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The effect of the grain boundary phase on the fracture toughness of beta-silicon nitride ceramics.

Peterson, Irene Mona

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THE EFFECT OF THE GRAIN BOUNDARY PHASE ON THE
FRACTURE TOUGHNESS OF β-Si₃N₄ CERAMICS

by

Irene Mona Peterson

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Materials Science and Engineering)
in The University of Michigan
1995

Doctoral Committee:

Professor Tseng-Ying Tien, Chair
Professor I-Wei Chen
Professor John Halloran
Professor Victor Li

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For my husband and my parents
ACKNOWLEDGMENTS

This thesis would not have been possible without the encouragement and assistance of many people. I would like to thank my advisor, Professor T. Y. Tien for his encouragement and assistance throughout my graduate career, and Dr. Z. K. Huang and Professor E. Hucke for many useful discussions. I am grateful for the comments and suggestions of the members of my dissertation committee.

The friendship and help of the graduate students in this department have been invaluable. I thank Mohan Menon for his comments on this thesis and N. Sridhar for his advice on modeling. Special thanks also go to Dr. S. L. Hwang and Dr. D. S. Jacobs for answering many questions about the behavior of silicon nitride.

This work was sponsored by the U. S. Department of Energy, Office of Transportation Technologies, Advanced Materials Development Program under Contract No. DEA CO5 84OR2140, administered by Oak Ridge National Laboratory. Their support is gratefully acknowledged.

Some of the work in this thesis was performed at Oak Ridge National Laboratory under the HTML User's Program, under Contract No. DEA ACO5 84OR21400. The successful completion of the experiments at ORNL was made possible by the advice and assistance of Dr. X-L. Wang and Dr. T. R. Watkins.
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CHAPTER 1

INTRODUCTION

Silicon nitride is one member of a family of ceramic materials developed for use in structural applications at high temperatures. Silicon nitride ceramics exhibit excellent mechanical strength up to 1000°C and good thermal shock resistance. The mechanical strength is provided by a three-dimensional network of strong covalent bonds, which also inhibit self-diffusion of silicon and nitrogen.

The slow self-diffusion rates in silicon nitride inhibit mass transport and densification during sintering. To prepare dense silicon nitride ceramics, sintering aids are added. The additives react with the silicon nitride to form a liquid which surrounds the silicon nitride particles. Since mass transport in the liquid occurs at a much faster rate than in the solid, full densification can be achieved by liquid phase sintering.

On cooling, some of the sintering liquid solidifies into a grain boundary phase which can be either amorphous or crystalline. The mechanical properties of the grain boundary phase influence the mechanical properties of the silicon nitride ceramic. For example, amorphous grain boundary phases can soften at high temperatures and lower the high temperature strength and creep resistance of the silicon nitride ceramic. In some cases, the grain boundary phase can be crystallized to improve the creep resistance and high temperature strength of the silicon nitride.

The effects of the grain boundary phase on the mechanical properties is not well understood. In order to design tougher, stronger silicon nitride ceramic materials, the effect of the grain boundary phase on the strength and toughness must be determined. The goal of this thesis was to determine the effect of the grain boundary phase on the fracture toughness of silicon nitride.
The fracture toughness of silicon nitride ceramics depends on the crack path in the material. On the microstructural level, the interaction between the crack and the grain boundary phase determines whether the crack will grow around or through the silicon nitride grains in its path. If either the interface or the grain boundary phase provides a weak path for the crack, then the crack will be deflected around the silicon nitride grains, and will leave intact grains in the crack wake. As the crack opens, intact grains which bridge the crack absorb energy as they stretch, rotate and pull out of the matrix. As a result, the bridging grains improve the fracture toughness of the material.

The behavior of the crack at the grain boundary is controlled by the bonding between the silicon nitride and the grain boundary phase, the mechanical properties of the grain boundary phase, and the presence of residual stresses. In this thesis, the properties of the grain boundary phases were explored by using bulk samples of oxynitride glasses with compositions similar to those of the grain boundary phases. The Young's moduli, glass transition temperatures, fracture toughness and thermal expansion coefficients of oxynitride glasses were measured.

After the properties of the grain boundary phases were measured, the effect of the grain boundary phase on crack propagation was determined. Different grain boundary phases were produced by sintering silicon nitride with a variety of sintering aids. Two sets of sintering aid compositions were used. The first set of compositions contained combinations of cordierite (2 MgO: 2 Al₂O₃: 5 SiO₂) and YAG (3 Y₂O₃: 5 Al₂O₃), both of which are commonly used additives. A second study used a series of alkaline earth aluminosilicate additives, 2 XO: 2 Al₂O₃: 5 SiO₂, where X is Mg, Ca or Ba. All of the grain boundary phases were amorphous after sintering, and could be crystallized by appropriate heat treatments.

Different sintering aids can affect the growth of the grains and the development of the microstructure. Low sintering temperatures (below 1880°C) were used to minimize
any differences in grain growth. Grain size analysis found that at the temperatures and for the particular compositions used in these studies, the composition of the sintering aid had negligible effect on the grain sizes, aspect ratios or distribution. Therefore, differences in the properties of the samples could be attributed to the grain boundary phase.

The grain boundary phase strongly influenced the crack path in and the fracture toughness of the silicon nitride. Crack deflection and the formation of bridging grains occurred in samples where the grain boundary phase had a high thermal expansion coefficient. In contrast, straight, transgranular cracks were found in samples where the grain boundary phase had a low thermal expansion coefficient.

The correlation between the crack path and the thermal expansion coefficient of the grain boundary phase can be explained by the presence of residual stresses in the silicon nitride ceramic. When the thermal expansion coefficient of the grain boundary phase was larger than that of the silicon nitride, hydrostatic tensile residual stresses developed in the grain boundary phase and compressive residual stresses developed in the silicon nitride. Fracture mechanics models suggest that the tensile stresses at the grain boundary promote crack deflection and grain bridging because they create a weak interface between the silicon nitride grains.

The magnitude of the residual stresses which arise from thermal expansion mismatch can be predicted from the thermal expansion coefficients and Young's moduli of the grain boundary phases and silicon nitride. As part of this thesis, the effect of the grain boundary phase on residual stresses in the silicon nitride grains was measured using x-ray and neutron diffraction. As expected, when the thermal expansion coefficient of the grain boundary phase increased, the compressive residual stress in the silicon nitride grains increased.

This thesis demonstrates that the thermal expansion coefficient of the grain boundary phase has a strong influence on the extent of crack deflection, grain bridging and the fracture toughness of the sample. The information about the role of the grain
boundary phase can be used to design a silicon nitride material with high fracture toughness.

This thesis is divided into several parts. A review of the literature on silicon nitride in Chapter 2 contains sections on crystallography, liquid phase sintering, microstructure and mechanical properties of silicon nitride, along with a discussion of fracture mechanics in structural ceramics. Descriptions of the work performed for this thesis begin in Chapter 3, with a discussion of the relationship between the composition and properties of oxynitride glasses. The effect of the thermal expansion coefficient of the grain boundary phase on fracture toughness in silicon nitride is discussed in Chapter 4. Thermal expansion mismatch between the grain boundary phase and the silicon nitride had a strong influence on the crack propagation path in the silicon nitride ceramic because of the development of residual stresses. The residual stresses in silicon nitride ceramics sintered with different additives were measured using x-ray and neutron diffraction, and are reported in Chapter 5. These stresses were higher than predicted from simple models. Reasons for the discrepancy were discussed. Chapter 6 contains a summary of the results found in this thesis and their application to the design of tough silicon nitride ceramics, along with suggestions for future work.
CHAPTER 2

BACKGROUND

2.1 Introduction

This chapter summarizes previous research about the crystallography, microstructure, processing and mechanical properties of silicon nitride. Factors which influence the fracture toughness of silicon nitride and other structural ceramics are discussed.

2.2 Crystallography of α and β-Silicon Nitride

2.2.1 α - Si3N4 / β - Si3N4

Both the α and β forms of silicon nitride have hexagonal structures. The hexagonal structure of silicon nitride is built from (SiN4) tetrahedra. The tetrahedra are joined at the corners so that each nitrogen atom is shared by three tetrahedra. The linked tetrahedra form two types of rings; small rings which contain which contain four silicon and four nitrogen atoms and large rings which contains six silicon atoms and six nitrogen atoms. The rings join to form sheets, as shown in Figure 2.1. The sheets can be stacked in two different arrangements. If the sheets are stacked with the rings aligned to form continuous channels, the β phase is formed. If the sheets are displaced from one another by a glide plane in the c-direction, so that the rings are no longer aligned, the α modification is formed. As a result of the displacement of the rings, the α phase contains
two large interstitial holes in each unit cell which can accommodate cations when solid solutions are formed. ¹ The formation of solid solutions stabilizes the α structure.

This displacement between layers also causes a distribution in silicon-nitrogen bond lengths and causes the tetrahedra to be tilted and distorted, which gives the α structure a higher entropy than the β structure. The extra entropy makes the α structure kinetically favored during the nitridation reaction which produces the silicon nitride powder from silicon. However, the displacement of the layers causes strain in the lattice. Because the α form contains more strain than the β form, pure α silicon nitride is considered to be less thermodynamically stable than pure β.²³ In the absence of impurities which stabilize the α structure, α-silicon nitride transforms to β silicon nitride by a solution-reprecipitation mechanism during sintering. Because this transformation involves the breaking of Si-N bonds, it requires considerable energy and time. ⁴⁻⁸

2.2.2 Solid Solution Formation - α'-SiAlON and β'-SiAlON

Solid solutions can form in both the α and β-Si₃N₄ structures. Gauckler proposed that solid solution formation in the β-Si₃N₄ structure occurred when Al-O pairs substituted for Si-N pairs.⁹ This simultaneous replacement of Si by Al and N by O preserved charge neutrality without the formation of extrinsic defects. Solid solutions which contain Al and O in the β-Si₃N₄ structure are called β'-SiAlONs. The general formula for a β' solid solution is Si₆₋ₓAlₓOₓN₈₋ₓ, with x ≤ 4.2.¹⁰⁻¹²

The α modification contains large interstitial holes which can accommodate cations. When Si⁴⁺ is replaced by Al³⁺, the charge imbalance can be corrected by either placing cation M²⁺ into an interstitial hole, or by replacing N with O. The formula for α'-SiAlON is Mₘ/₂Si₁₂₋(m+n)Al(m+n)OnN(16-n). The α phase can form a series of stuffed derivatives where the interstitial cation M is Y, Ca, Mg, Li, or any of the lanthanides except La and Ce.¹³⁻²²
The representation of the phase diagram of silicon nitride sintered with an oxide additive becomes complicated because of the number of elements involved. Gauckler was able to simplify the $\text{Si}_3\text{N}_4$-$\text{SiO}_2$-$\text{AlN}$-$\text{Al}_2\text{O}_3$ phase diagram because none of the elements involved changed their valency during any of the solid or liquid reactions inside the region bounded by the four compounds. In addition, the four components were related by the reversible reaction:

$$\text{Si}_3\text{N}_4 + 2 \text{Al}_2\text{O}_3 = 3 \text{SiO}_2 + 4 \text{AlN}$$

As a result, only three of the components are independent; the fourth is fixed by the reversible reaction above. Systems which contain elements of non-variant valency and in which the components are related by a reversible reaction are called reciprocal salt systems. Gauckler presented the phase diagram of the $\text{Si}_3\text{N}_4$-$\text{SiO}_2$-$\text{AlN}$-$\text{Al}_2\text{O}_3$ system as a reciprocal salts system, as shown in Figure 2.2. The percentage of the total number of positive charges which are supplied by Al$^{3+}$ is shown along the $\text{Si}_3\text{N}_4$/AlN side of the diagram, labeled as "equivalent % Al". Similarly, the percentage of negative charges which are supplied by O$^{2-}$ is shown along the AlN/$\text{Al}_2\text{O}_3$ side of the diagram, labeled as "equivalent % O". When silicon nitride is sintered with two oxide additives, the phase diagram can be drawn as a triangular prism. The phase diagram of the $\text{Y}$,$\text{Si}$,$\text{Al}$/O-N system is shown in Figure 2.3.

As shown in Figure 2.3, the $\beta'$ substitutional solid solutions form along the tieline between $\text{Si}_3\text{N}_4$ and $\text{Al}_2\text{O}_3$:AlN. The $\alpha'$ forms series of stuffed derivatives which lie on a plane which contains $\text{Si}_3\text{N}_4$ and $\text{M}_2\text{O}_3$: 9 AlN, and MN:AlN. The element "M" is $\text{Y}$ in Figure 2.3.
2.3 Sintering of Silicon Nitride

2.3.1. Stages of Liquid Phase Sintering

Silicon nitride is extremely difficult to densify without the use of sintering aids. The strong, covalent Si-N bonds cause a very low bulk diffusivity in silicon nitride. As a result, mass transport is too slow to allow full densification to occur by solid state sintering. To prepare dense samples, sintering aids are added which react with the silicon nitride to produce a liquid. Since mass transport in the liquid is much faster than in the solid, full densification can occur by liquid phase sintering.

Densification during conventional liquid phase sintering proceeds in three overlapping stages: particle rearrangement, solution-reprecipitation and particle coalescence (or grain growth). The chemistry of the sintering liquid is considered to play an important, though poorly understood, role in the densification of silicon nitride. A number of elements have been reported to enhance densification rates, including Mg, Sr, Be, Ba and Nd.

2.3.2 Particle Rearrangement

Particle rearrangement is the first stage of liquid phase sintering. Rearrangement of silicon nitride particles is assisted by the formation of a liquid phase, which lubricates the particles. The first liquid forms from the reaction between the sintering aid additives and the SiO2 which coats the Si3N4 particles. The temperature at which liquid forms depends on the eutectic temperature of the SiO2/sintering aid system - in the range of 1350°C-1400°C for many metal oxide/alumina/silica compositions. If some of the silicon nitride reacts with the additives before melting occurs, the first liquid will form at temperatures below the eutectic found in the oxide system.
Because only a small amount of eutectic liquid forms, only a small amount of particle rearrangement occurs at the eutectic temperature, accompanied by about 5 volume % shrinkage. The amount of shrinkage will be even smaller if the initial oxide melt does not wet the silicon nitride particles. Studies by Hwang 28 found a second shrinkage step which occurred at higher temperatures when the oxide melt fully wetted the silicon nitride powder. Approximately 15 volume % shrinkage occurred during this stage.

