without remounting the samples onto the support plate. All surfaces were left in the as ground condition. In the case of preannealed 150 microns or more was ground off all of the surfaces to pieces, remove any surface oxide and obtain the required sample size. Preannealing was done either on the 7mm lengths or on the 80mm bars prior to slicing.

Compression tests were performed on an MTS computer controlled, servo-hydraulic test machine. A SiC push-rod was used and the sample was placed between two SiC platens (see figure 4.17). Strain was monitored with a three probe extensometer. The two outer probes were attached to the sample side of the top platen, and inner probe to the underside of the bottom platen. The difference between the average of the outer two probe positions and the centre probe position was used to

calculate the change in length of the sample. The sample and platens were centered in the middle of a 320mm height clam-shell furnace with Room temperature fluctuations were found to have a a 75mm hot zone. profound effect on strain measurements. Thus extensive shielding of the probes extending from the furnace was necessary to ensure that there was a constant temperature air environment at the LVDT. Data was collected on a PDP11-23 computer. LVDT, load and time readings were taken every 0.5 seconds. Readings were recorded whenever a change in load greater than 20N occurred or every 400s. In the latter case, recorded values were the average of 800 readings. This procedure helped reduce noise while ensuring data were collected when sudden changes occurred. After converting elongation data to strain, the strain - time data were smoothed using the same curve fitting routine (FITG by E. McCaffery 1989) as used in analyzing the bend data. The strain rate was determined by taking the slope over 3 or 4 points. The stain rate was also determined after using a flexible curve to smooth the data. This produced the same result for all tests.

Tests were performed at 1200°C under loads of 60 and 80MPa on samples in both the as sintered condition and after annealing at the creep test temperature for 400 hours. At least two samples were tested at each condition in order to assess reproducibility.

4.4 RESULTS:

Typical strain vs. time curves, from the four point bend tests, are shown in figure 4.18. They show a constantly decreasing curvature (or strain rate). Tertiary creep leading to failure is never seen. Data at this stage of the creep tests was recorded either every

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20 minutes or whenever the strain increment was greater than some minimum level. Thus either tertiary creep was non-existent or was very short-lived. The scatter in the data due to both experimental and material variations is best seen by comparing tests done under the same test conditions. Figure 4.19a shows the strain vs time plots for two tests at 1200°C, 80MPa and two at 1250°C, 55MPa. The corresponding strain rate vs strain plots are shown in figure 4.19b. The constant initial strain rate regime is typical of all tests done.

The times and strains to failure are plotted as a function of stress in figures 4.20 and 4.21 respectively. Data points with arrows indicate tests which did not fail under load. The existence of a Monkman-Grant strain limited fracture condition was evaluated by plotting the time to failure against the initial steady state strain rate on a log-log scale in figure 4.22. Clearly a slope of -1, indicative of a Monkman-Grant relationship, can not be drawn.

Creep resistance was evaluated as a function of strain and time as shown in figures 4.23a and 4.23b respectively. The strain rate exhibits a much greater dependence on strain than time. It is initially constant up to strains of approximately 0.3 percent. At this point there is a dramatic decrease in the strain rate. The initial steady state creep rate has an activation energy of 700 \pm 10 kJ/mol (figure 4.24). The activation energy has been used to analyze the stress dependence of the initial constant strain rate of materials in the as sintered and preannealed condition, at all temperatures. As shown in figure 4.25, the stress exponent 'n' equals 4.0 \pm 0.5.

The effect of preannealing on the creep behaviour is most clearly seen by plotting the strain rate as a function of time and strain as shown in figures 4.26 and 4.27. The strain rate decreases as a function of creep test time with very little effect of prior

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annealing. The strain rate depends more on the test time than on the total time of the sample at temperature. It is worth noting that the initial strain rate does not vary significantly with preannealing time (or more specifically, with the extent of crystalline grain boundary phase). The strain at which the strain rate drops is slightly smaller for preannealed samples.

Analysis of the time to failure of the material shows a dramatic effect of preannealing time. Figure 4.28 shows the difference in lifetime for a variety of stresses at 1200°C for different preannealing times. Clearly even short preannealing times (25 hours) have a drastic effect on the time to failure.

The location of the neutral axes and the bend bars for which they were determined are shown in table 2. Although the error is rather large, the results indicate that the neutral axis has moved towards the compressive face.

Compression samples tested at the same applied stresses as those used for bend samples did not exhibit tertiary creep, nor did they fracture. Two tests done for each test condition showed the shape of the creep curves to be very reproducible. The strain - time data for tests done at 1200°C under 60 and 80 MPa on as sintered material and 60 MPa on material which had been preannealed for 400 hours to partially crystallize the intergranular phase are shown in figure 4.29. The strain scale is given in increments only due to the difficulty in assigning the point of zero strain, possibly a result of alignment difficulties. All tests have the same initial strain rate characteristics and are plotted so the initial strain behaviour of the curves overlap. Assuming this corresponds to the same strain for all materials, the material crept under 80MPa load achieves a higher strain than material tested at 60 MPa. The material which was preannealed has

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the same initial strain behaviour as the as sintered material although it deviates to a faster strain rate as time increases. Thus the preannealed material accumulates more strain than the as sintered material under the same applied load.

The error in the absolute strain value is taken into account in the error bars in the strain rate - strain plots shown in figure 4.30. The uncertainty obscures any possible differences due to applied load or preannealing. However these plots do indicate that the compression tests do not exhibit an initial constant strain rate regime at low strains (as found in the bend samples), but that the strain rate decreases continuously with strain.

(Note: observations of the bend bar fracture surfaces are presented in the chapter 3.)

4.5 DISCUSSION:

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4.5.1 COMPARISON OF SN220 DATA TO LITERATURE

Since the most complete bend test data con silicon nitride materials have been published by Grathwohl (1983, 1984), Ernstberger et al (1986) and Quinn (1986a,b), the bend test data for SN220 have plotted in the same format for ease of comparison.

Grathwohl (1984) found a threshold stress below which the rupture strain and time to failure increases dramatically (see figures 4.1 and 4.2). Quinn also found the slope of the stress rupture curve changes, separating the slow crack growth and creep fracture regimes (see figure 4.6). Figures 4.20 and 4.21 show the stress vs time to failure and failure strain vs. stress relationships from the current study on SN220. It is possible that a threshold stress exists. However

the scatter in the data and the strong dependence of failure time on stress makes this difficult to ascertain.

The above implies that fracture in SN220 is occurring in the slow crack growth region. Slow crack growth is a result of damage accumulation in a localized region, generally due to stress concentrations from inhomogeneities in the structure or on the surface. However the evidence of a larger damage zone (cracks behind the fracture surface) and considerable strain found in samples indicate a more diffuse damage zone exists. It is possible that creep throughout the sample and localized slow crack growth are occurring simultaneously.

It is clear from figure 4.21 that a constant failure strain does not exist. Whether or not the strain accumulated during the steady state regime limited the lifetime of the material was investigated by plotting the initial steady state strain rate against the time to failure. As figure 4.22 shows, no correlation between the two can be detected.

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The occurrence of a critical temperature above which a minimum creep rate has been found was also investigated. Ernstberger et al. (1986) determined the transition temperature with the bend data by plotting the change in strain rate with respect to time versus temperature. Difficulty applying this type of analysis to SN220 arose as SN220 does not exhibit either a constant or a minimum secondary creep rate.