A critical amount of liquid is necessary for particle rearrangement to occur during pressureless sintering. For example, Ekstrom and Nygren 3 found that at least 6 weight % \( \text{Y}_2\text{O}_3 \) had to be added in order to form dense silicon nitride by pressureless sintering. Particle rearrangement occurs more easily and the rate of densification increases if the amount of liquid increases or the viscosity of the liquid decreases. 30 Particle rearrangement is hindered by the formation of bridges between the particles.

2.3.3 Solution/Reprecipitation and Phase Transformation of \( \text{Si}_3\text{N}_4 \)

Bridges between particles must dissolve and collapse before the particles can be packed to full density by secondary particle rearrangement. 31 During the solution stage, the starting powder, which is usually primarily \( \alpha\)-\( \text{Si}_3\text{N}_4 \), starts to dissolve into the sintering liquid.

The dissolved silicon nitride can precipitate as either \( \alpha' \), \( \beta \) or \( \beta' \). Pure \( \alpha \) does not precipitate from the sintering liquid. Thermodynamic considerations usually favor precipitation of \( \beta \) or \( \beta' \) rather than \( \alpha' \). However, \( \alpha' \) solid solutions can precipitate if the appropriate sintering aids are present. The \( \beta \) phase can precipitate as new nuclei, or can grow epitaxially on existing \( \beta \) or \( \alpha \) grains. 28

The \( \alpha-\beta \) transformation obeys first order reaction kinetics. 30 The speed of the solution/reprecipitation process depends on the rate at which the initial \( \alpha \)-silicon nitride is
dissolved by the liquid and transported. The reaction kinetics depend on the amount, viscosity, and chemical characteristics of the liquid. Studies on silicon nitride sintered with different amounts of cordierite or YAG found that the transformation rate increased as the viscosity of the liquid decreased and the amount of liquid increased. A number of additives, including Y, Sc, La and Ac, have been reported to increase the phase transformation rates.

Densification occurs faster than phase transformation. The densification rate is much more sensitive to changes in the amount of liquid than the phase transformation rate is. The densification rate in liquid phase sintering is strongly influenced by the reactivity of the liquid with the solid particles, the wetting angle between the liquid and the silicon nitride particles, and by the diffusion rate of silicon nitride in the liquid.

2.3.4 Grain Growth of β Silicon Nitride

The two phases of silicon nitride exhibit different morphologies. The α'-SiAlON phase forms small equiaxed grains, but the β phase grows into elongated hexagonal prisms. Most studies have focused on the development of the elongated β-Si₃N₄ grains.

The formation of elongated grains indicates that the growth rates are different in different crystallographic directions. The anisotropic growth of β-Si₃N₄ is probably caused by differences in the grain boundary mobility in the [001] and [210] directions. Theories predict that the boundary mobility increases as the atomic step density (or roughness) of the boundary increases. TEM studies by Hwang showed that the solid/liquid interface in the [001] direction was semi-spherical, which indicated a rough boundary, which would be expected to grow quickly. The solid liquid interface in the [210] direction parallel to the (1010) prismatic plane, was smooth, and would be expected to grow slowly.

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The size distribution and aspect ratios of the β grains depend on a number of factors, including the characteristics of the starting powder, the sintering conditions and the sintering liquid. Studies indicate that both the physical properties of the liquid (such as viscosity and diffusion rates, the chemical properties and the amount of the liquid affect the development of the microstructure. 3, 26, 27, 30, 34 Both the growth rate and the average aspect ratio of β grains of a given length appear to depend on the sintering aid. 35, 36 A study on silicon nitride sintered with different Al₂O₃:Ln₂O₃, where Ln was La, Nd, Gd and Yb, indicated that the relative amount of growth in the width direction relative to the length direction increased as the radius of the cation in the sintering aid decreased. The authors suggested that the additive altered the Si₃N₄ surface energy. 37 Despite several studies, the effect of the chemistry of the sintering liquid on the growth of silicon nitride is poorly understood.

The volume fraction of sintering aid appears to have a small and indirect affect on grain growth. 30, 35 Studies by Hwang 30 and Lai 35 found that grain size distribution contained a smaller fraction of very long grains at very low volume fractions of liquid. Hwang proposed that the growth of the longest grains was halted because they impinge on neighboring grains.

Efforts to understand the effect of the sintering liquid on microstructure development are hindered by poor characterization of the microstructure. Several different methods are in use to measure the grain lengths and aspect ratios from 2-dimensional sections and from heavily etched samples. The most reliable method of measuring grain size is to disintegrate the sample by dissolving the grain boundary phase, collect the loose grains by filtration, and measure the sizes of the loose grains using the SEM. 35
2.3.5 Prevention of Oxidation and Decomposition Reactions During Sintering

Thermodynamic calculations provide insight into the reactions which occur during sintering of silicon nitride in a graphite furnace. Wada et al determined the effect of the furnace atmosphere on the stability of silicon nitride. Calculations of phase equilibria in the Si-C-N-O system were performed as a function of the partial pressures of nitrogen, oxygen and carbon. The stability regions of SiO$_2$, Si$_2$N$_2$O, β-SiC and β-Si$_3$N$_4$ were determined. These calculations predicted the sintering conditions for Si$_3$N$_4$ and for Si$_3$N$_4$/SiC composites.

The thermodynamic calculations also provided insight into the decomposition reactions which occur during sintering. The high temperatures used in sintering promote decomposition reactions. At high temperatures, the decomposition of Si$_3$N$_4$ was controlled by the partial pressure of SiO gas in the furnace atmosphere:

\[
\text{Si}_3\text{N}_4 (s) + 3 \text{CO}_2 (g) \rightarrow 3 \text{SiO (g)} + 3 \text{CO (g)} + 2 \text{N}_2 (g)
\]

The decomposition reaction was assisted when the activity of carbon in the system was high - for instance, when the crucible or the furnace was made from graphite. The decomposition reactions could be suppressed by decreasing the partial pressure of oxygen, and increasing the partial pressure of nitrogen in the system. The formation of Si$_2$N$_2$O and of SiC were both inhibited by the use of 10 atmospheres overpressure of nitrogen.

Silicon nitride can react with oxygen in the furnace atmosphere, constituents of the liquid sintering aid and the crucible during sintering. Bubbles of nitrogen, SiO, metal oxides and other volatile species are produced during these reactions, resulting in weight loss, porosity and bloating. To prevent the oxidation of the silicon nitride by the furnace atmosphere, highly reducing conditions are maintained. The local activity of SiO and N$_2$...
in the gas are raised by the use of powder beds or closed crucibles which prevent transport of the gases. Gas pressure sintering, under a modest nitrogen overpressure (10-20 atmospheres) is often used to suppress decomposition reactions.

Materials which contact the silicon nitride must be chosen for their thermodynamic stability under sintering conditions. For example, sintering aids are usually metal oxides which are thermodynamically stable relative to the products of the Si₃N₄ oxidation reaction under reducing conditions. 39 The crucible must also be thermodynamically stable with respect to the oxidation of silicon nitride and the sintering aid constituents. Because of the stability of boron nitride under sintering conditions, boron nitride crucibles are frequently used. When graphite crucibles are used, boron nitride powder prevents contact between the crucible and the silicon nitride sample.

2.4 Formation of Grain Boundary Phases

2.4.1 Amorphous Grain Boundary Phases

When the silicon nitride is cooled from sintering temperature, the sintering liquid solidifies as a grain boundary phase. The grain boundary phases which form are often amorphous, because the high viscosity of the oxynitride liquids prevents crystallization.

The composition of the grain boundary phase is controlled by the composition of the sintering liquid. The compositions which are possible for the sintering liquid in equilibrium with silicon nitride are shown on the solid/liquid phase diagrams. All the grain boundary phase compositions contain at least small amount of SiO₂, which is present as a coating on the Si₃N₄ starting powder. From 1.2 to 2.1 weight percent oxygen is present in commercial silicon nitride powders. 40

The grain boundary phase also contains dissolved Si₃N₄. The amount of Si₃N₄ which dissolved into the grain boundary phase has been determined by solid/liquid phase
equilibria studies. The solid/liquid phase equilibria in the cordierite-β-Si₃N₄-β′-SiAlON system was determined by Hayashi and Tien, Bonnell, and Hwang. As shown in Figure 2.4, about 10 wt% Si₃N₄ dissolves into a liquid formed from the cordierite additive at 1650°C. The maximum nitrogen content found in calcium aluminosilicate oxynitride glasses and barium aluminosilicate oxynitride glasses are very similar to the amount found in magnesium oxynitride glasses.

When YAG (Y₃Al₅O₁₂) is used as a sintering aid, the grain boundary phase contains Y₂O₃, Al₂O₃, a small amount of SiO₂ from the Si₃N₄ starting powder, and dissolved Si₃N₄. The solid/liquid equilibria in the Si, Al, Y/O/N system was determined by Wisnudel and Huang et al. As shown in Figure 2.5, there is a eutectic between Si₃N₄ and YAG which occurs at 1650°C. The eutectic composition contains 25 wt% Si₃N₄.

When alumina is present in the sintering aid, some of the alumina can leave the sintering liquid and enter into a β′SiAlON solid solution. When the sintering aid composition is very close to the composition of a stable crystalline phase, almost all of the Al₂O₃ remains in the sintering liquid and becomes part of the grain boundary phase, rather than entering into solid solution. For example, when cordierite (Mg₂Al₄Si₅O₁₈) is added to Si₃N₄, the phases which appear on cooling are a magnesium aluminosilicate oxynitride glass and β-Si₃N₄, not β′ SiAlON. EDX analysis of the grain boundary phase by Bonnell found that the Mg:Al ratio in the grain boundary phase was 1:2; the same as in the cordierite additive. This confirmed that the Al from the cordierite additive remained at the grain boundary, rather than entering into a β′-SiAlON solid solution.
2.4.2 Crystallization of Grain Boundary Phases

The high temperature strength and creep resistance can be improved by crystallizing the grain boundary phase. Bonnell demonstrated that through careful control of composition, crystallizable grain boundary phases could be produced. The ability to crystallize the grain boundary phase depends on both thermodynamic and kinetic factors. Extensive crystallization is favored when the glass composition is similar to that of a solid phase which is thermodynamically compatible with silicon nitride.

Crystallization is hindered when the crystalline and glass phases have different densities, because changes in volume during crystallization must be accommodated. Volume changes during crystallization of the grain boundary phase create stress in the silicon nitride. A fraction of the stress can be relaxed by viscous flow of liquid in the grain boundaries and solution/reprecipitation of primary grains. If the stress is not relieved, it can increase the activation energy for crystallization and result in incomplete crystallization.

However, in many systems, nearly complete crystallization of the grain boundary phase has been observed by TEM. For example, magnesium aluminosilicate oxynitride grain boundary phases can be crystallized. The crystalline phases which can form in the Si, Al, Mg/O,N system were reported by Nunn et al, as shown in Figure 2.6. Both cordierite and N phase (MgAl₂Si₄O₆N₄) are compatible with silicon nitride.

Other crystallizable grain boundary phases are formed in the yttrium aluminosilicate oxynitride system. Subsolidus phase relationships in the Si,Al, Y/O,N system were reported by Naik et al and by Sun et al. Both YAG and Y₂Si₂O₇ are compatible with silicon nitride, as shown in Figure 2.7.
2.4.3 Distribution and Structure of Amorphous Grain Boundary Phases

During liquid phase sintering, the silicon nitride grains are surrounded by a thin film of liquid. Most of the sintering liquid collects in the junctions where three or more grains meet. When the volume fraction of liquid increases, most of the liquid flows into the junctions, which expand. The thickness of the liquid film along the grain boundaries between two grains remains constant as long as the volume fraction of liquid is less than 20%, according to TEM studies. \(^{58,59}\) TEM studies found that the variation in thickness of the grain boundary film along the length of the grain boundary was less than 0.1 nm. \(^{60}\)

Clarke suggested that there was an equilibrium grain boundary thickness which was independent of the volume fraction of liquid. The equilibrium thickness was determined by the balance between two forces: an attractive van der Waals dispersion force and a repulsive steric force which opposed distortion of the SiO\(_4\) tetrahedra in the glass. \(^{58,59}\)

The forces which determine the thickness of the grain boundary phases depend on the composition and structure of the sintering liquid. Kleebe et al. \(^{60,61}\) measured the effect of changes in chemistry on the thickness of the grain boundary phase in silicon nitride. The silicon nitride was sintered with 5 volume % of sintering aids which contained different amounts of CaO. The thickness of the glassy grain boundary increased from 0.8 nm to 1.5 nm when amount of CaO present in the glass increased. \(^{60-62}\)

In addition to Van der Waals forces and steric forces, electrostatic forces from the crystal field of the silicon nitride also act on the glass. The interaction between the (SiO\(_4\)) tetrahedron and the crystal field of the silicon nitride causes the glass adjacent to the silicon nitride to become partially ordered. TEM evidence for ordering in an amorphous grain boundary phase was found by Thorel et al. \(^{63}\) and Kleebe. \(^{48}\)
2.5. Properties of Oxynitride Glasses

Information on the structure and properties of grain boundary phases can be found in the literature on oxynitride glasses. One of the earliest studies on oxynitride glasses was conducted by Mulfinger.64, 65 Mulfinger suggested that nitrogen could substitute for oxygen in the glass structure. Spectroscopic measurements by x-ray photoelectron spectroscopy, raman spectroscopy and $^{29}$Si NMR spectroscopy 66-68 indicate that the nitrogen bonds to silicon in the glass network, as suggested by Mulfinger.

Incorporation of nitrogen changes the structure of the glass because nitrogen can bond to three silicon atoms, while oxygen can only bond to two Si atoms. As a result, the presence of nitrogen would increase the number of links between Si(O,N)$_4$ tetrahedra, and therefore increase the rigidity of the glass network and change the mechanical properties of the glass. 64, 65

Early studies found a strong relationship between the nitrogen content and the properties of oxynitride glasses. The properties of Y-Si-Al-O-N glasses were measured by Shillito 69 and Loehman. 70, 71 Shillito correlated an increase in Knoop hardness to an increase in nitrogen content. Loehman reported increases in glass transition temperature, microhardness and fracture toughness, and decreases in thermal expansion coefficient as the nitrogen content increased. Loehman reported the same trends in other M-Si-Al-O-N glasses, where M was Mg, Ca or Li. 71 However, the cation ratios in the glasses were not held constant in the studies by Loehman or Shillito. Therefore, the changes in properties were influenced by both the change in cation ratios and the change in nitrogen content.