The steady state creep rate in SN220 is found at low strains (less than 0.3%). At higher strains the strain rate decreases continuously. From the bend test K45, plotted as strain vs time in figure 4.19, one can see how the apparent steady state strain rate one would obtain if the sample fractured after 60000 sec. is different from the one obtained after 80000 sec. 'Minimum' or 'steady state' strain

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rates can then be misleading. Due to the observed creep behaviour, a new model describing creep due the linear viscous flow was developed. The initially constant strain rate regime occurs when the fluid flows around grains, and the strain rate decreases when all the fluid has been squeezed out from between grains under compression.

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An initial constant stain rate regime has not been noted by other groups looking at creep of silicon nitride for two reasons. Very few have looked at strain rate data carefully at low strains. The Grathwohl group is one exception (Grathwohl 1983, 1984, Ernstberger et al. 1986). They however do not see a constant strain rate. This may be due to a lower viscosity of the intergranular phase and creep due to viscous flow occuring faster. As a result the strain due to viscous flow may be hidden in the primary creep strain regime.

To summarize, the four point bend data for SN220 does not exhibit a threshold stress which Quinn and Grathwohl have found to separate slow crack growth and creep regimes. In addition, SN220 does not follow a Monkman Grant relationship, or even exhibit steady state secondary creep regime as found by the Grathwohl group. This, together with the observation of an initial constant strain rate regime at low strains, indicates that SN220 has creep properties unlike those found by either Quinn or the Grathwohl group. The initial constant strain rate behaviour as shown by the bend data for SN220 has led to the development of a creep model based on non linear viscous flow of the grain boundary phase.

4.5.2 CREEP MODEL BASED ON VISCOUS FLOW:

4.5.2a Viscous Flow Model Applied to Uniaxial Creep

In this section, a model is developed for creep due to viscous flow. This model extends the model of Dryden et al. (1989) by inclusion of non-linear viscous flow. The model assumes that the glass is squeezed out from between adjacent grains and that the grains become interlocked leading to a decrease in strain rate with strain. The constitutive creep equations are based on phenomenological behaviour observed in fluids and do not assume steady state. The procedure for converting the rate of squeezing of the amorphous phase to the strain rate in the material in both uniaxial creep and in bending are similar to that developed by Dryden et al (1989) for the case of a linear viscous fluid.

The intergranular glass is treated as a non-Newtonian fluid described by a constitutive equation of the form:

$$\gamma = \Phi T^n$$

(1)

where γ is the shear strain rate, T is the shear stress, n is the stress exponent and Φ is a material constant. The rate of separation of two parallel plates $\delta(2H)/\delta t$ separated by a non-Newtonian fluid is calculated following the procedure outlined by Bikerman (1968) (details of this calculation can be found in the appendix, section 4.7). For two parallel plates with end pressure P, the rate of separation or squeezing of the plates is given by:

 $2H = \frac{2}{n+2} \left[\frac{2n+1}{2n} \right]^n \frac{H^{n+2}}{2n} (F + 2LP)^n \operatorname{sgn}(F + 2LP)$ (2a)

By applying this result to the case of a hexagonal array of grains, as

shown in figure 4.31, a constitutive equation for flow in a polycrystal can be developed. The grains are assumed to be incompressible and the rates of change of lengths A, B and C are assumed to be taken up entirely by the boundary phase (i.e. rigid grains). Following Dryden et al (1989) this results in the following relationships between boundary layer thickness and strain:

$$2H_{A} = (\sqrt{12}) L \epsilon_{11}$$

$$2H_{B} = \sqrt{3} L (\sqrt{3}\epsilon_{12} - \epsilon_{11})$$

$$2H_{C} = \sqrt{3} L (\sqrt{3}\epsilon_{12} + \epsilon_{11})$$
(2b)

Dryden et al (1989) also obtained relationships between the applied forces on each grain boundary facet, and the resulting stresses:

 $F_{A} = 2L (3/2 \sigma_{11} - 1/2 \sigma_{22})$ $F_{B} = 2L (\sigma_{22} + \sqrt{3} \sigma_{12})$ $F_{C} = 2L (\sigma_{22}^{\circ} - \sqrt{3} \sigma_{12})$ (2c)

(3)

In the current treatment, only uniaxial applied stresses are considered, in which case:

$$\sigma_{11} = \sigma, \ \sigma_{22} = \sigma_{12} = 0$$

 $\epsilon_{11} = \epsilon, \ \epsilon_{12} = 0$

Thus combining equations 2a, b, and c, leads to two separate equations for strain rate:

$$\dot{\epsilon} = \frac{1}{\sqrt{3} (n+2)} \left[\frac{2n+1}{2n}\right]^{n} \Phi \left[\frac{H_{A}}{L}\right]^{n+2} (3\sigma + 2P)^{n} \operatorname{sgn}(3\sigma + 2P)$$

$$(4)$$

$$\dot{\epsilon} = -\frac{2}{\sqrt{3} (n+2)} \left[\frac{2n+1}{2n}\right]^{n} \Phi \left[\frac{H_{B}}{L}\right]^{n+2} (2P)^{n} \operatorname{sgn}(2P)$$

In equating equations 4," it is important to realize that $sgn(3\sigma+2P)$ is the negative of sgn(2P). Solving for P then gives:

$$2P = \frac{-3\sigma H_A^{(n+2)/n}}{H_A^{(n+2)/n} + 2^{1/n} H_B^{(n+2)/n}}$$
(5)

At any time during deformation, the following relations hold true (Dryden et al, 1989):

$$\epsilon_{11} = \frac{(H_A - H)}{\sqrt{3} * L}$$
(6)

where $3H = H_A + 2H_B$ and $H_B = H_C$ due to conservation of volume. Thus we obtain:

$$\frac{3^{(n+1)/2}}{2^{n+1}} \left[\frac{2^{n+1}}{2^n} \right]^n \Phi(\sigma)^n f^{n+2} R(\epsilon_N) \operatorname{sgn}(2P) (7)$$

Since applying a positive stress induces a negative pressure at the grain junctions:

$$\epsilon_{11} = C \Phi (\sigma)^n R(\epsilon_N) sgn(\sigma)$$
 (8)

where

$$C = + \frac{3^{(n+1)/2}}{2^{n+1} (n+2)} \begin{bmatrix} 2n+1 \\ -\frac{2n}{2n} \end{bmatrix}^n f^{n+2} \operatorname{sgn}(\sigma)$$

and

$$R(\epsilon_{N}) = 3^{n} \frac{(1 + 2\epsilon_{N})^{n+2} (1-\epsilon_{N})^{n+2}}{[(1 + 2\epsilon_{N})^{(n+2)/n} + 2^{1/n} (1-\epsilon_{N})^{(n+2)/n}]^{n}}$$

Here ϵ_N is the normalized strain equal to ϵ/f , f being the normalized grain boundary layer thickness (f= 2H/v3L). Equation 8 reduces to the equivalent result from Dryden et al (1989) for the case of linear viscous flow (when n=1 and $\Phi=1/\eta$).

The strain dependent part of the strain rate $R(\epsilon_N)$ is plotted against the normalized strain in figure 4.32 on a log-log scale. The general shape of the curve is very similar to that found in figure 4.14 for the case of linear viscous flow. The initial strain rate is relatively constant for low strains but decreases drastically as the strain approaches a limiting value. The limiting strain is, as in the linear case, equal to the nominal volume fraction of the intergranular phase in tension and one half of that value in compression. The only difference is a slightly sharper drop in strain rate as the limiting strain is approached for the case where n>1 (non-linear flow). In both cases the pressure at the triple points is zero at the maximum compressive strain ($H_A=0$) and is $-3\sigma/2$ at the maximum tensile strain ($H_B=0$). It is important to realize that creep strain is not limited by a build up of pressure at the triple points, but by the amount of fluid which can be squeezed out from between grains.

4.5.2b Viscous Flow Model Applied to Creep in Bending

It is well known that the stress distribution and location of the neutral axis within a bend bar changes with time. However previous models which have predicted this behaviour have been of a purely phenomenological nature (Cohrt et al 1981, 1984; Chuang 1986), unlike the present mechanistic based model. Dryden et al (1989) calculated the stress distribution with time for a linear viscous material flowing around incompressible hexagonal grains. The redistribution and movement of the neutral axis is the result of the different strain rates predicted in tension and in compression. The following analysis (summarized from Chadwick et al 1990) for the stress redistribution in a bend bar of a material containing a non-linear viscous fluid also includes the strain accommodated by elastic deformation of the hexagonal

grains¹.

The total strain ϵ_t in the material is assumed to be accommodated solely by the viscous flow ϵ_v (as given by the integral of equation 8 above) and by elastic strain ϵ_F . Thus:

$$\epsilon_{\rm t} = \epsilon_{\rm v} + \epsilon_{\rm E} \tag{9}$$

For small increments of time:

$$\frac{\delta \epsilon_{t}}{\delta t} = C \Phi R(\epsilon_{N}) \sigma^{N} + \frac{\delta \sigma / E}{\delta t}$$
(10)

This equation can be normalized by dividing by the volume fraction intergranular phase f, i.e. $\epsilon_{N} = \epsilon_{t}/f$, and substituting normalized terms for stress $\sigma_{N} = \sigma/(Ef)$, and time $\delta t_{u} = C\Phi E^{n} f^{n-1} \delta t$:

$$\frac{\delta \epsilon_{\rm N}}{\delta t_{\rm N}} = R(\epsilon_{\rm N})\sigma^{\rm n} + \frac{\delta \sigma_{\rm N}}{\delta t_{\rm N}}$$
(11)

The stress distribution as a function of time is calculated numerically following the procedure given by Chuang et al (1988). First, for a constant total strain, the $\Delta \epsilon_v$ for an initial elastic stress distribution is calculated. This destroys the equilibrium conditions of no net axial forces and constant moment for a fixed applied load as described by:

$$\int_{-h}^{h} \Delta \sigma_{\rm E}({\rm y}) \, {\rm d}{\rm y} = 0$$

 $\Delta \sigma_{\rm E}({\rm y}) {\rm y} {\rm d} {\rm y} = 0$

'(12)

The second step restores these conditions by calculating a new $\sigma_{_{
m E}}$

¹John Dryden of the University of Western Ontario is acknowledged for his contribution in developing the computer prgram for this calculation. distribution (i.e. ϵ_v is constant, ϵ_t changes). These steps are used to provide the stress distribution within a bend bar as a function of viscous creep. This distribution is shown in figure 4.33 at several creep strains. Note that the initial stress distribution is symmetric. As strain accumulates the amorphous phase is first squeezed out from between grains on the compressive side of the bar. These grains lock together and can then support a larger load. While this occurs the neutral axis shifts towards the compressive face. As creep continues, grains on the tensile surface will also become locked together and all of the load will be supported on the tensile and compressive faces. Thus the limiting strain in bending (the maximum outer fibre tensile strain) is the same as found in compression. The total outer fiber tensile stress and strain rate are shown as a function of time and maximum outer fibre strain in figure 4.34a and 4.34b. The outer fibre strain rate is also plotted on a log-log scale with those for uniaxial creep in figure 4.35. The difference in the constant strain rate for bending and uniaxial creep under the same normalized stress is due to the redistribution of stresses in the bend bar. In addition, the limiting strain in bending approaches the limiting strain in tension.

4.5.3 COMPARISON OF MODEL AND EXPERIMENT: °

4.5.3a Creep Resistance vs Strain and Intergranular Film Thickness

The model and the experimental creep results are compared on the basis of the strain rate - strain relationship in figure 4.36. A stress exponent of n = 4 is used to analyze the data (based on the

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experimentally determined stress exponent for strains less than .2%). The left and bottom axes are the strain rate and strain of the experimental data. The right and upper axes are for the theoretical curves. These are plotted as normalized strain rate versus normalized strain. The normalized and experimental values are related via:

$$\epsilon_{N} = \epsilon_{t} / f$$

$$\frac{\delta \epsilon_{N}}{\delta t_{u}} = \frac{\delta \epsilon_{t} / f}{C \Phi E^{n} f^{n-1} \delta t}$$

and

δtu

The experimental and theoretical curves are plotted on a log-log scale with the same increments. In this way, changing the normalizing terms simply shifts the theoretical curve.

Both the experimental and theoretical bend data show an initial constant strain rate followed by a rapid decrease in strain rate as the strain approaches a limiting value. The fact that the drop is not as sharp in the experimentally obtained curves as predicted theoretically may result from the non-uniform distribution of initial grain boundary phase in the real material. From the viscous flow model the limiting strain depends on H/L. As this value varies from grain boundary to grain boundary, a range of limiting strains will exist.

According to the viscous flow model, the strain rate and the strain at which the strain rate drops depends on the initial value of H/L.Experimentally the drop in strain rate occurs at a strain of approximately 0.2-0.3%. From the model, this drop occurs at a normalized strain ($\epsilon_{\mu}=\epsilon/f$) of .32, which corresponds to an initial normalized glass layer thickness, $f = 2H/\sqrt{3L}$, of 0.006-0.01. If one assumes an average silicon nitride grain size of about 1 micron (an approximate value as seen in figure 3.2), this in turn corresponds to a grain boundary thickness of 14-20nm. This value can be compared to those measured by Clarke (1989) on a MgO doped silicon nitride which had

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(14)

been quenched from 1450°C to room temperature. Using high resolution electron microscopy Clarke measured the intergranular amorphous phase thickness to occur in a range from 2 to 10nm. Possible reasons for this difference will be given shortly. Nevertheless, in terms of the strain at which the strain rate decreases, it is clear that the model is in approximate agreement with experiment.

4.5.3b Effect of Applied Stress in Bending

The strain at which the strain rate starts to decrease depends on the applied bending stress as shown in figure 4.37. It occurs at a 0.1% lower strain for samples loaded under 63MPa than those under 74MPa. Given that $\epsilon_{11}=H_A/(\sqrt{3}L)$ and assuming a grain size of approximately 1 micron, this measured strain difference corresponds to a difference in intergranular thickness of 3.5nm. The stress dependence cannot be due to the elastic deformation of the silicon nitride grains since this would account for a strain difference of only 0.004%. The discrepancy can be partially explained in terms of the equilibrium intergranular phase thickness which, as will be shown below, is expected to decrease as the applied stress increases.