The first studies which isolated the effects of increasing the nitrogen content from the effects of changing the cation ratio were performed by Drew. 72 Drew reported that the incorporation of nitrogen increased the viscosity, refractive index, glass transition temperature and resistance to devitrification of the glasses. The increase in glass...
transition temperature with increasing nitrogen content is shown in Figure 2.8. The crystallization temperature is higher for oxynitride glasses than for their oxide counterparts because the nitrogen containing glasses have higher viscosity than their oxide equivalents. For example, the crystallization temperature of a Y-Si-Al-O-N glass was 200° higher than that of an oxide glass with the same cation ratio. 73

Subsequent studies found that the Young's modulus of the glass increases as the nitrogen content increases, as shown in Figure 2.9. 74-76 The density 74 and fracture toughness 73, 77 also increase with increasing nitrogen content. The influence of the nitrogen content on the density and mechanical properties of the glass is consistent with the structural model suggested by Mulfinger. 64, 65

2.6 Mechanical Properties of Silicon Nitride

2.6.1 Effect of Microstructure

The mechanical properties of dense silicon nitride ceramics are controlled by two factors: the shape and size distribution of the silicon nitride grains and the properties of the grain boundary phase. The relationship between the mechanical properties and the microstructure of the silicon nitride has been the subject of intensive study. Silicon nitride ceramics which contain β-Si3N4 or β'-SiAlON have higher fracture toughness, but lower hardness and strength than those which contain primarily α'-SiAlON. Lange suggested that the elongated β grains increased the fracture toughness because they interfered with crack propagation. 78-80 Efforts to develop tough silicon nitride ceramics have focused on β-Si3N4.

β-Si3N4 ceramics exhibit a range of fracture toughness and flexure strength values. Fracture toughness values ranging from 2 MPa-m^{1/2} to 10 MPa-m^{1/2} have been reported. The fracture toughness of the silicon nitride increases as the diameter and the
aspect ratio of the β-silicon nitride grains increase until the aspect ratio reaches a critical limit, as shown in Figure 2.10. When the aspect ratio reaches a critical limit, microcracking occurs, which reduces the fracture toughness. The critical aspect ratios for the onset of microcracking depend on the grain boundary phase. 26, 82

In some compositions, the critical aspect ratio for microcracking is never reached, because grain coarsening occurs. When the grains coarsen, the aspect ratio begins to decrease even though the grain diameter continues to grow. Even if the aspect ratio decreases, the fracture toughness continues to increase linearly with the square root of the grain diameter if microcracking does not occur. 83, 84

In silicon nitride ceramics with large, elongated grains, the fracture toughness increases as the crack length increases. As the crack grows, more energy is absorbed per unit length. This behavior, called rising R-curve behavior, reflects toughening mechanisms which are cumulative. 85-88 Rising R-curve behavior is associated with an increase in flaw tolerance and reliability.

The value of the fracture toughness in R-curve materials depends on the crack size relative to the scale of the microstructure, and on the crack shape. As a result, fracture toughness values measured by different techniques on the same material can be different by a factor of two. The measured fracture toughness increases as the crack size used in the measurement method increases. The smallest values of fracture toughness come from indentation fracture toughness measurements, which rely on the measurements of small cracks. The largest values come from SENB samples, which contain large precracks which are introduced before testing. For example, one study reported fracture toughness values measured on the same sample by four different methods. The fracture toughness was determined by indentation crack length (5.8 MPa·m$^{1/2}$), indentation strength (8.5 MPa·m$^{1/2}$), single-edge pre-cracked beam (SEPB) (10.2 MPa·m$^{1/2}$) and Chevron-notched beam method (10.7 MPa·m$^{1/2}$). 89 Belise and Steinbrech also cautioned that long-crack measurement techniques such as single-edge
notched beam (SEN'B) overestimate the toughening which would be provided by natural cracks in the material. 90

The shape of the crack is also different when different measurement methods are used. Bleise and Steinbrech found that propagation of cracks from indentation produced a flat R-curve response in very coarse grained alumina, while SEN'B methods measured a rising R-curve. They attributed the different responses to differences in the way the crack opened.

Different crack patterns can also be produced even when the same technique is used to produce them. Belise and Steinbrech 90 observed that the indentation crack pattern in alumina changed with increasing load. This problem was caused partially by the coarse grain size (16 μm) in their sample.

The fracture toughness is not the only mechanical property which depends on the microstructure. The microstructure also influences the flexure strength and the creep resistance. The flexure strength of fine grained Si3N4 exceeds 1 GPa. The flexure strength of silicon nitride ceramics decreases as the aspect ratio of the β-silicon nitride grains increases according to studies by Lai et al 91 and Greil et al 59. The strength decreases because clusters of large grains can act as flaws. 92 The decrease in strength could be avoided and narrow strength distributions could be achieved if the elongated grains were well distributed 81, 92, 93 When the grains were well distributed, strengths of over 800 MPa and Weibull moduli of 26 have been achieved in samples with grain diameters as large as 9 μm. 81

The shape and size of the grains also affect the creep resistance. Studies by Chen suggest that interlocking elongated grains improve the creep resistance of silicon nitride ceramics. 51
2.6.2 Effect of the Grain Boundary Phase on Mechanical Properties

Silicon nitride loses strength at high temperatures because the amorphous grain boundary phase becomes soft. For example, Rouxel et al. demonstrated that the decrease in Young's modulus of Si$_3$N$_4$ sintered with Y$_2$O$_3$ and Al$_2$O$_3$ coincided with the decrease in Young's modulus of a Y-Si-Al-O-N glass at temperatures above the glass transition temperature of the glass, as shown in Figure 2.11.

One method to improve the mechanical properties of silicon nitride ceramics is to design a more refractory grain boundary phase. A grain boundary phase which retains its strength at high temperatures can be produced using additives that increase the refractory nature of the glass (primarily rare earths) or by crystallizing the glass at the grain boundary. Alternatively, the grain boundary phase can be eliminated by using compositions in which the sintering aid liquid additives dissolve into solid solution.

Since MgO was the first sintering aid used to densify silicon nitride, the first grain boundary phases were Mg-Si-O-N glasses. However, the amorphous Mg-Si-O-N grain boundary phase softened above 1000°C, causing the strength to deteriorate rapidly.

In order to produce a more refractory grain boundary phase, yttria was used as a sintering aid. The glass transition temperature of the Y-Si-O-N glasses were expected to be higher than in the Mg-Si-O-N system, because the eutectics in the Y-Si-O-N system are 150° higher than in the Mg-Si-O-N system. Unfortunately, quaternary Y-Si-O-N phases form which undergo large volume increases (up to 30%) on oxidation. In addition, large volume changes which occurred the crystallization of different yttrium silicate polytypes caused mechanical properties to deteriorate. The use of Al$_2$O$_3$ and Y$_2$O$_3$ together avoided the crystallization of the unwanted Y-Si-O-N and yttrium silicate polytypes and produced refractory glass grain boundary phases. Other sintering aids which produce refractory grain boundary glasses include CeO$_2$, Nd$_2$O$_3$, La$_2$O$_3$, Dy$_2$O$_3$, Sm$_2$O$_3$, and Yb$_2$O$_3$. 

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Unfortunately, refractory grain boundary glasses arise from refractory sintering aid compositions. These compositions make poor sintering aids, because they remain very viscous at high temperature. Efforts to develop silicon nitride with very refractory amorphous phases are limited by the difficulty of sintering with very refractory and viscous liquids.

Another method to produce refractory grain boundary phases was to crystallize the amorphous material at the grain boundary. When the grain boundary phase is crystalline, the temperature at which the strength dropped would be limited by the formation of liquid along the join between the silicon nitride and the crystalline phase. The temperature at which liquid forms is up to several hundred degrees higher than the glass transition temperature.

Phase equilibrium studies were undertaken to identify sintering aids compositions which would lead to crystallizable grain boundary phases. Bonnell found that it was possible to design a sintering aid compositions which produced crystallizable grain boundary phases in the MgO-Al₂O₃-SiO₂-Si₃N₄ and Y₂O₃-Al₂O₃-SiO₂-Si₃N₄ systems. The creep resistance of the silicon nitride improved after crystallization of the grain boundary phase. In addition, the strength of silicon nitride with crystalline grain boundary phases was retained at higher temperatures than that of samples with amorphous grain boundary phases.

Another strategy to improve the high temperature properties is to eliminate the grain boundary phase. The amount of grain boundary phase is reduced if the amount of sintering aids is reduced. The amount of additives can be minimized if pressure is applied during sintering, by using hot pressing or hot isostatic pressing.

Another option was to use sintering aids which did not remain at the grain boundaries. The discovery of extensive solid solution regions in both the α and β forms of silicon nitride led to the development of compositions which could be sintered without the formation of grain boundary phases. The sintering aids formed a transient liquid
phase which allowed densification. The elements from the sintering liquid subsequently dissolved into the silicon nitride solid solution. Because the liquid disappears during the sintering process, the grain boundary contains only a small amount of glass. Elimination of most of the grain boundary phase resulted in excellent high temperature strength. The high temperature strength of an \( \alpha'/\beta' \) composite was 1.0 GPa at 1400°C.\(^9\) The reduction in the amount of grain boundary glass also improved the hardness of \( \alpha' \) ceramics. Various \( \alpha' \) compositions were produced with Vickers hardness from 1900-2100\(^3,\)\(^100\)

Unfortunately, it was difficult to sinter combinations of \( \alpha' \) and \( \beta' \) to full density without adding enough sintering aid to leave a grain boundary phase.\(^3\) In addition, development of a desirable microstructure of elongated \( \beta' \) grains also required the presence of more liquid than was available when transient liquid phase sintering was used. In dense \( \alpha'/\beta' \) materials, the aspect ratio of the \( \beta' \) grains decreased when the amount of sintering aid was small enough to disappear into solid solution.\(^3\)

Materials which contained very little grain boundary phase showed poor fracture toughness. The fracture toughness of \( \alpha'/\beta' \) compositions decreased as the amount of sintering aid decreased.\(^3\) \( \beta' \) compositions designed to contain very little glass at the grain boundaries showed fracture toughness of less than 3 MPa-m\(^{1/2}.\)\(^3\) Some of the decrease in fracture toughness was microstructural: a result of the absence of elongated grains. However, Tanaka et al.\(^{101}\) demonstrated that the presence of elongated \( \beta- \text{Si}_3\text{N}_4 \) whiskers was not sufficient to increase the fracture toughness in a dense material sintered without additives. In the absence of a weak grain boundary phase, the cracks were not deflected by the whiskers. The grain boundary phase provides a weak interface between silicon nitride grains, which allows debonding, crack deflection and other toughening mechanisms to occur. When the grain boundary phase is eliminated, the mechanisms which enhance the fracture toughness don't operate.\(^{101}\)
The effect of the grain boundary phase on fracture toughness in silicon nitride has not been the subject of systematic study, despite many comments in the literature about a connection between the grain boundary phase and the fracture toughness. Existing experimental evidence indicates that strong bonding between the intergranular phase and the silicon nitride hinders crack deflection. As a result, crack paths become transgranular and the fracture toughness is poor. Tanaka 101 prepared dense silicon nitride without any sintering aid and noticed that the fracture toughness was very low - only 3 MPa-m$^{1/2}$ - and that the crack path was transgranular. Tanaka suggested that strong interfacial bonding in the brittle samples prevented crack deflection.

The bonding between the silicon nitride and the grain boundary phase can be affected by chemical composition and residual stresses. Studies by Tajima 102 on Si$_3$N$_4$ sintered with MgO, ZrO$_2$ and small amounts of Al$_2$O$_3$ found that the fracture toughness and the amount of crack deflection in the sample decreased as the amount of Al$_2$O$_3$ increased. The amount of Al$_2$O$_3$ had not affected the microstructure, so the authors attributed the decrease in fracture toughness to an increase in the interfacial bond energy caused by the Al$_2$O$_3$. Pyzik 103 observed that the amount of crack deflection and the fracture toughness changed when different compositions in the Y$_2$O$_3$-MgO-Al$_2$O$_3$-CaO system were used as sintering aids. When several of the samples had similar microstructures but different fracture toughness, the difference in fracture toughness was attributed to the difference in grain boundary phase chemistry.

Interfacial bonding is strongly influenced by residual stresses. One source of residual stress is thermal expansion mismatch between the grain boundary phase and the silicon nitride grains during cooling. When the thermal expansion coefficient of the grain boundary phase is greater than that of silicon nitride tensile stresses weaken the grain boundary. Studies by Bonnell 42 and Nunn 47 on silicon nitride sintered with cordierite and YAG suggested that the fracture toughness depended on the thermal expansion coefficient of the grain boundary phase. When the grain boundary phase was crystallized,
the thermal expansion coefficient of the grain boundary phase changed, and the fracture toughness changed. A study by Nagoaka et al on silicon nitride sintered with Y₂O₃ and Al₂O₃ found that after grain boundary phases which had a high thermal expansion coefficient were crystallized, the fracture toughness of silicon nitride increased. \(^{104}\)

In contrast, when the thermal expansion coefficient of the grain boundary phase is smaller than that of silicon nitride, compressive stresses strengthen the grain boundary phase. Van Weeren et al suggested that the low fracture toughness \((2.5-3.0 \text{ MPa-m}^{1/2})\) exhibited by silicon nitride densified without additives was caused by compressive residual stresses in the grain boundary phase due to the low thermal expansion coefficient of silicon oxynitride glass.\(^{105}\)

Studies on other ceramics which contain elongated grains also suggest that residual stresses have a strong affect on crack deflection. Ohashi et al studied the effects of different dopants, including \(\text{ZrO}_2, \text{Al}_2\text{O}_3, \text{MgO}, \text{CeO}_2\) and \(\text{Ln}_2\text{O}_3\) (where \(\text{Ln} = \text{Nd, Sm, Gd, Dy, Er, Yb and Y}\)), on the fracture toughness of silicon oxynitride \((\text{Si}_2\text{N}_2\text{O})\).\(^{106}\) The compositions which contained the lanthanide oxide addition had higher fracture toughness and more crack deflection than the other samples. The authors attributed the increase in crack deflection to residual stresses which weakened the bonding between the intergranular phase and the silicon oxynitride. These stresses were caused by the large difference in thermal expansion coefficient between the \(\text{Si}_2\text{N}_2\text{O}\) and the lanthanide-containing grain boundary phase.