The equilibrium thickness can be estimated using a model developed by Clarke (1987). Clarke considers a number of forces which act across a viscous layer between two grains. These include the applied and capillarity forces, the van der Waals force (an attractive term acting on the grains on either side of the grain boundary), the steric force (a repulsive term due to the structure of the liquid adopting an orientational order close to each grain), the force due to the formation of an electrical double layer in the liquid, and

forces due to solute adsorption on the grain surfaces and hydrogen bonding. However, in the absence of experimental evidence indicating that electrical double layer interactions, solute adsorption and hydrogen bonding occur in ceramics at high temperatures, Clarke neglects their effects. However, as Clarke also states, double layer interactions and adsorption are likely to occur and contribute to the repulsive forces acting to separate the grains. Clarke also assumes capillarity effects are negligible. The energy due to the applied force is simply the force times the intergranular thickness h. The van der Waals force is given by Clarke to be:

 $F(vdw) = HaBa/(6\pi h^3)$

where $H\alpha\beta\alpha$ is the Hamaker constant for two α surfaces separated by β . The van der Waals energy contribution, calculated by integrating the force over the grain separation, is:

 $G(vdw) = -H\alpha\beta\alpha/(12\pi h^2)$

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The energy contribution due to steric forces is given by:

 $G(\text{steric}) = 2an^2 \epsilon \operatorname{coth}(h/2\epsilon)$

where an² is a measure of the free energy difference between ordered and disordered states (Clarke lets this term equal the free energy of melting of pure silica) and ϵ is the length of orientational fluctuations in the intergranular phase (assumed equal to .3nm, the length of a SiO₄ tetrahedral unit). Using Clarke's values for the Al₂O₃-SiO₂-Al₂O₃ system at 2000K, the equilibrium thickness is calculated to be approximately 2.3nm for the case of no applied force. This value is in the range of 2.1 to 2.4nm that Clarke gives. Clarke also provides a table in which he lists the Hamaker constants for different systems and their corresponding equilibrium grain boundary thicknesses.[©] It should be noted that the Hamaker constants given are for room temperature. To calculate to thicknesses at elevated temperatures these

constants must be multiplied by T/300 (as the Hough-White expression, equation A-1 in Clarke 1987, shows). The theoretical equilibrium grain boundary height for Si₃N₄-SiO₂-Si₃N₄ of 1.7nm compares well with measurements of 0.6-2nm for a number of silicon nitrides (Krivanek et al 1979, Ahn and Thomas 1983, Lou et al 1978), although thicknesses of up to 10nm have been measured by other researchers on materials of the same nominal composition as well as silicon nitrides of different compositions (Clarke 1989, Clarke and Thomas 1978). These differences may result from a number of approximations used in calculating the equilibrium thickness. Haßa and an² values for a pure SiO₂ boundary were used as values are not available for the correct grain boundary composition. Electrical double layer and adsorption effects were also neglected in the calculation of the equilibrium thickness. These would contribute to the repulsive energy between grains and would lead to an increase in the equilibrium thickness. Not included in Clarke's calculation is a term which minimizes the amount of interfacial area (i.e. a large triple junction and a thin grain boundary film has less interfacial area than if no triple junction exists and all the amorphous phase is in a thick grain boundary layer). As the difference in energy between a thick boundary and one of minimum thickness is small (of the order of lmJ/m^2), any of these factors could have a significant effect. on the equilibrium thickness of the film.

The above equilibrium thickness values are expected to increase slightly with temperature as the thermal expansion of the amorphous boundary is likely to be larger than that of the crystalline grains (Clarke 1989). An order of magnitude calculation can be made using a thermal expansion coefficient for silicate glasses of order 20 to 100 $\times 10^{-7} \circ C^{-1}$ (Loehman, 1980; Hyatt and Day, 1987) and assuming the glass is not constrained by the silicon nitride grains. At 1000°C the

amorphous phase will expand by .2 to 1%. This change is much less than the uncertainties in the data and in the model, i.e. it is insignificant.

Evaluating the effect of temperature on the other terms in the force balance equation is more difficult. Clarke's work on the effect of temperature on the van der Waals forces is confusing. In one paper Clarke (1987) provides Hamaker constants for the same system at two temperatures. The value at 2000K is greater than at 273K. Using these values the equilibrium grain boundary height is estimated to be 0.9nm smaller at the higher temperature. In a subsequent paper (Clarke 1989) in which the first paper is referred to, it is stated that as the van der Waals force is proportional to temperature (as given by the Hough-White expression in appendix A), the grain boundary thickness is expected to increase logarithmically. However an increase in the van der Waals force is expected to decrease, not increase, the boundary height.

Steric forces are also expected to change with temperature. As Clarke (1987) states, this effect comes into effect through the term an², the difference in energy between ordered and disordered states. Small differences in this value are not expected to have a large effect on the equilibrium boundary thickness.

The discrepancy seen in comparing Clarke's intergranular film thickness as measured by AEM (Clarke 1989) with the equilibrium value calculated for the Si_3N_4 -SiO₂ system (Clarke 1987) indicates that the above effects may be significant. Clarke's measured thicknesses of 2-10nm on the MgO doped Si_3N_4 quenched from 1450°C are larger than the approximately 1nm value obtained for MgO doped samples which have not been quenched. These in turn are approximately equal to the predicted room temperature equilibrium value of approximately 1.7nm.

Clearly the lack of experimental variables to calculate the magnitudes of the various forces limits the ability of Clarke's net force model to provide accurate estimates of the boundary thickness. However the model does provide a good theoretical basis for the existence of an equilibrium grain boundary thickness as observed experimentally. With this in mind, the above model can be applied to the silicon nitride system. For the $Si_3N_4-SiO_2-Si_3N_4$ system at 1200°C a Hamaker constant of 380 x 10⁻²¹J will be used. The equilibrium thickness in the absence of stress is calculated to be 1.9nm. This value drops to 0.9 and 0.8 nm when stresses of 60 and 80MPa are applied respectively. The energy-thickness dependence for each of the energy terms as well as the sum of the terms are shown in figure 4.38. In the absence of any applied stress the difference in energy between a boundary of minimum thickness and a very thick boundary is of the order of $2mJ/m^2$. As shown in appendix 4b, although the rate of diffusion due to this small difference in free energy is small, it is attainable.

The calculated difference in minimum intergranular thickness due to differences in the applied stress of the order of 20MPa is approximately .1nm, corresponding to a strain of .005% (assuming $\epsilon_{11}=H_A/\sqrt{3L}$ and L=1 micron). This is less than the measured difference in the strain (of the order of 0.1%) at which the strain rate starts to decrease under applied loads of 60MPa versus 80MPa. However, it does predict the correct trend. The magnitude of the grain boundary thicknesses, both the initial minimum thickness and the difference in equilibrium thicknesses under 60 and 80MPa, are considerably greater than the theoretical values. An additional factor to consider in using

the thickness values obtained from the strain rate vs strain plots of the bend data is that the thicknesses are average values calculated assuming an average silicon nitride grain size of 1 micron. These average values include boundaries of the minimum (equilibrium) thickness as well as those containing large amounts of glass as a result of an intergranular pocket of glass extending between grains (as shown in figure 3.2). Thus the calculated grain boundary thicknesses should not be expected to accurately forecast the difference in total strain under different applied stresses.

4.5.3c Effect of Preannealing on Creep:

The experimental bend test data for samples which were tested following annealing can be analyzed in terms of the viscous flow model. The analytical electron microscopic results combined with an elemental mass balance (as detailed in chapter 3) have been used to quantify the fraction of the amorphous phase present after annealing at 1250°C. Approximately 60 volume percent residual glass is found in the centre of air annealed samples and 30 % near the surface. If all of the glass were evenly distributed in all the grain boundaries with no pockets, the volume fraction of glass would equal f, the normalized grain boundary layer thickness. Assuming a value of 50% residual glass (as the exact value is not critical), the non-linear viscous flow model can be used to calculate the expected drop in the initial strain rate. From equation 8 the strain rate is proportional to f^{n+2} . For the case of n=4, and a 50% reduction in the volume fraction of glassy phase from f=.01to .005, a drop in the initial strain rate by two orders of magnitude is predicted. Experimentally, there is less than half an order of

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 ϵ^{-1}

magnitude difference in the initial strain rate. However, it is clear from the TEM micrographs (figure 3.2) that the glass is not evenly distributed. Instead, the majority of the amorphous phase is found in the triple points between silicon nitride grains. Thus the volume fraction glass does not equal the normalized grain boundary thickness Moreover, when partial grain boundary crystallization occurs layer. these pockets crystallize. As shown in the dark field micrograph of figure 3.3, the crystallized grain boundary phase can extend around several silicon nitride grains. Thus some of the grain boundaries must also be crystalline. However, as the majority of the crystalline phase is in pockets or in channels between three or more grains, crystallization of 50% of the glass does not imply crystallization of 50% of the material at the grain boundaries between two grains. The smaller strain at which the strain rate decreases as a result of preannealing may be a due to the additional crystalline material limiting grain movement.

4.5.3d Compression Tests

The strain rate-strain behaviour of samples tested in compression shows a rapidly decreasing strain rate at strains considerably less than in the bend case. In addition, an initial constant strain rate regime is not visible. A comparison of the theoretically predicted strain rate-strain behaviour for bend and compression tests (figure 4.35) shows that the limiting strain in bending approaches that expected for uniaxial tension (i.e. maximum strain occurs when all the amorphous phase on the sajacent grain boundaries has moved to the boundaries perpendicular to the stress
axis). The smaller limiting strain in compression occurs when all of the intergranular phase has been squeezed out from between faces under compression. In addition, the constant initial strain rate plateau ends at much smaller strains in compression than in bending. This makes it difficult to detect the constant strain rate regime with the strain resolution available in these tests. The greater difference between the observed data (compression vs. bending) as compared with that predicted (see figure 4.36) is in keeping with the trends seen in the previous sections.

4.5.3e Additional Support for Viscous Flow Model

Additional support for the viscous flow model discussed earlier can be found in work by Vaandrager and Pharr (1989) on the compressive creep of copper containing liquid bismuth. The strain rate behaviour as a function of strain as shown by Vaandrager and Pharr is shown in figure 4.12. Although none of the plots show an initial constant strain rate, they do show a rapid decrease in strain rate and a large initial strain. Vaandrager and Pharr discuss this large initial strain in terms of viscous flow of the grain boundary phase (as described in section 4.2.5). Using the viscosity of bismuth, the applied stress and various estimates of the grain boundary phase thickness, they calculate that the time for the maximum strain to occur by viscous flow is approximately 10^{-5} seconds. Thus a constant strain rate at low strain would not be observed under these stresses.

Determining whether or not viscous flow is important on the basis of an initial constant strain rate is difficult for data taken from the literature. This is because most authors are concerned with

a secondary or steady state regime. As a result limited data is collected or published for low strains. However, in most cases evidence for an initial creep regime can be found by extrapolating the steady state creep rate back to the starting time. An initial plus primary creep strain of close to 1% (Grathwohl, 1984; Todd and Xu, 1989) generally exists. Although some of this may occur during the time required for stress redistribution, it is more likely that most of this is a result of creep due to viscous flow. A second creep mechanism such as cavitation or solution/reprecipitation may occur after the grains have started to lock together. One would then expect the strain rate to be constant at low strains, decrease as viscous flow nears completion and then become constant as a second slower steady state creep mechanism becomes dominant. Tertiary creep may be seen prior to failure. This sequence is depicted schematically in figure 4.40. It appears that this may indeed occur in SN220 at higher temperatures (although with the absence of tertiary creep) as shown in the creep data taken at 1325°C (figure 4.41). The temperature range over which both regimes are easily seen is likely to be quite small. At low temperatures observing creep due to viscous flow would be easy (provided premature fracture does not occur). However the temperature may be too low for a significant amount $creep^{i}$ to occur via а second mechanism such of as solution/reprecipitation. At high temperatures viscous flow may occur rapidly and be difficult to detect. In this case only the creep resistance in the second creep regime would be recorded. However, a large initial strain due to viscous flow would still occur.

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4.5.4 CREEP FRACTURE

4.5.4a Stress Redistribution

The viscous flow creep model predicts that the neutral axis in a bend test moves with time. This is shown in figure 4.33. Measurements of the tensile and compressive lengths of the bend bars indicate that the neutral axis moves towards the compressive face during the test (table 4.2) as is expected from previous work (Wiederhorn et al 1986).

The model also predicts that the outer fiber tensile stress decreases with time. This is shown clearly in figure 4.34. Here stress redistribution reduces the outer fiber tensile stress to 23% its original value in the time it takes for a normalized outer tensile fibre strain of .033 to accumulate. For an initial f of 0.006, this corresponds to a strain of 0.02%. In the case of 63MPa applied load, this occurs in less than 20 minutes. As this is less than the time required for formation of oxide pits, the surface flaws in the preannealed case are subject to much higher tensile stress than the surface flaws which form during the bend test. This may account for the effect of pit removal on increased creep lifetime.

4.5.4b Effect of Partial Grain Boundary Crystallization on Failure Time

Although preannealing has very little effect on the creep behaviour, it does have a dramatic effect on the lifetime of the material. As shown in figure 4.28 even short preanneals have a pronounced effect on the time to failure. There are several possible explanations for this behaviour: degradation of the surface finish

resulting in the formation of critical flaws, internal cavity generation as the microstructure evolves, or a decruase in the amount of amorphous phase in the intergranular pockets reducing material ductility. Each of these possibilities will now be examined.

Preannealing SN220 does lead to the formation of large surface pits as shown in chapter 3. The effect of these on the creep properties can be seen by comparing the bend data for samples crept at the same temperature and stress but after different annealing conditions and different surface sample preparation. Figure 4.39 shows the creep data for 3 samples; one crept in the as received condition after polishing the tensile surface, the second polished and annealed in air for 25 hours prior to the creep test, and the third sample annealed in air for 25 hours and then polished prior to the creep test. Clearly polishing after oxidation to remove any surface scale and pits does increase the creep time and strain. As stresses redistribute more rapidly than new pits form, new surface flaws are not subject to the same applied stress as pits on annealed materials (see section 4.5.4a). However, removal of these flaws does not increase the creep life expectancy to the level found in the as sintered material. Thus surface finish alone does not account for the decrease in time to failure with preannealing.

The possibility of microstructural evolution causing the formation of cavities was investigated through a series of density measurements on samples before and after annealing, and before and after removal of any oxide scale. As discussed in chapter 3, the decrease in density found after annealing results from the formation of the oxide scale. However it is possible that a small amount of cavitation or cracking could reduce the lifetime without a significant decrease in density.

During annealing, partial grain boundary crystallization occurs.

As described in chapter 3, this leads to a decrease in the number of large amorphous triple pockets. As a result, the ability of the material to accommodate stresses arising from the viscous flow of the glassy phase and subsequent grain movement is reduced. Thus stress concentrations leading to failure occur earlier in the preannealed material.

These stress concentrations may also account for the higher strain rate seen at longer times in compression tests on samples which have a partially crystalline grain boundary phase compared to samples crept in the as sintered condition (figure 4.29). It is postulated that a secondary creep damage mechanism is occurring at a faster rate than in material with amorphous intergranular pockets.