A study by Padture et al\(^{107}\) on alumina with one volume \% of anorthite \((\text{CaO-Al}_2\text{O}_3-\text{SiO}_2)\) grain boundary phase also found that residual tensile stress at the grain boundary can promote crack deflection and fracture toughness. In this study, the fracture toughness of the alumina was measured before and after crystallization of the anorthite phase. Two sources of residual stress arose because of the crystallization of the grain boundary phase: an increase in thermal expansion mismatch stress, and a change in the volume of the grain boundary phase. The thermal expansion coefficient of the
crystalline phase is more than twice that of the glass. Since the volume of the glass increased only 2% on crystallization, the residual stresses were attributed to the mismatch in thermal expansion coefficient. The flaw tolerance of the alumina increased after crystallization, when the grain boundary phase was under residual tensile stress.

Previous observations suggest a strong connection between the properties of the grain boundary phase and the fracture toughness of the material. However, none of these studies were intended to evaluate the effect of systematically varying particular measurable properties of the grain boundary phase on the fracture toughness of silicon nitride in order to establish trends. In addition, since the grain sizes and the volume fraction of the grain boundary phase varied in different compositions within a study, it was difficult to separate the effect of the grain boundary phase from the effects of other microstructural parameters.

Although the role of the grain boundary phase is not well understood experimentally, models of crack propagation behavior assign a critical role to the grain boundary phase. The two major toughening mechanisms in silicon nitride are crack bridging and pullout, which both require debonding to occur either inside the grain boundary phase or between the grain boundary phase and the silicon nitride: behavior controlled by the properties of the grain boundary phase and the grain boundary/silicon nitride interface. The thermal expansion coefficient, elastic properties and fracture energy of the grain boundary phase as well as the bonding between the grain boundary phase and the grains strongly influence crack paths.

Becher noted that interfacial debonding allowed the crack to propagate through the material while the whiskers were left intact. If the crack was not deflected around the whiskers, grain bridging and pullout would be impossible, and toughness values would be low. 108
2.7 Toughening Mechanisms in Non-Transforming Ceramics

Silicon nitride is one member of a family of whisker-reinforced ceramic composites. The elongated $\beta$-Si$_3$N$_4$ grains act as randomly oriented whiskers in a matrix of the grain boundary phase. The fracture toughness mechanisms which operate in silicon nitride are the same as those which operate in other non-transforming, whisker-toughened ceramics. In this section, the toughening mechanisms of crack deflection, grain bridging and pullout which operate in silicon nitride will be discussed.

The toughness of polycrystalline ceramics depends on the mechanisms available to absorb energy in the material. Some mechanisms are not affected by the length of the crack, so the fracture toughness of the material does not change as the length of the crack increases. In contrast, in some ceramics, the fracture toughness increases as the crack length increases until the crack length reaches a critical size. After the crack exceeds the critical length, the fracture toughness does not increase any further. When the fracture resistance of the material increases as the crack length increases, the material exhibits R-curve behavior. The critical crack length where the fracture toughness reaches its maximum value occurs at crack lengths which are very long in comparison to the scale of the microstructure. For example, rising R curves at crack lengths of several millimeters have been reported for alumina. Discussion of the mechanisms which control the fracture toughness of ceramics with R-curve behavior must explain why energy absorption would increase with crack length over such large length scales.

Energy absorption can occur ahead of the crack tip, at the crack tip or behind the crack tip. Ahead of the crack tip, microcracks can form as described by models developed by Hoagland and Evans. The formation and growth of microcracks absorbs energy that would otherwise be used to extend the main crack. Since the size of the microcrack cloud would increase as the crack length increased, this mechanism would lead to R-curve behavior. However, no evidence for extensive microcracking has been
reported in tough samples of alumina or silicon nitride. Swansson et al used microscopy and surface profilometry to search for evidence of microcracking in coarse grained alumina (grain size > 20 um) alumina, and were not able to find any microcracks. 113 Becher et al found limited microcracking in coarse grained alumina (> 15 um), but did not consider this to be an important energy absorption mechanism. 114 However, Becher pointed out that microcracking at the crack tip helped other toughening mechanisms to operate. 108 Microcracking resulted in crack bifurcation, twisting and tilting, which led to incomplete fracture and the presence of bridging grains behind the crack tip. 108

At the crack tip, energy absorption occurs by cleavage of the crystalline grains, debonding of the grain/grain boundary interface, or fracture of the grain boundary phase. Cleavage and debonding do not absorb very much energy. For example, the intrinsic fracture resistance to cleavage in silicon nitride is only about 2.0 MPa-m1/2. 101, 115 The intrinsic fracture resistance of the grain boundary phase can be estimated from fracture toughness measurements on oxynitride glasses. The fracture toughness of oxynitride glasses near their maximum nitrogen solubility limits ranges from 0.8 MPa-m1/2 to 1.8 MPa-m1/2, depending on the composition and crystallinity. 41, 83, 116

At the crack tip, crack deflection can lead to higher toughness because the stress intensity of the crack tip is reduced by crack deflection, as discussed by Evans and Faber. 117 However, as pointed out by Mai and Lawn, the energy absorbed by crack deflection is not cumulative. 109 Therefore, crack deflection cannot account for R-curve behavior. However, ceramics with high toughness usually show crack deflection, as noted by Evans and Faber. 117 Observations made by Rodel et al during fracture in SiC-reinforced alumina found that crack deflection allowed the crack to grow around grains in its path. 118 Intact grains were left behind the crack tip, and held the crack closed.

The most important toughening mechanisms in whisker toughened ceramics occur behind the crack tip. The first strong evidence for crack wake toughening by elongated grains came from studies by Knehans and Steinbrech. 119 R-curve measurements were
made on an alumina sample. As expected, the fracture toughness rose as the crack length increased. After sawcuts were made behind the crack tip, the fracture toughness fell. Knehans and Steinbrech 120 postulated that bridging grains behind the crack tip had held the crack faces together. After the bridges were destroyed by the sawcut, the fracture toughness fell. Therefore, the bridging grains in the crack wake must have been responsible for the R-curve behavior.

Bridging grains were found in alumina by Swanson et al. 113 The bridging grains were 2-5 grain diameters apart. The length of the crack which was bridged by the grains (called the bridging zone) in this sample was remarkable. Bridges were found more than 100 grain diameters away from the crack tip. Bridging by elongated grains was also observed in silicon nitride by Li and Yamanis. 88

A schematic of a bridging grain is shown in Figure 2.12. As the crack opens, energy is required to stretch the intact grains. The bridges can fail by bending, by fracture, or by debonding from the grain boundary phase. If the critical strain to fracture of the grain is exceeded, the grain breaks. Many of the bridges fracture far from the fracture plane, so the broken ligaments still bridge the crack. As the crack faces move apart, the broken or detached grains slide out of the matrix. Energy is required to overcome the frictional forces which oppose sliding of grains. The energy required to stretch and pull out bridging grains contributes to the toughness of the material.

A simple model was developed by Mai and Lawn 121 and Foote et al 122 to describe the relationship between the bridging stresses and the distance between the crack faces, called the crack opening displacement. The maximum bridging stress, \( \sigma_m \), is at the crack tip. The crack bridging stress, \( \sigma_b \), decreases with increasing distance behind the crack tip and with increasing crack opening displacement, \( w \):

\[
\frac{\sigma_b}{\sigma_m} = \left[ 1 - \frac{w}{w_c} \right]^{n}
\]

(1)

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where $w_c$ is the crack opening displacement at the end of the bridging zone, where the bridging stress falls to zero. The exponent $n$ is called the softening index. An exponent of $n = 0$ indicates that the bridging stress has a constant value until the bridge breaks: the bridging stress is either present or absent. This would occur if the bridges fractured without pulling out of the matrix. An exponent of $n = \infty$ indicates that bridging does not occur in the material. If the major toughening mechanism in the material is frictional pullout of bridging grains, the exponent $n=1$.

The bridging stresses can be derived from several different types of measurements. Hu et al.\textsuperscript{123} calculated crack tip bridging stress from measurements of the change in compliance as a function of crack length in alumina during R-curve testing. They found a maximum crack tip bridging stress of 50 MPa in coarse-grained alumina. The bridging stress dropped to its minimum value about 2.6 mm behind the crack tip. The bridging stress/crack opening relationship derived from their measurements could be fit to the equation above with the softening exponent $n=2$.

Fett et al.\textsuperscript{124} calculated crack tip bridging stresses by comparing measurements of the crack opening profiles with calculated values of the crack opening profiles expected from a material without bridging interactions. Their data was fit to a power series, so no softening exponent was obtained. For their sample of fine-grained alumina, they found a maximum bridging stress of 25 MPa, which dropped to its minimum value at a distance of 2 mm behind the crack tip.

The existence of bridging grains in alumina required an explanation. Why would a crack detour around particular grains? Grain bridges can result from debonding at grain boundaries with low fracture energy, and from the presence of residual stresses.\textsuperscript{125, 126} Swain\textsuperscript{110} proposed that localized stresses caused by the anisotropic thermal expansion coefficients in non-cubic materials interacted with the crack front. An advancing crack would detour around interfaces in compression, and proceed along interfaces which were under tension. Interfaces which surrounded the largest grains would be under the largest...
amount of stress. Therefore, very large grains would be particularly likely to form bridges across the crack. He also suggested that the extent of the R-curve was controlled by the grain size. However, the toughness increase from increasing grain size would eventually be limited by the onset of microcracking from the interfaces which were under tension. Measurement of residual stresses in alumina by piezospectroscopic methods found tensile stresses of 100 to 300 MPa in the c direction. The stresses increased with increasing grain size, as predicted.

Grain bridging is also considered the cause of R-curve behavior in boron carbide and silicon nitride. However, in silicon nitride, the thermal expansion anisotropy between the a and c directions is not sufficient to cause grain bridging, as shown by the transgranular fracture behavior of dense samples prepared with a minimal amount of grain boundary phase. In fact, the amount of grain bridging increases in the presence of grain boundary phases, even though the grain boundary phases may relieve some of the internal stresses from anisotropic expansion of the silicon nitride. This thesis will demonstrate that thermal expansion mismatch between the grain boundary phase and the silicon nitride provides the residual stresses which allow the grain bridging to occur.

The amount of energy absorbed by bridging and pullout depends on the strength and toughness of the bridging grains, the strength of the interface, the roughness of the interface, the interfacial friction and the maximum pullout length of the grains. Many models for the increase in toughness due to grain bridging and pullout have been developed. The following section is not intended to be a complete description of the range or development of bridging models. Instead, the following section describes a few models which describe fracture mechanisms which operate in silicon nitride, and which can be affected by changes in the microstructure and grain boundary phase of the material. The models fall into two categories depending on the purpose of the model. One set of models was developed to analyze microstructural contributions to fracture
toughness. The second set of models was developed to explain and predict the shape of the R curve.

The first type of model was developed to guide the design of the microstructure and interface to achieve maximum fracture toughness. The models by Becher fall into this category.\textsuperscript{81, 82, 108, 114} Three types of energy dissipation are considered in Becher's models: 1) crack bridging 2) rotation of bridging grains and 3) pullout of grains. The first energy term in the model,\textsuperscript{82} called $\Delta J_{fb}$, accounts for the energy dissipated from frictional motion and elastic stretching of elongated grains before the grains fail:

$$\Delta J_{fb} = \frac{d}{36E_r} A_r \left[ \frac{2 \gamma_f}{\gamma_i} \right]$$  \hspace{1cm} (2)

where $d$ is the grain diameter, $A_r$ is the area fraction, $\sigma_{fg}$ is the tensile strength, $\gamma_f$ is the fracture energy, $E_r$ is the Young's modulus of the bridging grains, and $\gamma_i$ is the debonding energy of the interface. The debonded length, $l_d$, hidden in this expression is assumed to be equal to $d \gamma_f / 12 \gamma_i$.\textsuperscript{129}

The frictional energy dissipated during rotation of a debonded grain, $\Delta J_{gr}$ is described by\textsuperscript{130}:

$$\Delta J_{gr} = \left[ \frac{\pi A_{gr} \mu \sigma_{fg}}{2} \right] d$$  \hspace{1cm} (3)

and the frictional energy dissipated during pullout of a grain, $\Delta J_{po}$, is described by:\textsuperscript{82}

$$\Delta J_{po} = \left[ \frac{\pi A_{po} (\sigma_{fg})^2}{8\tau_i} \right] d$$  \hspace{1cm} (4)

where $\mu$ is the coefficient of friction and $\tau_i$ is the shear stress at the interface. The shear stress is proportional to the radial compressive stress acting at the interface, $\sigma_r$.
The fracture toughness of the whisker reinforced ceramic, $K$, depends on the energy absorbed by the crack bridging process and the energy absorbed by other mechanisms:

$$K = \frac{E_c(\Delta J_m + \Delta J_{cb})}{E_c}^{1/2}$$

(6)

where $E_c$ is the Young's modulus of the composite, $\Delta J_m$ is the energy expended during crack extension in the absence of crack bridging and $\Delta J_{cb}$ is the energy expended by crack bridging processes. The change in fracture toughness from the bridging process, $\Delta K_{cb}$, can also be expressed as:

$$\Delta K_{cb} = \sigma_{f,g} \left[ \frac{V_f d}{12(1-v_g^2)} \frac{E_c \sigma_{f,g}}{E_g \tau_i} \right]^{1/2}$$

(7)

This model makes several predictions. The fracture toughness is predicted to increase linearly with the square root of the diameter of the bridging grains, the square root of the area fraction of bridging grains and the square root of the ratio of the Young's modulus of the composite to that of the bridging grain. For the purposes of this thesis however, the most important relationship is the increase in fracture toughness with the square root of the ratio of the fracture energy of the grain to that of the interface. This model implies that a weak interface would increase the fracture toughness of the silicon nitride ceramic.
Becher's model includes the energy absorbed by intact grain bridges and the energy absorbed when the grains are pulled out of the matrix. In contrast, the Evans model 132 ignores the energy absorbed when the grains are pulled out. Evans argues that in the case of whiskers, pullout is negligible because the whiskers usually fail by bending. Becher 82 disagrees, and argues that spalling of the matrix partially relieves the bending stresses, allowing pullout to proceed.