4.6 CONCLUSIONS

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SN220 has been crept in both bending and compression under a variety of loads. Samples have been tested in the as sintered condition and after annealing for various lengths of time. The intergranular amorphous phase is known to be partially crystalline in the latter (see chapter 3).

All samples crept in bending exhibit an initial constant strain rate at strains less than 0.3%. The strain rate decreases rapidly at larger strains. This decrease occurs at higher strains for samples crept under larger loads. Preannealing the material does not affect the initial constant strain rate. It does however cause the strain rate to decrease at smaller strains than for the as sintered material crept under the same conditions. Preannealing reduces the lifetime of the material for samples whether or not they have been repolished prior to

creep testing. Removal of the oxide scale does however increase the life of preannealed materials.

Samples crept in compression do not exhibit the same initial constant strain rate as found in bending. In addition, creep compression samples showed little effect of prior annealing.

A model has been developed which describes the creep behaviour of sintered silicon nitride. It assumes creep occurs due to the nonlinear viscous flow of an amorphous phase around rigid grains. An initial constant strain rate is predicted at low strains. The strain rate decreases as the strain approaches a limiting value. The maximum strain in compression occurs when essentially all of the fluid is squeezed out from between grain faces perpendicular to the stress axis. In tension, the maximum strain occurs when essentially no fluid is left on faces adjacent to those perpendicular to the stress axis. In bending an initial constant creep rate is predicted. This value decreases after grains on the compressive side begin to lock together. The limiting outer fibre strain in a bend bar however approaches the limiting strain predicted in tension.

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The maximum amount of strain in the bar depends on the initial intergranular film thickness and the equilibrium film thickness which exists under an applied load. An estimate of the film thicknesses can be obtained using a model developed by Clarke (1987). A larger creep strain would be expected under a larger load. The initial intergranular film thickness also affects initial strain rate.

Both the viscous flow creep model and the experimental bend tests show the same initial constant creep rate at low strains. The decrease in the strain rate occurs at a normalized strain of 0.32. This corresponds to an initial intergranular phase thickness of 14 to 20 nm. The decrease in strain rate at slightly smaller strains for tests under smaller loads is partially explained by the presence of an equilibrium boundary layer thickness which depends on the applied load. Although the difference in boundary height under different applied loads and the initial equilibrium film thickness as calculated with Clarke's model are less than that obtained from the viscous flow model and bend tests, the correct trends are predicted. In fact exact values are not expected as this would imply that all boundaries are of an equilibrium height. This is not the case as large pockets of amorphous phase extend into the grain boundaries.

Strain rates in compression do not show the same initial constant behaviour as found in bending. The strain rate in compression is also lower than in bending for the same strains. The viscous flow model predicts that the strain rate decreases at a lower strain in compression than tension. It is likely that, due to limitations in the compression testing, the constant creep rate region was not detected. A slower strain rate in compression than bending for the same strain is expected from the viscous flow model. The observed difference is however greater than that predicted. Again this may be due to difficulties in obtaining accurate strain measurements.

Partial grain boundary crystallization was found to have little effect on the initial creep rate in bending or compression. The viscous flow creep model predicts a strong dependence of the initial strain rate on the fraction of intergranular phase present. This suggests that annealing has very little effect on the thickness of the intergranular phase. Support for this was found in microstructural analysis showing that most of the amorphous phase exists in large pockets. Annealing leads to crystallization of most of these. Although not examined in this work, annealing has never been found to lead to crystallization of the film at two-grain boundaries.

Partial grain boundary crystallization does however have a large effect on the time to failure. The reduction in lifetime of samples crept with their oxide surface intact is partially due to oxide pits being subjected to high surface stresses. In the case of creep testing of as sintered material, stress redistribution occurs before pits form on the surface. Thus oxide formation during the creep test does not have the same catastrophic effect found in testing annealed bars with their oxide surface intact. Repolishing an annealed sample prior to testing increases the time to failure, although not to the level found for as sintered material. This is thought to be due to the intergranular pockets losing their ability to accommodate stresses arising from the viscous flow of the grain boundary phase. Thus stress concentrations leading to failure occur earlier in the annealed material.

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4.7 TABLES AND FIGURES

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Table 4.1:	BEND TEST	CONDITIONS	
TEMPERATURI C	E STRESS MPa	TEST	ŧ
1100	212 185.5	6 7	
1150	174.9 159 159 159 137.8	9 5 4 13 14	
	132.5 127.2 121.9 111.3	20 21 12 10	
1200	79.5 265 212 159	8 1 2 3	
	85 85 80 80	42 43 40 45	
s.	79.5 79.5 76.8 74.2	16 19 24 18	
1215 1225 1250	53.6 53.6 63.6 63.6 58.3 58.3 58.3	17 15 28 27 26 34 35 37	
1325	53 47.7 42.4 42.4 37.1	36 38 30 33 31	
1400	37.1 21.2	32 29	
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Table 4.1 (cont)

TEMPERATURE C	STRESS MPa	ANNEAL hours	TEST 🛊	
1200	85	25	48	
	85	25	49	
	85	100	44	
	85	100	46	
	80	25	41	
	80	100	50	
	80	400	52	
	74.2	25*	22	
	74.2	25	25	
	74.2	100	51	
	74.2	400	53	
	63.6	25	23	
	63.6	100	54	
•	63.6	400	55	

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* sample not polished after oxidation

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Table 4.2: NEUTRAL AXIS LOCATION

TEST TEMP	TEST #	STRESS	FAILURE TIME	FAILURE STRAIN	RELATIVE N.A. HIEGHT
(C)		(MPa)	(hr)	(\$)	FROM COMP. SURFACE
1200	45	80	>26	>1.2	.22 ± .20
1215	28	63.6	>310	>2.3	.29 ± .08
1250	37	58.3	49.6	1.23	.19 ± .15
1250	36	53	97.5	2.68	.17 ± .10
1325	32	37.1	>51.5	2.78	.26 ± .06

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4.7 FIGURES

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Figure 4.1. Dependence of rupture strain and rupture time on applied stress indicating a threshold stress exists below which atmosphere influences rupture behaviour of Si_3N_4 (Grathwohl 1983). Slope change has been drawn in for clarity for tests done in air.

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 $\sum_{i=1}^{n}$







Figure 4.4. Example of creep data from one of four different Si_3N_4 materials all showing the same behaviour. Bending stress is 160MPa (Ernstberger et al 1986).

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Figure 4.6. Flexural stress rupture in air for HPSN (as-machined specimens). The change of slope, as drawn in for clarity, indicates the creep fracture regime. (Quinn 1986a)



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Figure 4.7. Nucleation and growth process for oblate holes in thin glass films and spherical holes in three grain pockets. Oblate holes form a full facet cavity by coalescence. Spherical holes grow to full facet size by viscous flow at high local stresses and by solution/reprecipitation at low local stresses. (Marion et al 1983)

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Figure 4.10. Model for creep due to viscous flow unrealistic as grains movement is not limited by grains 'jamming' into each other as they would in a real material. (Pharr and Ashby 1983)



Figure 4.11. (a) Two dimensional model for incompressible material between rigid hexagons. (b) Expanded view of three grain junction. Velocity gradients of fluid in boundary are shown. (Drucker 1964)

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Figure 4.12. Theoretical predictions of strain produced by percolation of liquid around solid grains for copper-bismuth system (Vaandrager and Pharr 1989).

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Figure 4.13. (a) Model for unconstrained fluid flow from between two parallel plates. (b) Constrained fluid flow.



Figure 4.14. Strain dependent term S(E) of the strain rate as a function of normalized strain ε_N (where $\varepsilon_N =$ strain ϵ / fraction boundary phase f).

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Figure 4.15. Creep of alumina at 1044°C, under 60MPa. (a)No prior annealing. (b) Annealed 96hr prior to testing. Note annealing results in a 200-fold increase in lifetime, primarily as a result of grain boundary devitrification. (Wiederhorn et al 1986)



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Figure 4.17. Compression testing rig for MTS.

compression testing rig for MTS.



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Figure 4.18. Typical creep curves for SN220 crept in four point bending at 1200°C under a variety of stresses.



Figure 4.19. Examples of SN220 sample to sample variations in four point bend creep results. (a) Strain - time plots (b) Corresponding strain rate - strain plots.

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Figure 4.20. SN220 stress rupture data for comparison to data obtained by Grathwohl (fig. 4.1.) and Quinn (fig. 4.6). Arrows indicate samples which have not fractured.



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Figure 4.21. Failure strain as a function of stress for SN220 crept in bending. Arrows indicate samples which have not fractured.



Figure 4.22. Monkman-Grant type plot using initial constant strain rates vs. time. Arrows indicate samples which have not fractured.

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Figure 4.26. Effect of preannealing SN220 (in order to partially crystallize grain boundary phase) on the strain rate dependence on (a) time (b) strain. Tests and preanneals done at 1200°C, 63.5MPa.



Figure 4.27. Effect of preannealing SN220 (in order to partially crystallize grain boundary phase) on the strain rate dependence on (a) time (b) strain. Tests and preanneals done at 1200°C, 74.0MPa.



Figure 4.28. Creep life as a function of preannealing time. Bend tests at 1200°C.



Figure 4.29. Creep curves for compression tests at 1200°C, on both assintered and preannealed material.



Figure 4.30. Creep resistance as a function of strain for as-sintered and preannealed material. Compression tests at 1200°C, 80MPa.

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Figure 4.31. Two dimensional solid consisting of hexagonal grains of length 2L with intergranular phase of width $2H_A$, $2H_B$ and $2H_C$. The surrounding material exerts stresses σ_{ij} on the system. These can be related to the squeezing forces F_A , F_B and F_C which are aligned with A, B and C, the vectors joining grain centers. (Dryden et al 1989)



Figure 4.32. Strain rate dependence on strain as predicted from creep model due to non-Newtonian flow. $R(\epsilon_N) =$ strain dependent term of the strain rate (eqn 13) and $\epsilon_N =$ normalized strain = ϵ/f where f is the normalized grain boundary layer thickness.

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Figure 4.33. Stress distribution in a bend bar at several strains as predicted by creep model due to non-Newtonian flow for the case of stress exponent n = 4 and normalized stress $\sigma_N = \sigma/(Ef) = 0.01$.



Figure 4.34. Outer fibre stress and strain rate in a bend bar as a function of (a) normalized time and (b) normalized outer fibre strain for n = 4 and $\sigma_N = 0.01$.



normalized strain

Figure 4.35. Normalized outer fibre strain rate versus normalized strain for n = 4, $\sigma_N = 0.01$ in tension, compression and bending. Normalized strain rates for uniaxial creep are related to $R(\epsilon_N)$ (for comparison with $R(\epsilon_N)$ vs ϵ_N in figure 4.33) through ϵ_N = normalized strain rate = $R(\epsilon_N)\sigma^N$.

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Figure 4.36. Creep resistance as a function of strain as predicted theoretically (top and right hand axis) for n = 4, $\sigma_N = 0.01$; and as found experimentally for bend and compression tests at 1200°C (left hand and bottom axis). The increments of the two scales are the same.





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INTERGRANULAR FILM THICKNESS (nm)



 $\langle \underline{\lambda} \rangle$







STRAIN

Figure 4.40. Expected creep resistance behaviour as a function of strain for material exhibiting viscous flow followed by a second creep mechanism such as solution/reprecipitation or cavitation. Tertiary creep then leads to failure.



Figure 4.41. Creep resistance vs strain for bend tests at 1325C. Initial and final constant strain rate regions are found.

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4.8 APPENDICES

APPENDIX 4a: CALCULATION OF SEPARATION RATE OF PARALLEL PLATES SEPARATED BY NON-NEWTONIAN FLUID.

The rate of separation of two parallel plates $(2\delta H/\delta t)$ separated by a non-Newtonian fluid is calculated following the procedure outlined in Bikerman (1968). According to Newton's second law, the sum of the forces per unit volume equals the density times the acceleration. Assume that the flow is fully developed (i.e. no acceleration). Therefore the sum of the forces equal zero. These forces include gravitation, pressure and viscous contributions. Gravitation is

are neglected as plates The pressure of the horizontal. fluid varies as a function of x (reducing to p=P at x=L). The viscous force T acts in the x direction on a plane perpendicular to the z axis. Thus:

 $\delta p / \delta x = \delta T_{yx} / \delta z \quad \{A-1\}$

Assume that the viscosity of the fluid is described by the from between two parallel plates. constitutive equation of the form:

 $\dot{\mathbf{v}} = \Phi \mathbf{T}^{\mathbf{n}}$



Figure 4al: Geometry for fluid flow

{A-2}

 γ is the shear strain rate, equal to where T is the shear stress. $\delta u/\delta z$, where u is the linear velocity of the fluid moving in the xdirection and z is the direction perpendicular to this as shown in

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figure 4a1. Thus

Integrating equation A-1 from the mid-point of the fluid height H to z and inserting the solution for the shear stress T gives:

$$\delta u/\delta z = \Phi (\delta p/\delta x)^n (z - H)^n \qquad \{A-4\}$$

On integrating the following is obtained:

$$u = \Phi \left(\frac{\delta p}{\delta x} \right)^{n} \left[\frac{(z-H)^{n+1}}{(z-H)^{n+1}} - \frac{(H)^{n+1}}{(n+1)} \right]$$
 (A-5)

In order to find an expression for $\delta p/\delta x$ and solve for p, the volume velocity of the fluid between the plates is calculated:

$$V = 2y \int_{H}^{2H} u \, \delta z$$

= 2y $\Phi \, (\delta p / \delta x)^n \, (H)^{n+2} / (n+2)$

This equals the volume of liquid flowing out between the bottom plate at x = 0 and any other plane x which is 2Hx/unit length. Thus:

$$yx \ \delta 2H/\delta t = V \qquad \{A-7\}$$

Equating A-6 and A-7, rearranging and integrating over x, with the boundary conditions p = P at x = L gives:

$$p = \frac{n}{a(n+1)} [x^{(n+1/n)} - L^{(n+1/n)}] + P$$
 {A-8}

where $\alpha = [2\Phi(H)^{n+2}/[(n+2)\delta 2H/\delta t]]^{1/n}$.

Since the pressure difference in the fluid is balanced by the pressure F/2L on the plate:

$$\int_{0}^{L} p \, \delta x = LF/(2L) \qquad \{A-9\}$$

integration gives:

$$\frac{2}{2H} = \frac{2}{n+2} \left[\frac{2n+1}{2n} \right]^n \qquad \frac{H^{n+2}}{\Phi} = \frac{1}{L^{2n+1}} (F + 2LP)^n \operatorname{sgn}(F + 2LP) \qquad (A-10)$$

where the sgn(F + 2LP) allows for the change in grain boundary height * in the appropriate direction for net tensile or compressive forces.