Evans' model predicts that the change in fracture toughness of the ceramic caused by bridging, \( \Delta K_c \), will follow the relationship derived by Shum: 133

\[
\Delta K_c = 2.5fE\alpha\Delta T\sqrt{R}
\]  

(8)

where \( f \) is the volume fraction of bridging grains, \( E \) is the Young's modulus of the bridging grains, \( \Delta\alpha \) is the difference in thermal expansion coefficient which causes the mismatch strain to arise in the material, \( R \) is the radius of the bridging grain and \( \Delta T \) is the temperature drop over which the residual stresses are developed. In this model, the fracture toughness depends linearly on the residual stresses in the material and on the volume fraction of bridging grains, rather than on the square root of these quantities as in Becher's model. The residual stresses in this model originate from the thermal expansion anisotropy in different directions in non-cubic materials, as described by Swain. 110

The importance of an interface which is sufficiently weak to allow debonding to occur is mentioned, but not explicitly included in the mathematics of the bridging model. Campbell mentions the importance of the roughness of the interface, and argues that the energy absorbed during debonding should also be included in models. 134

The second type of model was developed to explain the shape of the R or T curve as a function of the crack length, \( c \). The R and T curves are two related expressions used by authors of fracture mechanics models. Both R and T curves describe the conditions necessary for a crack to propagate. The R curve describes the energy, \( R \), expended
when the crack extends. The T curve describes the toughness, T, available in the material to oppose crack propagation. Crack propagation is driven by the extrinsic stress intensity factor, $K_A$. The crack grows when the stress intensity factor exceeds the toughness of the material:

$$K_A(c) \geq T(c)$$  \hspace{1cm} (9)

Crack propagation becomes unstable when the stress intensity factor increases more rapidly than the toughness does as the crack length increases:

$$\frac{\partial K_A(c)}{\partial c} \geq \frac{\partial T(c)}{\partial c}$$  \hspace{1cm} (10)

The expressions for R and T are related by:

$$T = \left[ RE \right]^{\frac{1}{2}}$$  \hspace{1cm} (11)

where E is the Young's modulus of the material. 135

The R and T curve models also describe the relationship between the strength and the fracture toughness of bridging-toughened ceramics. The models by Mai and Lawn 121 and Bennison and Lawn 135 relate the dependence of the strength on the crack size to the fracture toughness of the material. These models contain more detailed descriptions of the form of the R or T-curve.

The model by Bennison and Lawn considers the growth of a crack in a material which contains grains under tension and grains under compression. 136 (The sum of all the microstructural stresses in the material is zero.) Three stages of crack growth are considered, as shown in Figure 2.13.
When the crack length \( c \) is smaller than the distance between bridging grains, \((c<d)\) the crack only encounters grains under tensile stress, \( \sigma_T \). The tensile stresses tend to open the crack. Since there are no bridging grains yet, the contribution from the closure stress, called \( p(u) \), is zero. The measured toughness of the material, \( T \), when \( c<d \) can be expressed as:

\[
T_\mu(c) = T_0 - \psi \sigma_R c^{1/2}
\]

where \( T_0 \) is the intrinsic toughness of the material and \( \psi \) is a geometric constant for penny-shaped cracks. The value of the "intrinsic" toughness, \( T_0 \), in a two-phase material is the toughness of the phase in which the crack grows. In a material which contained predominantly intergranular fracture, \( T_0 \) would be the grain boundary fracture energy. In a material which failed by transgranular fracture, \( T_0 \) would be the cleavage fracture energy of a single crystal.

When \( c>d \), bridging grains are left behind the crack tip. The bridging grains remain intact as long as the strain on the bridges is less than their fracture strain. (The effect of bending stresses on fracture are not included in this model.) Note that the tensile stresses open the crack when the crack is short, which decreases the fracture toughness before the crack intercepted the first potential bridge. After the crack intercepted the first bridge, the tensile stresses promote crack deflection and the formation of bridging grains, and enhance the fracture toughness.

As the crack extends into regions under compressive stress, the sum of internal residual stresses on the crack approaches zero. In the region \( d<c<c^* \), the toughness is increased by contributions from closure forces from the elastic bridging, debonding in the crack wake, and pullout of the grains.

The first bridge reaches its critical fracture strain when the crack length reaches \( c^* \). When \( c=c^* \), the first bridging grain in the crack wake fractures. As the crack grows,
the entire bridging zone translates with the crack. At \( c > c^* \), only the contributions to the toughness from grain bridging and pullout are considered. The toughness of the material at \( c > c^* \) is expressed as:

\[
T_\mu (c) = T_0 + \frac{E_{\mu} u^*}{2T_0}
\]  

(13)

where \( E \) is the Young's modulus of the bridging grains, \( u^* \) is the maximum pullout distance of the grains, and \( p_m \) is the closure stress function for grain pullout. The maximum pullout distance \( u^* \) is less than the length of the grain because the grain usually breaks before the entire grain pulls out of its socket. The closure stress function, \( p_m \), can be expressed as:

\[
p_m = \left[ \frac{\mu \sigma R \lambda u^*}{d^2} \right] \left[ \frac{2d^2}{l^2} - 1 \right]
\]  

(14)

where \( \mu \) is the coefficient of friction between the sliding grain and its socket, \( \lambda \) is the circumference of the bridging grain and \( l \) is the grain diameter.

The T-curve model was extended to include the effects of residual stresses from thermal expansion mismatch between two phases and the scale of the bridging particles by Lawn et al.\(^{136}\) and Padture et al.\(^{137}\) for the Al\(_2\)O\(_3\)/Al\(_2\)TiO\(_5\) system. However, the results are complicated by the onset of spontaneous microcracking in the Al\(_2\)O\(_3\)/Al\(_2\)TiO\(_5\) system. A similar model was developed by Cook and Liniger\(^{138}\) included additional parameters which related to the effect of the microstructure at small flaw sizes and the effect of lateral cracks at large flaw sizes.

Two important predictions are made by the theories in this section. The first is that the fracture toughness of the material is expected to increase linearly as the pullout length of the bridging grains increases. The fracture toughness also increases as the area
fraction of bridging grains increases. The second is that the presence of a weak grain boundary phase or of weak regions produced by residual stresses can enhance the fracture toughness by changing the crack path.

2.8 Crack Deflection at Interfaces

Crack deflection is a prerequisite for the formation of bridging grains. In-situ studies of crack propagation in alumina toughened with silicon carbide whiskers identified crack deflection sites as the precursors for bridge formation. Crack deflection at an interface between silicon nitride grains is favored when the fracture resistance of the interface is low compared to the fracture resistance of the silicon nitride. Crack deflection can be enhanced by either increasing the fracture resistance of the silicon nitride or decreasing the fracture resistance of either the grain boundary phase or the Si$_3$N$_4$/grain boundary interface.

The fracture resistance of the silicon nitride/grain boundary phase interface is controlled by the chemistry of the grain boundary phase and the presence of residual stresses. The effect of glass chemistry on crack deflection at the silicon nitride/glass interface was investigated by Becher et al. In Becher’s study, $\beta$-Si$_3$N$_4$ whiskers were embedded in Y-Si-Al-O-N glasses. Cracks were introduced at various angles to the Si$_3$N$_4$/glass interface using a Vicker’s indenter. The amount of crack deflection decreased with increasing Al$_2$O$_3$ /Y$_2$O$_3$ ratio and increasing nitrogen content. The study concluded that the addition of Al$_2$O$_3$ increased the interfacial bond strength.

Similar conclusions on the effect of the Y$_2$O$_3$/Al$_2$O$_3$ ratio on crack deflection were reached in another study. Wotting et al determined that increasing the Al$_2$O$_3$:Y$_2$O$_3$ ratio in the sintering aid used to densify silicon nitride decreased the amount of crack deflection in silicon nitride. In the studies by both Becher and Wotting, the crack deflection behavior may have also been influenced by the residual stresses present.
in the silicon nitride and glass. Residual stresses arise from thermal expansion mismatch between the silicon nitride and the grain boundary phase. If $\alpha_{\text{SiN}_4} < \alpha_{\text{grain boundary}}$, then when the material is cooled, the grain boundary phase will be under tensile stress and the silicon nitride grains will be under compressive stress. In this case, the fracture resistance of the grain boundary phase would decrease, while the fracture resistance of the silicon nitride grain would increase; crack deflection would be promoted. A decrease in the $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ ratio in the glass decreases the thermal expansion coefficient of the glass, so the glass would be under less tensile stress and would be stronger.

A study by Cai et al examined the effect of residual stress on crack deflection in a SiC/glass system. When the thermal expansion coefficient of the glass was only slightly higher than the thermal expansion coefficient of the silicon carbide, ($\alpha_{\text{glass L}} = 4.6 \times 10^{-6} \degree \text{C}, \ \alpha_{\text{SiC}} = 4.5 \times 10^{-6} \degree \text{C}$) the cracks propagated through the silicon carbide particles. No T-curve behavior was observed. The fracture toughness was similar to that predicted from the rule of mixtures, and lower than that obtained when the high $\alpha$ glass was used. When the thermal expansion coefficient of the glass ($\alpha_{\text{glass H}} = 12.7 \times 10^{-6} \degree \text{C}$) was much higher than the thermal expansion coefficient of the SiC, cracks were deflected around the silicon carbide particles. The intergranular fracture resulted in the formation of bridging grains, a rising T-curve, and fracture toughness which was higher than expected from the rule of mixtures. The presence of tensile residual stress in the glass decreased the fracture resistance of the grain boundary phase, while compressive residual stress in the silicon carbide increased the fracture resistance of the silicon carbide. The residual stress distribution promoted crack deflection and the formation of bridging grains.

The effects of residual stresses on fracture resistance of an interface was measured directly in tests of crack propagation along bimaterial interfaces by Charalambides et al. A compressive residual stress of 10 MPa at the interface of a sandwich specimen
changed the measured fracture resistance of the interface from the intrinsic material value of 2 J-m⁻² to 7 J-m⁻².

Another method to measure the effect of residual stresses on fracture resistance is to add small, strong, spherical, rigid, non-bridging particles to a matrix. Since only a small increase in fracture resistance is expected from crack deflection at and debonding of these particles, the largest source of changes in fracture resistance would be caused by changes in residual stress for thermal expansion mismatch between the particles and matrix. When Taya et al. added TiB₂ particles to a SiC matrix, the fracture resistance increased from 3.0 MPa-m¹/² to 5.3 MPa-m¹/². Most of the increase was attributed to the presence of compressive stress in the SiC matrix.

Studies which used silicon nitride as the matrix revealed the same trend. Kohsaka et al. added particles with a high thermal expansion coefficients to silicon nitride to produce compressive stress in the silicon nitride grains. The samples contained a grain boundary phase with a high α and exhibited a high degree of intergranular fracture even before the particles were added. After Kohsaka et al. added up to 15 volume % TaSi₂ particles (α TaSi₂ = 7.8 x 10⁻⁶/°C) to Si₃N₄ (α Si₃N₄ = 3.1x10⁻⁶/°C), the compressive stress in the silicon nitride was measured by x-ray diffraction and the fracture toughness of the composites was measured by indentation. As the compressive stress in the silicon nitride increased by 115 MPa, the fracture toughness increased from 7.5 MPa-m¹/² to 8.9 MPa-m¹/². In a similar study, Nagaoka et al. added up to 15 volume % TiN particles (α = 9.4 x 10⁻⁶/°C) to Si₃N₄. The maximum increase in fracture toughness was from 6.6 MPa-m¹/² to 7.5 MPa-m¹/².

Experimental evidence suggests that the residual stress distribution has a large effect on the relative fracture resistances of different phases in a material. Areas of low fracture resistance provide an easy path for the crack to follow. If an interface of low fracture toughness surrounds a grain, conditions are favorable for a crack to be deflected along the interface.
The conditions for crack deflection along the interface between a fiber and a matrix were determined by Evans and He. The crack will deflect if:

\[
\frac{G_i}{G_f} > \frac{T_i}{T_f}
\]

(16)

where \( G_i \) = crack energy release rate along the interface

\( G_f \) = crack energy release rate through the fiber

\( T_i \) = fracture energy of the interface

\( T_f \) = fracture energy of the fiber

The ratio of the critical energy release rates depends on the alignment between the loading stress and the fibers and the elastic properties of the fiber and interface. If the angle between the approaching crack and the interface is small, or if the fracture energy of the interface is low, the crack is more likely to be deflected. The \( \frac{G_i}{G_f} \) ratios increase as the angle between the approaching crack and the fiber axis decreases. The \( \frac{G_i}{G_f} \) ratios were calculated as a function of the angle of crack deflection by Evans et al. for the case where the elastic properties of the fiber and matrix were the same. The analysis was extended by He and Hutchinson to account for an interface between materials with different elastic constants. When \( \frac{G_i}{G_f} = \frac{T_i}{T_f} \), then the energy release rates have reached the critical ratio for crack deflection. The ratio of critical energy release rates, \( \frac{G_i}{G_f} \), was calculated as a function of the angle of deflection and the ratio of the Young’s moduli by He and Hutchinson.

Crack deflection is enhanced when the fracture energy of the interface is low relative to the fracture energy of the fiber. Local residual stresses change the fracture resistance of the fiber and interface according to models proposed by Evans et al. and Cutler and Virkar. When the silicon nitride is under compressive stress, the fracture resistance of the silicon nitride particles increases:
\[ K_R = K_{10} + 2\sigma_{\text{sn}} \sqrt{\frac{2\lambda}{\pi}} \]  
\[ \Delta K_{q\text{sn}} = 2\sigma_{\text{sn}} \sqrt{\frac{2\lambda}{\pi}} \]

where

- \( \sigma_{\text{sn}} \) = local average compressive stress in the silicon nitride
- \( \lambda \) = distance over which stress is exerted (grain diameter)
- \( K_R \) = fracture resistance for silicon nitride/particle composite
- \( K_{10} \) = fracture toughness of silicon nitride without particles
- \( \Delta K_{q\text{sn}} \) = change in critical stress intensity factor in the silicon nitride caused by residual stress

When the silicon nitride grains are under compressive stress, the grain boundary phase is under tensile stress. Therefore, the fracture resistance of the grain boundary phase would decrease. As a result, the ratio of the fracture energies would decrease, which would promote crack deflection and debonding along the interface.\(^ {129}\)

Since the fracture toughness of silicon nitride ceramics depends on crack deflection and grain bridging, the fracture toughness of the silicon nitride would be expected to increase as the amount of tensile residual stress in the grain boundary and the amount of compressive residual stress in the silicon nitride grains increased.

2.9 Residual Stresses - Calculation and Measurement

There are many equations in the literature to calculate residual stresses. One equation which is widely used to calculate hydrostatic residual stresses is based on
Eshelby's inclusion theory. This theory assumed that there was one particle embedded in an infinite matrix. The particle was removed from the matrix and allowed to contract freely as the temperature dropped. The matrix was also allowed to deform freely. Since the particle and the hole in the matrix would not deform by the same amount, the particle would not fit back into the hole in the matrix, unless hydrostatic stress was applied to the particle and matrix. Eshelby calculated the stresses which would be necessary in order to force the particle to fit back into the hole in the matrix. Eshelby's inclusion theory was extended to the case where there was more than one particle by Hsueh et al and Taya et al:

\[ \sigma_{sn} = (\alpha_{sn} - \alpha_g) \times \Delta T \times \left[ \frac{1 - 2\nu_{sn} + 1 + f_{sn} + \nu_g(1 - 4f_{sn})}{E_{sn}} \right]^{-1} \]

and

\[ \sigma_g = - \frac{f_{sn}}{1 - f_{sn}} \times \sigma_{sn} \]

where \( \sigma_{sn} \) and \( \sigma_g \) are the stresses in the silicon nitride and glass matrix, \( \alpha_{sn} \) and \( \alpha_g \) are the thermal expansion coefficients of the silicon nitride and glass matrix, \( \Delta T \) is the difference in temperature over which the stresses are locked in, \( f_{sn} \) is the volume fraction of the silicon nitride, \( \nu_{sn} \) and \( \nu_g \) are the Poisson's ratios of the silicon nitride and glass, \( E_{sn} \) and \( E_g \) are the Young's moduli of the silicon nitride and glass.

If glass was assumed to be the continuous phase and the particles are Si3N4, the residual stress can also be calculated if the glass phase acts as the particles and the silicon nitride as the matrix. For the calculations in this thesis, \( \Delta T \) was taken as the difference.
between the glass transition temperature of the amorphous grain boundary phase and room temperature, which was approximately 1000°C.

Residual stresses in crystalline phases can be measured using x-ray and neutron diffraction techniques. Residual stresses are determined from the difference in lattice spacing between an unstressed (reference) sample and a stressed sample. The strain, $\varepsilon$, in any particular crystallographic direction [h k l] can be determined from the lattice spacing:

$$\varepsilon = \frac{d - d_o}{d_o}$$

where $d$ is the lattice spacing along [hkl] and $d_o$ is the lattice spacing in the unstressed samples.

If the stress in the sample is hydrostatic, the residual stresses $\sigma$ can be determined from the measured strains using:

$$\sigma = \frac{E}{(1-2v)}\varepsilon$$

where $E$ is the elastic constant and $\varepsilon$ is the measured strain.

The residual stresses predicted by this theory were compared to measured stresses in an experiment by Wang et al. Wang et al measured the effect of ZrO2 particles on residual stresses in Al2O3 using x-ray and neutron diffraction. The measured stresses agreed with the stresses predicted by the modified Eshelby inclusion model.

2.10 Summary

There is a large amount of literature available about silicon nitride. However, the vast majority of the literature focuses on only a few of the many unanswered questions about how to design and process a tough, strong, creep-resistant silicon nitride ceramic.
The usual approach to the design of a tough silicon nitride material is to increase the size and aspect ratio of the silicon nitride grains in an attempt to increase the amount of crack deflection and grain bridging. While this approach has been successful, it has an inherent problem: very large grains act as flaws and degrade the strength.

Another strategy to produce a tough silicon nitride material is to design a grain boundary phase which will enhance crack deflection. While this approach has been successful in alumina and in glass/SiC composites, it had not been attempted with silicon nitride ceramics. In order to design a grain boundary phase, it is necessary to know what properties the phase should possess.

Fracture mechanics models suggest that the grain boundary phase or the silicon nitride/grain boundary phase interface should be "weak" in order to enhance debonding and crack deflection. One method to produce a relatively weak interface is to take advantage of the residual stresses in the material. If the grain boundary phase has a higher thermal expansion coefficient than the silicon nitride grains, then the grain boundary phase will be under residual tension and the silicon nitride grains will be under residual compression after the material is cooled from processing temperatures. This type of stress distribution would weaken both the grain boundary phase and the interface.

The work in this thesis demonstrates that the grain boundary phase has a large effect on the fracture toughness of silicon nitride ceramics. The influence of the grain boundary phase on fracture toughness and crack deflection can be understood from existing models on toughening mechanisms in non-transforming ceramics.
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Figure 2.1. Structures of $\alpha$ and $\beta$-Si$_3$N$_4$ (After Ref. 30)
Figure 2.2. Gauckler representation of the Si$_3$N$_4$-SiO$_2$-AlN-Al$_2$O$_3$ system (After Ref. 9)
Figure 2.3. Formation of $\alpha'$ and $\beta'$ solid solutions (After Ref. 20)
Figure 2.4. Solid/liquid phase equilibria in the Mg, Si, Al/O, N system (After Ref. 30)

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Figure 2.5. Solid/liquid phase equilibria in the Y, Si, Al/O, N system (After Ref. 47)

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Figure 2.12. Schematic of a bridging grain
a) intact grain in crack wake
b) grain fractures and pulls out of matrix
Figure 2.13. The three regions of crack growth a) crack length is shorter than distance between potential bridging grains: \( c < d \) b) crack length is equal to the bridging zone length: \( c = c^* \) c) crack length is longer than the bridging zone length: \( c > c^* \)
3.1 Introduction

Oxynitride glasses are present at the grain boundary in many silicon nitride ceramics. The mechanical behavior of the grain boundary phases influences the mechanical behavior of the silicon nitride ceramics. For example, the high temperature strength and creep resistance of the silicon nitride deteriorates above the glass transition temperatures of amorphous grain boundary phases.

Even at low temperatures, the properties of the grain boundary phase control the fracture toughness of the material. The thermal expansion coefficient and Young’s modulus of the grain boundary phases determine the magnitude and distribution of residual stresses in the silicon nitride. In addition, the crack paths inside the silicon nitride body are determined by the debonding behavior along the grain boundary/silicon nitride interface and by the fracture energy of the grain boundary phase.

In order to develop desirable grain boundary phases, the properties of the grain boundary phases must be known. Some information on the properties of the grain boundary phases can be found in the literature on oxynitride glasses. For example, the thermal expansion coefficients, glass transition temperatures and elastic properties have been reported for several Mg, Si, Al/O,N and Y, Si, Al/O,N glasses. However, little data is available on Y, Si, Al, Mg/N, O glasses with compositions similar to those found at the grain boundaries of the silicon nitride samples used for the fracture toughness studies in this thesis. Measurements of the glass transition temperatures, thermal...
expansion coefficients, Young’s moduli and fracture toughness of a variety of oxide and oxynitride glasses were measured for this thesis.

3.2 Literature Review

The mechanical properties of the glass, such as the glass transition temperature, Young’s modulus, thermal expansion coefficient and fracture toughness, depend on both the bond strength between elements in the glass and the structure of the glass. The glass transition temperature depends on the coordination number of elements in the glass, and the strength of the attraction between elements in the glass. Cations which have high coordination numbers and non-directional bonds raise the glass transition temperature. For example, IR investigations on oxynitride glasses have shown that 

\[ \text{Mg}^{2+} \] participates in the formative network, while \[ \text{Ca}^{2+} \] is a network modifier and is surrounded by six anions. Drew et al\(^5\) found that oxynitride glasses containing \[ \text{Ca}^{2+} \] (6-fold coordination) had higher glass transition temperatures than those containing \[ \text{Mg}^{2+} \] (4-fold coordination).

When different cations which have the same coordination number are used, the glass transition temperature increases as the ionic field strength of the cation increases. For example, replacement of \[ \text{Nd}^{3+} \] by the smaller \[ \text{Y}^{3+} \] raises the glass transition temperature. Drew et al\(^5\) replaced \[ \text{Mg}^{2+} \] by \[ \text{Y}^{3+} \], which has both a higher field strength and a higher coordination number than \[ \text{Mg}^{2+} \], and found that glass transition temperature of the glass increased, as expected.

The glass transition temperature is also affected by the structure of the glass. Mulfinger suggested the presence of nitrogen would change the structure of the glass because each nitrogen ion was able to bond to three silicon atoms, while oxygen could only bond to two silicon atoms. As a result, the number of bonds between \[ \text{Si} \,(\text{O, N})_x \] tetrahedra in the network would increase. Spectroscopic measurements by x-ray
photoelectron spectroscopy, raman spectroscopy and $^{29}$Si NMR spectroscopy indicate that the nitrogen bonds to silicon in the glass network, as Mulfinger suggested. NMR spectroscopy has revealed evidence of some Al-N bonding, although not as prevalent as Si-N bonding. An increase in the number of bonds between tetrahedra in the glass network would be expected to increase the density of the glass. Homeny and McGarry measured a linear increase in density with increasing nitrogen content in Mg-Al-Si-O-N glasses.

Since the substitution of nitrogen for oxygen increases the coordination number of the anion in the structure, the glass transition temperature would be expected to increase as the nitrogen content of the glass increased. Large increases in the glass transition temperature have been observed as the amount of nitrogen increases in many systems, including Mg-Si-Al-O-N, Ca-Si-Al-O-N, Y-Al-Si-O-N, Nd-Si-Al-O-N and Ba-Al-Si-O-N systems. When the cation ratios are held constant, the Tg increases linearly with the atomic % nitrogen in the glass.

The thermal expansion coefficient of the glass depends on the asymmetry of the amplitude of thermal vibrations in the glass. The amplitude of the thermal vibrations is small when there are many strong bonds present in the network. As a result, the thermal expansion coefficient decreases as the rigidity of the network increases.

Modifying cations decrease the rigidity of the glass network by introducing non-bridging oxygen atoms, and therefore increase the thermal expansion coefficient of the glass. Other changes in the structure or chemistry of the glass also change the thermal expansion coefficient. The change in the thermal expansion coefficient of the glass which is caused by an additive is often directly proportional to the amount of additive. If the change in the thermal expansion coefficient, $\Delta \alpha$, is divided by the amount of additive, $x$, the result is the thermal expansion prefactor for that additive, $\alpha_j$.

The thermal expansion coefficient of the glass can be calculated from the weighted sum of the thermal expansion prefactors of the constituents of the glass.
\[ \alpha = \sum \alpha_i X_i \] (1)

where \( X_i \) is the mole fraction of the constituent and \( \alpha_i \) is the empirically determined thermal expansion coefficient prefactor. 17

The thermal expansion prefactors of many glass constituents have been determined. Takahashi 18 had determined the thermal expansion coefficient prefactors for \( \text{Al}_2\text{O}_3 \) and \( \text{MgO} \). Appen 19 had determined the prefactors for \( \text{MgO} \) and \( \text{SiO}_2 \). The thermal expansion prefactors depend on the field strength of the ion and the structural role of the ion in the glass. Takahashi found that thermal expansion prefactors of modifying cations increased linearly as the field strength of the ions decreased. 18

The thermal expansion prefactors also correspond with the role of the ion in the glass structure. The substitution of nitrogen for oxygen increases the number of bonds between tetrahedra in the network, so the network becomes more rigid and the thermal expansion coefficient decreases. 14, 20-22

Soga et al 23 explored the effect of the attraction between ions of the Young’s modulus of the glass. The Young’s modulus of the glass depends on the attraction between different ions in the glass structure. Soga et al substituted different alkaline earth elements into alkaline earth silicate glasses. As the field strength of the modifying cations decreased, the Young’s modulus decreased. 23. A similar trend was seen in rare earth and lanthanide aluminosilicate glasses. 24, 25

The Young’s modulus also depends on the number of bonds between structural units in the glass. Because oxynitride glasses contain an extra bond between the tetrahedral structural units, the glass network of oxynitride glasses would be expected to be more rigid than in oxide glasses. As expected, the Young’s modulus of oxynitride glasses increases as the nitrogen content increases. 25, 26 Several authors reported a linear increase in Young’s modulus with weight or atomic % N. 12, 27
The fracture toughness of glasses is primarily determined by the amount of energy per unit volume which is needed to break the bonds in the glass structure. Since the oxynitride glasses have a larger number of bonds per unit volume than their oxide counterparts, the fracture toughness of oxynitride glasses is higher than that of oxide glasses.

3.3 Experimental Procedures

3.3.1 Determination of glass transition temperatures and thermal expansion coefficients

The glasses were synthesized from the starting powders, Al₂O₃, Si₃N₄, SiO₂, Y₂O₃ and MgO. The compositions prepared are listed in Table 3.1. The powders were mixed by hand with isopropyl alcohol with an agate mortar and pestle, dried, and cold pressed into pellets. The pellets were melted at 1650°C, for two hours under 10 atmospheres of nitrogen. The samples were cooled by turning off the power to the furnace, and cooled to room temperature in approximately 3 hours. The presence of crystalline phases was determined by x-ray diffraction. Only samples which did not show any crystalline peaks were used to determine the thermal expansion coefficient and glass transition temperature of the glass. The composition of the glasses were verified using EPMA.