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{A-3}

{A-6}

Equation A-10 reduces to the result found by Bikerman (1965) for the case where P = 0. It also reduces to the result found by Dryden et al (1989) for linear viscous flow (when $\Phi=1/\eta$, n=1).

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APPENDIX 4b: CALCULATION OF FLUX DUE TO DIFFERENCE IN ENERGY BETWEEN EQUILIBRIUM AND NON-EQUILIBRIUM BOUNDARY LAYER THICKNESSES

Clarke's (1988) theoretical calculation of the intergranular film thickness predicts that an equilibrium film thickness exists for $Si_3N_4-SiO_2-Si_3N_4$. As shown in figure 4.38, only the lower limit to the thickness is well defined. The following calculation will show that the difference in excess free energy between an intergranular film of equilibrium thickness and one much greater than this will not lead to a significant flux of atoms. Therefore an upper limit on the intergranular thickness is not well defined.

The excess free energy of the system due to the layered structure is:

 $G = \gamma(h) A$

where $\gamma(h)$ is the excess free energy at an intergranular film layer thickness h, and A is the area of the interface. Suppose the film thickness is increased by one monolayer of height a (the atomic height). Therefore the change in free energy is:

 $\Delta G = (\partial \gamma / \partial h) a A$

The corresponding change in chemical potential μ is :

 $\Delta \mu = \Delta G / (N_A A)$

= $(\partial \gamma / \partial h) a / N_{A}$

= $(\partial \gamma / \partial h) \Omega$

where N_{A} is the number of atoms per unit area, and Ω is the atomic volume.

The gradient in chemical potential $\nabla \mu$ is given approximatly by $\Delta \mu$ /grain facet length 1. The flux is (Herring, 1950):

 $\sigma J = D \nabla \mu / (\Omega kT)$

The difference in excess free energy between an equilibrium

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thickness of a few nanometres and a 45 nm thickness is approximately $0.002J/m^2$ for Si₃N₄-SiO₂-Si₃N₄. For a facet length 1 of 1 micron, $\nu\mu$ is $5 \times 10^{10} (J/m^4) \ \Omega(m^3)$. For a diffusion coefficient of $10^{-7} \text{cm}^2/\text{s}$ at 1473K, the flux is 2 x $10^{19} \text{atoms/m}^2\text{s}$. The time required to reach the equilibrium height can be calculated with a mass balance. The decrease in volume of the boundary phase when boundary material is removed is $\partial h l^2$. The boundary height decreases as a result of the flux of material through the open edges of the boundary. Assuming square grains, this area is 41h. A mass balance gives:

 $\partial hl^2 = -J\partial t 4lh\Omega$

Integrating from h_0 at time t equals 0, to h_{eouil} at time t gives:

 $\ln(h_o/h_{eouil}) = 4J\Omega t/1$

For an order of magnitude calculation, let h_0 equal 45nm, h_{equil} equal 2nm, and Ω equal $4\pi r^3/3$ where r is the ionic radius (approximately 1A). Together with the values of J and 1 given above, the time for the boundary to reach equilibrium height is 2 hours.

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5 OVERALL CONCLUSIONS:

Sintered silicon nitride SN220 was analyzed on a microstructural level to differentiate between the effects of annealing and creep A methodology for quantitative electron energy loss damage. spectroscopy was developed for this purpose. The as sintered material contains $B-Si_{3}N_{4}$ grains surrounded by an amorphous intergranular phase. This phase is inhomogeneously distributed, existing mainly in large intergranular pockets. It was found that annealing leads to partial crystallization of the intergranular phase. The crystalline phases formed depend on the atmosphere used and position within the sample. The residual glass however, was found to be of the same composition, regardless of annealing environment. Thus the formation of a stable glass is suspected although attempts to verify this proved unsuccessful. Impurities in the silicon nitride material may have been responsible for the difference between intergranular and bulk crystallization behaviour.

In all cases the amorphous phase was found to be homogeneous, regardless of the adjacent crystalline phases. Thus diffusion channels must still exist between grains, possibly through thinner amorphous boundaries between two adjacent grains.

Creep deformation of as sintered or annealed material had no effect on the crystallization products or glass composition. As the glass composition was the same regardless of the degree of stress on the area, it appears that silicon nitride grains are not dissolving to any discernable degree. Additional effects of stress, such as cavitation and dislocations, were infrequently observed.

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Four point bend creep tests on samples with an amorphous or a partially crystalline grain boundary phase had very similar creep characteristics. Both showed an initial constant strain rate at low strains followed by a decrease in strain rate at higher strains. The strain at which the creep rate decreased was slightly smaller for samples crept under smaller loads and samples which had been preannealed. A more significant effect of preannealing was to decrease the time to failure. Compression tests of as sintered and preannealed material had the same initial creep rate behaviour, although a steady state was not observed.

The above creep behaviour can be explained using a model for creep due to non-linear viscous flow. The initial constant strain rate in bending is due to the redistribution of glass around the grains. The creep rate decreases as essentially all the amorphous phase is squeezed out from between grains near the compressive and tensile surface. As the thickness of the residual amorphous film between grains depends on the applied stress, the strain at which the strain rate drops will also The viscous flow creep model also depend on the applied stress. predicts a strong dependence of the initial strain rate on the initial intergranular film thickness. As partial grain boundary crystallization has little effect on observed strain rates, preannealing the material must not affect the intergranular film thickness. Microstructural observations indicate this is possible as diffusion channels must still exist between grains. The smaller strain at which the strain rate drops e for annealed material is due to the crystalline pockets limiting grain movement.

Although partial grain boundary crystallization has little effect on the creep resistance of the material, it does have a dramatic effect on the time, to failure. Lifetimes have been reduced

significantly due to the crystalline pockets loosing their ability to accommodate stresses due to viscous flow. As a result stress concentrations leading to fracture occur earlier in annealed material.

In a broader context, some suggestions can be made regarding the ideal microstructure of a structural ceramic component for use in high temperature applications. The intergranular phase in silicon nitride is present as a result of oxide additives used to enhance densification. As an amorphous phase softens at high temperatures and is detrimental to high temperature behaviour, crystallization of the glass has been suggested. This work has shown that partial grain boundary crystallization has a negligible effect on creep due to viscous flow. As the strain due to viscous flow can be as high as the fraction of intergranular phase present (intergranular film thickness divided by the grain size), a significant creep strain can occur. In SN220, this accounts for a 0.3% strain. This value can be decreased by increasing the grain size or decreasing the equilibrium film thickness. In the first case, a material with a larger grain size may be expected to accumulate stress concentrations faster and fail sooner. Poorer packing density would also be expected, leading to larger amorphous pockets. These may meet the criterion for cavitation and have detrimental oxidation characteristics. An inhomogeneous grain size distribution containing large and small grains may alleviate this problem. This configuration is also expected to have good fracture toughness. The second option of decreasing the equilibrium intergranular film thickness is more difficult. Clarke (1987) has modelled the forces across a grain boundary to calculate equilibrium intergranular thickness. The grain boundaries are expected to be thicker than the minimum equilibrium level due to poor grain packing and the presence of large intergranular amorphous pockets. Thus changing the chemistry to lower the minimum

equilibrium thickness is not likely to decrease the strain due to viscous flow. Again an inhomogeneous grain size distribution is recommended. Crystallization of the large pockets also alleviates the problem of large glassy pockets. However, this leads to the accumulation of stress concentrations and premature failure.

For high temperature applications it is therefore recommended to fabricate a material with small amorphous pockets and allow for strain due to viscous flow in the design of the part.

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