The thermal expansion coefficient was measured from room temperature to 1200°C using an alumina single rod dilatometer calibrated with a fused silica standard. The heating rate was 2°C/min. The value of the thermal expansion coefficient from room temperature to 515°C was calculated. The T₉ was determined from the dilatometer trace. A typical dilatometer trace is shown in Figure 3.1, with the T₉ indicated.
The thermal expansion coefficient prefactor for \( \text{Y}_2\text{O}_3 \) was determined from glasses which contained \( \text{MgO} \), \( \text{Al}_2\text{O}_3 \), \( \text{SiO}_2 \) and \( \text{Y}_2\text{O}_3 \) only. The amount of the thermal expansion which was due to Y-O bonds, called \( \alpha_{\text{Y}_2\text{O}_3} \), was determined from equation 2 below:

\[
\alpha_{\text{Y}_2\text{O}_3} = \alpha_{\text{Measured}} - \{\alpha_{\text{MgO}}X_{\text{MgO}} + \alpha_{\text{SiO}_2}X_{\text{SiO}_2} + \alpha_{\text{Al}_2\text{O}_3}X_{\text{Al}_2\text{O}_3}\} \quad (2)
\]

where

\[
\alpha_{\text{Y}_2\text{O}_3} = \alpha_{\text{Y}_2\text{O}_3}X_{\text{Y}_2\text{O}_3} \quad (3)
\]

(Equation 2 is an expansion of equation 1.) The thermal expansion prefactor of \( \text{Si}_3\text{N}_4 \) was determined using the glass compositions in Table 3.1. The amount of thermal expansion which was due to Si-N bonds, called \( \alpha_{\text{Si}_3\text{N}_4} \), was calculated using equation 4:

\[
\alpha_{\text{Si}_3\text{N}_4} = \alpha_{\text{Measured}} - \{\alpha_{\text{MgO}}X_{\text{MgO}} + \alpha_{\text{Al}_2\text{O}_3}X_{\text{Al}_2\text{O}_3} + \alpha_{\text{SiO}_2}X_{\text{SiO}_2} + \alpha_{\text{Y}_2\text{O}_3}X_{\text{Y}_2\text{O}_3}\} \quad (4)
\]

where

\[
\alpha_{\text{Si}_3\text{N}_4} = \alpha_{\text{Si}_3\text{N}_4}X_{\text{Si}_3\text{N}_4} \quad (5)
\]

3.3.2 Young’s Modulus Measurements

The glasses were synthesized from the starting powders, \( \text{Al}_2\text{O}_3 \), \( \text{Si}_3\text{N}_4 \), \( \text{SiO}_2 \), \( \text{Y}_2\text{O}_3 \), \( \text{BaCO}_3 \) and \( \text{MgO} \). The starting compositions of the powder batches are shown in Table 3.2. They were mixed by hand with isopropyl alcohol with an agate mortar and
pestle, dried, and cold pressed into pellets. The pellets were melted at temperatures between 1650°C and 1700°C, depending on the composition, for two hours under 10 atmospheres of N₂. The samples were quenched by turning off the power to the furnace, and cooled to room temperature in approximately 3 hours. The presence of crystalline phases was determined by x-ray diffraction: only samples which did not show any crystalline peaks were used to determine the Young’s modulus. Compositions were verified by EPMA.

Two silicon nitride samples, one with a cordierite sintering aid and one with a barium aluminosilicate sintering aid were prepared. The compositions of the starting powder batches are shown in Table 3.3. The oxide powders were attrition milled with silicon nitride for four hours. The samples were sintered at 1640 °C for 3 hours under 10 atmosphere of nitrogen, then at 1840°C for three hours, and then at 1640 °C for two hours to re-equilibrate the grain boundary phase. The power to the furnace was turned off, allowing the samples to cool to room temperature in about 3 hours. The sample containing the barium aluminosilicate was heated to 1450°C for six hours to crystallize the grain boundary phase.

The glass samples were cut into rectangles approximately 0.5 cm thick x 1 cm wide x 1 cm long. The silicon nitride samples were cut into bars about 5 cm long and 1 cm thick. The surfaces of the samples were ground with 600 grit paper. The dimensions of the samples were measured with a micrometer. The density of each sample was measured using Archimedes method.

The Young’s modulus was measured by the ultrasonic pulse echo technique. A 10 kHz signal was put into the sample, and the time between the initial pulse and the arrival of the reflected wave in the material was measured using a transducer and an oscilloscope. Both the shear wave velocity and the longitudinal wave velocity were measured.
The velocity of sound in the material, \( V \), can be calculated from the thickness of
the sample, \( l \), and the reflection time, \( t \):

\[
V = \frac{2l}{t}
\]  

(6)

The Poisson’s ratio, \( \nu \), of the material can be calculated from the velocity in the
transverse directions \( V_t \), and the velocity in the longitudinal direction, \( V_l \):

\[
\nu = \frac{1 - 2 \left( \frac{V_t}{V_l} \right)^2}{2 - 2 \left( \frac{V_t}{V_l} \right)^2}
\]  

(7)

The Young’s modulus of the material, \( E \), can be calculated from the density, \( \rho \), the
Poisson’s ratio, \( \nu \), and the longitudinal velocity of sound in the material, \( V_l \):

\[
E = \frac{V_l^2 \rho (1 + \nu)(1 - 2\nu)}{(1 - \nu)}
\]  

(8)

The Young’s modulus of the intergranular phase can be estimated from the rule of
mixtures from the modulus of the silicon nitride samples.

3.3.3 Fracture toughness measurements

The glasses were synthesized from the starting powders, \( \text{Al}_2\text{O}_3 \), \( \text{Si}_3\text{N}_4 \), \( \text{SiO}_2 \),
\( \text{Y}_2\text{O}_3 \) and \( \text{MgO} \). The compositions prepared are listed in Table 3.4. The powders were
mixed by hand with isopropyl alcohol with an agate mortar and pestle, dried, and cold
pressed into pellets. The pellets were melted at 1650°C, for two hours under 10
atmospheres of nitrogen. The samples were quenched by turning off the power to the furnace, and cooled to room temperature in approximately 3 hours. The samples were polished with 0.1 um diamond paste. The presence of crystalline phases was determined by x-ray diffraction. The compositions of the glasses were verified by EPMA.

The fracture toughness was determined from the crack lengths produced by Vicker's indentation. A load of 3 kg was used. The fracture toughness was calculated using the equation of Anstis et al: 

$$K_c = 0.016 \left[ \frac{E}{H} \right]^{\frac{1}{2}} \left[ \frac{P}{c^\frac{3}{2}} \right]$$

(9)

where $K_c$ is the fracture toughness, $E$ is the Young's modulus, $H$ is the hardness, $P$ is the peak load on the Vicker's indenter and $c$ crack length from the center of the indent to one tip of the crack.

3.4. Results

3.4.1 Thermal Expansion Coefficients and Glass Transition Temperatures

The thermal expansion coefficients and the glass compositions are listed in Table 3.1. The error in the thermal expansion coefficient measurements is about $2 \times 10^{-7}/\degree C$, based on the calibration of the dilatometer. The error in temperature measurements is $\pm 2\degree C$ according to the calibration of the dilatometer thermocouple.

Using previously reported $\alpha_i$ values for MgO, Al2O3 and SiO2, 18, 19 $\alpha_i$ values for Si3N4 and Y2O3 were determined. The $\alpha_i$ values are listed in Table 3.5. The $\alpha_i$ value for SiO2 is only valid when the mole fraction of SiO2 is less than 0.67. The $\alpha_i$ values were determined from plots of $\alpha_i$ as a function of $X_i$. Figure 3.2 a shows the plot of
HY2O3 as a function of XHY2O3. The slope of the plot in Figure 3.2a is αHY2O3. Figure 3.2b shows the plot of αSi3N4 as a function of XSi3N4. The slope of the plot in Figure 3.2b is αSi3N4.

Using the αi values listed in Table 3.5, the expected values of the thermal expansion coefficient were calculated. Figure 3.3 shows the excellent agreement between the calculated and measured values - the maximum difference is 10%.

The addition of small amounts of Y2O3 and Al2O3 in a 3:5 ratio (YAG) to the base cordierite glass had little effect on the glass transition temperature of the oxide glass, as shown in Figure 3.4.

Figure 3.5 shows the glass transition temperature as a function of silicon nitride content for MgO-Al2O3-SiO2-Si3N4 and Y2O3-MgO-Al2O3-SiO2-Si3N4 glasses. A best-fit line through the data in Figure 3.5 results in an empirical equation for the glass transition temperature:

\[ T_g \, (^\circ C) = 839 + 15.3 \, X \]  

(10)

where X is the mole % of silicon nitride in the glass.

3.4.2 Young's Moduli

The measured Young's moduli of the glasses increased as the amount of YAG added to the glass increased, as shown in Figure 3.4. The modulus of the glass also increased from as the amount of silicon nitride in the glass increased, as shown in Table 3.6a. The Young's moduli of the silicon nitride samples are listed in Table 3.6b. Using the rule of mixtures, a rough estimate of the Young's modulus of the intergranular phase can be calculated. A Young's modulus of 300 GPa was assumed for silicon nitride. The Young's modulus estimated using the rule of mixtures for the barium aluminosilicate
The glass-ceramic phase is 100 GPa. The Young’s modulus measured for the barium aluminosilicate oxynitride glass was 90 GPa. The Young’s modulus estimated using the rule of mixtures for the magnesium aluminosilicate oxynitride phase is 167 GPa. The Young’s moduli reported for Mg-Si-Al-O-N glasses of similar composition to the grain boundary glass range from 110 GPa to 140 GPa. 12, 30

3.4.3 Fracture toughness measurements

The fracture toughness values measured are shown in Figure 3.7. As expected, the fracture toughness increased with increasing nitrogen content.

3.5 Discussion

The thermal expansion coefficients and glass transition temperatures of Y-Mg-Si-Al-O-N glasses can be predicted from simple equations using the thermal expansion prefactors of the ions. The thermal expansion prefactors can be correlated with the field strength of the ions and the structural role of the ions in the glass, as expected form theory. For example, Y³⁺ has a high thermal expansion prefactor, consistent with its position as a network modifier, but not with its high field strength.

The thermal expansion coefficient of the glass increased as the nitrogen content increased, consistent with previous measurements. The linear decrease in thermal expansion coefficient with increasing nitrogen content is similar in magnitude to that observed in previous studies. 14, 20-22

The linear increase in glass transition temperature with increasing nitrogen content was similar to that observed in systems where the cation ratios were held constant 16, 9 Although the cation ratios were not held constant in this study, the effect of the additional Si added along with the N to the melt appeared to be minor. 14 The glass
transition temperature of 840°C for the cordierite composition melt was 10 ° higher than the value reported by Hayashi et al, probably because the melting and quenching conditions were different.14

The increase in Young's modulus with increasing Y content is consistent with the increase in packing efficiency of the glass as well as previous reported data on Mg-Si-Al/O,N and Y, Si, Al/O, N glasses. The Young's moduli of the cordierite based glass with less than 10 weight % 3Y2O3:5Al2O3 added was the same as that reported previously for a cordierite glass.12 The Young's moduli reported for Y-Si-Al/O glass containing 4 SiO2: 1 Y3Al5O12 was 125 GPa,24 which is similar to the value measured for the 60 wt % Mg2Al4Si5O18: 40 wt % Y3Al5O12 composition in this study.

The Young's modulus of the Ba, Al, Si/O, N glass was lower than that of the Mg, Si, Al/O, N glass, as expected since the field strength of Ba is lower than the field strength of Mg. The decrease in Young's modulus with decreasing field strength of the modifier cations was observed in a study by Soga et al on alkaline earth silicate glasses.23

The difference in Young's modulus between the two alkaline earth aluminosilicate oxynitride glasses may also be affected by the difference in the structure of the glass. In oxynitride glasses, the Mg and the Ba do not necessarily have the same coordination. Mg can have 4-or 6- fold coordination, while the Ba has 6-fold coordination.

The increase in Young's modulus with increasing nitrogen content is consistent in magnitude with that reported for the Mg, Si, Al/O,N26, Ca, Si, Al/O,N20 and Y, Si, Al/O,N glasses.13,30

The increase in fracture toughness with increasing amount of nitrogen is consistent with that reported by Messier13 for Y, Si, Al/O,N glasses and by Homeny and McGarry for Mg, Si, Al/O,N glasses.12 However, a maximum fracture toughness value of about 1.4 MPa-m1/2 was reported for both Y, Si, Al/O,N13 and Mg, Si, Al/O,N12 glasses. The fracture toughness of the Y, Mg, Si, Al/O,N was higher than that reported for
either the Y,Si, Al/O,N glasses or Mg,Si, Al/O,N glasses. Glasses in the Y,Mg,Si, Al/O,N system should be explored further.

3.6 Conclusions

The properties of the oxynitride glasses measured in this study are consistent with those measured by other authors. The variations of thermal expansion coefficient, Young's modulus and fracture toughness with changes in chemistry and nitrogen content are consistent with the changes expected from theoretical considerations.

Acknowledgments: Thanks to Carl Henderson for his assistance with the EPMA measurements.
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19. A.A. Appen, Silikattechn. 3 113 (1953)


Table 3.1 Compositions of Glasses Used for Thermal Expansion Measurements (mole fraction)

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<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Y₂O₃</th>
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<th>Si₃N₄</th>
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<tr>
<td>0.60</td>
<td>0.06</td>
<td>0.33</td>
<td>0</td>
<td>0</td>
<td>7.5</td>
</tr>
</tbody>
</table>

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Table 3.2 Compositions of Glass Used for Young’s Modulus Measurements (wt %)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Y₂O₃</th>
<th>Si₃N₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 C/ 10 Y</td>
<td>12</td>
<td>36</td>
<td>46</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>80 C/ 20 Y</td>
<td>11</td>
<td>36</td>
<td>41</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>70 C/ 30 Y</td>
<td>10</td>
<td>37</td>
<td>36</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>65 C/ 35 Y</td>
<td>9</td>
<td>38</td>
<td>33</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>60 C/ 40 Y</td>
<td>8</td>
<td>38</td>
<td>31</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>60 C/ 40 Y + 10% Si₃N₄</td>
<td>8</td>
<td>34</td>
<td>28</td>
<td>21</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>BaCO₃</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Si₃N₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAS + 10% Si₃N₄</td>
<td>40</td>
<td>21</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3.3 Compositions of Silicon Nitride Specimens Used for Young’s Modulus Measurements (wt %)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si₃N₄</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>BaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>85 Si₃N₄/ 15 C</td>
<td>90</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>75 Si₃N₄/ 25 BAS (crystal)</td>
<td>77</td>
<td>7</td>
<td>9</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.4 Compositions of Glasses Used for Measurement of Fracture Toughness
( wt %)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Y₂O₃</th>
<th>Si₃N₄</th>
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<tbody>
<tr>
<td>C</td>
<td>14</td>
<td>35</td>
<td>51</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C + 10 wt % Si₃N₄</td>
<td>12</td>
<td>31</td>
<td>46</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>80 C/20 Y</td>
<td>11</td>
<td>36</td>
<td>41</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>80 C/20 Y + 5 wt % Si₃N₄</td>
<td>11</td>
<td>34</td>
<td>39</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>80 C/20 Y + 10 wt % Si₃N₄</td>
<td>10</td>
<td>32</td>
<td>37</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>60 C/40 Y</td>
<td>8</td>
<td>38</td>
<td>31</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>60 C/40 Y + 10 wt % Si₃N₄</td>
<td>8</td>
<td>34</td>
<td>28</td>
<td>21</td>
<td>10</td>
</tr>
</tbody>
</table>
### Table 3.5 Thermal Expansion Prefactors

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Takahashi(^\text{19})</th>
<th>Appen(^\text{20})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\alpha_j \times 10^6/°\text{C}))</td>
<td>((\alpha_j \times 10^6/°\text{C}))</td>
<td>((\alpha_j \times 10^6/°\text{C}))</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>3.8</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>3.1</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>Y(_2)O(_3)</td>
<td>15.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Si(_3)N(_4)</td>
<td>-7.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrO</td>
<td></td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>CaO</td>
<td>13</td>
<td>14.5</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.6a Comparison of Young’s Moduli of an Oxide and Oxynitride glass

<table>
<thead>
<tr>
<th>Sample</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 C/40 Y</td>
<td>123</td>
</tr>
<tr>
<td>60 C/40 Y + 10 wt % Si(_3)N(_4)</td>
<td>150</td>
</tr>
</tbody>
</table>

### Table 3.6b Young’s Moduli of Silicon Nitride with Different Grain Boundary Phases

<table>
<thead>
<tr>
<th>Sample</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85 Si(_3)N(_4)/15 C</td>
<td>280</td>
</tr>
<tr>
<td>75 Si(_3)N(_4)/25 BAS (crystal)</td>
<td>250</td>
</tr>
</tbody>
</table>
Figure 3.1. A typical dilatometer trace

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Figure 3.2a. The thermal expansion coefficient of the glass increases when Y$_2$O$_3$ is added. The slope of the plot is the thermal expansion prefactor of Y$_2$O$_3$, $\alpha_{Y_2O_3}$. 

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Figure 3.2b. The thermal expansion coefficient of the glass decreases when Si$_3$N$_4$ is added. The slope of the plot is the thermal expansion prefactor for Si$_3$N$_4$, $\alpha_{\text{Si$_3$N$_4$}}$. 

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Figure 3.3. Comparison of calculated and measured thermal expansion coefficients
Figure 3.4. Small additions of $\text{Y}_3\text{Al}_5\text{O}_{12}$ to Mg-Si-Al-O oxide glasses show no effect on $T_g$.

Figure 3.5. $\text{Si}_3\text{N}_4$ additions raise the $T_g$ of oxynitride glass
Figure 3.6. Increase in Young's modulus with increasing Y content
Figure 3.7. Increase in fracture toughness with increasing Si$_3$N$_4$ content and increasing Y$_2$O$_3$ and Al$_2$O$_3$ content
CHAPTER 4

EFFECT OF DIFFERENT GRAIN BOUNDARY PHASES ON FRACTURE TOUGHNESS OF SILICON NITRIDE

4.1 Introduction

Because the diffusion rates in silicon nitride are very slow, silicon nitride is difficult to densify without a sintering aid. Sintering aids affect the properties of the silicon nitride ceramic in two ways: by influencing the development of the microstructure and by controlling the properties of the grain boundary phase formed by the sintering aids.

Both the microstructure and the properties of the grain boundary phases affect the fracture toughness of the silicon nitride ceramic. There is a large amount of literature on the effect of grain diameter and aspect ratio on fracture toughness. However, several authors have observed that silicon nitride samples which were sintered with different sintering aids had the same microstructure but drastically different values of fracture toughness. The differences in fracture toughness were attributed to differences in the grain boundary phase. Properties of the grain boundary phase such as the thermal expansion coefficient, Young's modulus and fracture resistance would be expected to influence the fracture toughness by controlling the crack path.

Despite the importance of the behavior of the grain boundary phase, the effect of the grain boundary phase on crack morphology and fracture toughness is poorly understood. The purpose of this study was to determine the effect of the grain boundary phase on crack path and fracture toughness in silicon nitride. This study focused on the
effects of the thermal expansion coefficient of the grain boundary phase on the fracture toughness of silicon nitride. To accomplish this, sintering aids which produced similar microstructures, but which produced grain boundary glasses with different thermal expansion coefficients were used.

Two different sets of sintering aid compositions added to silicon nitride. The first set contains combinations of MgO, Y$_2$O$_3$, Al$_2$O$_3$ and SiO$_2$. These additives are commonly used as sintering aids. The second set of sintering aids was designed to separate the effects of differences in chemistry from differences in the properties of the grain boundary phases. The second set of sintering aids consisted of three different alkaline earth aluminosilicate combinations, with MgO, CaO or BaO chosen as the alkaline earth.

The fracture toughness of silicon nitride samples which contained different grain boundary phases was compared. The thermal expansion coefficient of the grain boundary phase was found to have a strong influence on the fracture toughness of the silicon nitride samples.

4.2 Literature Review

In order to determine the thermal expansion coefficients of the grain boundary phases, the compositions of these phases had to be determined. The composition of the oxynitride glass phase was assumed to be the composition of the liquid at the temperature of the final sintering step. The solid/liquid equilibria relevant to many of the systems in this study have been determined by other authors. The solid/liquid phase equilibria in the Mg,Si,Al/O,N system were determined by Hayashi and Tien, Bonnell and Hwang, as shown in Figure 4.1. The solid/liquid equilibria in the Y,Si,Al/O,N system were determined by Wisnudel and Huang et al as shown in Figure 4.2. The compositions of the liquid in the Y, Mg,Si,Al/O,N system were determined from a phase
equilibria study. Liquid/solid equilibria in two alkaline earth aluminosilicate oxynitride systems: Mg, Si, Al/O,N and Ca,Al,Si/O,N were compared by Huang et al\textsuperscript{10} as shown in Figures 4.3a and 4.3b. The solid/liquid equilibria in the Ba,Al,Si/O,N system has not yet been reported. However, studies on oxynitride glasses indicate that the maximum nitrogen content which could be dissolved in the glasses in the composition range of interest to this study was nearly identical in the Mg Si, Al, O,N system, Ca,Al, Si/O,N and Ba,Al,Si/O,N systems.\textsuperscript{11}

The compositions of some of the crystalline grain boundary phase in equilibrium with silicon nitride have been reported. Subsolidus phase relationships in the Si, Al, Mg/O,N system were reported by Nunn et al\textsuperscript{12} Both cordierite and N phase are compatible with silicon nitride.\textsuperscript{12} Subsolidus phase relationships in the Si,Al, Y/O,N system were reported by Naik et al\textsuperscript{13} and by Sun et al.\textsuperscript{14} Both YAG and Y\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} are compatible with silicon nitride.

The effect of the grain boundary phase on toughness and crack propagation was demonstrated by Tanaka et al\textsuperscript{15}, who densified silicon nitride without additional sintering aids. Their dense silicon nitride sample, which contained 20 volume % Si\textsubscript{3}N\textsubscript{4} whiskers, had a fracture toughness of only 3.5 MPa-m\textsuperscript{0.5}. Their photo of the crack path revealed nearly transgranular fracture, with little sign of crack bridging, deflection or pullout by the whiskers. Therefore the whiskers did not contribute much to the fracture toughness. Clearly, elongated grains are only useful if the fracture path is primarily intergranular.

When the crack path is intergranular, the crack is deflected around the silicon nitride grain, leaving the grain intact in the crack wake. Crack deflection is affected by the presence of residual stresses in the material. Residual stresses caused by thermal expansion mismatch between the grain boundary phase and the silicon nitride interact with the crack tip. For smooth grains, tensile stress in the grain boundary phase would be expected to draw the crack along the weaker grain boundary phase, enhance
debonding, and lead to intergranular fracture. Compressive stress in the grain boundary phase would be expected to limit debonding and lead to transgranular fracture. The use of thermal expansion mismatch stresses to improve fracture toughness was demonstrated by Taya et al in a SiC/TiB_2 composite. Local residual stresses were also observed to effect the crack path in a SiC/glass composite.

The conditions for crack deflection along a fiber were determined by Evans and He. The crack will deflect if:

\[ \frac{G_i}{G_f} > \frac{T_i}{T_f} \]  

where \( G_i \) = crack energy release rate along the interface  
\( G_f \) = crack energy release rate through the fiber  
\( T_i \) = fracture energy of the interface  
\( T_f \) = fracture energy of the fiber

The ratio of the critical energy release rates depends on the alignment between the loading stress and the fibers and the elastic properties of the fiber and interface. The \( G_i/G_f \) ratios were calculated as a function of the angle of crack deflection by Evans et al for the case where the elastic properties of the fiber and matrix were the same. The analysis was extended by He and Hutchinson to account for an interface between materials with different elastic constants. The elastic constants of the material were taken into account through the Dundar's parameter, \( \alpha_{Dundar} \):

\[ \alpha_{Dundar} = \frac{G_1(1-v_2) - G_2(1-v_1)}{G_1(1-v_2) + G_2(1-v_1)} \]  

where  
\( G_1 \) = Shear modulus of the silicon nitride  
\( G_2 \) = Shear modulus of the glass  
\( v_1 \) = Poisson's ratio of the silicon nitride

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\[ v_2 = \text{Poisson's ratio of the glass} \]

The ratio of critical energy release rates, \( \frac{G_i}{G_f} \), was calculated as a function of the angle of deflection and \( \alpha_{\text{Dundar}} \) by He and Hutchinson. \(^{21}\)

Local residual stresses change the fracture resistance of the fiber and interface according to models proposed by Evans et al.\(^{22}\) and Cutler and Virkar.\(^{23}\) When the silicon nitride is under compressive stress, the fracture resistance of the silicon nitride particles increases:

\[
K_R = K_{10} + 2\sigma_{sn}\sqrt{\frac{2\lambda}{\pi}} \tag{3a}
\]

\[
\Delta K_{qsn} = 2\sigma_{sn}\sqrt{\frac{2\lambda}{\pi}} \tag{3b}
\]

where:
- \( \sigma_{sn} \) = local average compressive stress in the silicon nitride
- \( \lambda \) = distance over which stress is exerted (grain diameter)
- \( K_R \) = fracture resistance for silicon nitride/particle composite
- \( K_{10} \) = fracture toughness of silicon nitride without particles
- \( \Delta K_{qsn} \) = change in critical stress intensity factor in the silicon nitride caused by residual stress

The fracture resistance of the glass decreases because the glass is under tensile residual stress. If the silicon nitride is under compression and the glass is under tension, the relative fracture energy ratio would decrease, which would promote crack deflection:

\[
T = \frac{K^2}{E} \tag{4a}
\]
where \( E_{sn} \) and \( E_j \) are the Young’s moduli of the silicon nitride and glass. The effects of residual stresses on apparent fracture resistance had been observed in tests of crack propagation along bimaterial interfaces by Charalambides et al.\textsuperscript{24} A residual stress of 10 MPa at the interface of a sandwich specimen changed the measured fracture resistance from the intrinsic material value of 2 J-m\(^{-2}\) to 7 J-m\(^{-2}\).

There are many equations in the literature to calculate residual stresses. One widely used one is based on Eshelby’s inclusion theory\textsuperscript{25} as arranged by Hsueh et al.\textsuperscript{26} and Taya et al.\textsuperscript{17}:

\[
\frac{T_i}{T_{sn}} = \frac{\left[K_{10i}\right]^2 - \left[\Delta K_{qi}\right]^2}{\left[K_{10sn}\right]^2 + \left[\Delta K_{qsn}\right]^2} \frac{E_{sn}}{E_j} \tag{4b}
\]

\[
\sigma_{sn} = \left(\alpha_{sn} - \alpha_g\right) * \Delta T * \left[\frac{1-2v_{sn} + 1 + f_{sn} + v_g(1-f_{sn})}{E_{sn} + 2E_g(1-f_{sn})}\right]^{-1} \tag{5a}
\]

and

\[
\sigma_g = - f_{sn} \sigma_{sn} \tag{5b}
\]

where \( \sigma_{sn} \) and \( \sigma_g \) are the stresses in the silicon nitride and glass matrix,

\( \alpha_{sn} \) and \( \alpha_g \) are the thermal expansion coefficients of the silicon nitride and glass matrix

\( \Delta T \) is the difference in temperature over which the stresses are locked in

\( f_{sn} \) is the volume fraction of the silicon nitride

\( v_{sn} \) and \( v_g \) are the Poisson’s ratios of the silicon nitride and glass

\( E_{sn} \) and \( E_g \) are the Young’s moduli of the silicon nitride and glass.
The glass was assumed to be the continuous phase and the particles are Si$_3$N$_4$. $\Delta T$ was taken as the difference between the glass transition temperature of the grain boundary glass and room temperature, which was approximately 1000°C.

Models developed by Becher$^{27}$ and Swansson et al.$^{28}$ for alumina relate fracture toughness to the presence of bridging grains behind the crack tip. The crack tip bridging stresses are determined by the size and shape of the silicon nitride grains, the residual stresses present in the material, and the details of the stress vs. separation curve of the bridging grains.$^{29}$ The models attribute the residual stresses to thermal expansion mismatch between grains of different orientations.$^{29}$ Additional residual stresses are introduced by thermal expansion mismatch between the grain boundary phase and the silicon nitride.

According to Becher's model, the increase in fracture toughness caused by bridging grains can be expressed as:

$$\Delta K_{gb} = \sqrt{\frac{A_{gb} \tau_{gb} E_c d}{2(1 - \nu^2)}}$$  \hspace{1cm} (6)

where

$\Delta K_{gb}$ = increase in fracture toughness from bridging grains

$A_{gb}$ = area fraction of bridging grains

$\tau_{gb}$ = frictional sliding stress

$E_c$ = Young's modulus of the composite

$d$ = grain length

$\nu$ = Poisson's ratio of the composite

The change in fracture toughness, $\Delta K^{gb}$, caused by bridging grains was also calculated by Shum$^{30}$:

$$\Delta K^{gb} = 2.5fE\alpha \Delta T \sqrt{R}$$ \hspace{1cm} (7)
where \( f \) is the volume fraction of bridging grains and \( R \) is the radius of the bridging grains. In Shum's model, the fracture toughness depends linearly on the residual stresses in the material and on the area fraction of bridging grains, rather than on the square root of these quantities as in Becher's model. According to both models, the fracture toughness of the silicon nitride is expected to increase as the area fraction of bridging grains increases.

4.3 Experiment

4.3.1 Silicon nitride with mixed \( 3Y_2O_3:5Al_2O_3 \) and \( 2 MgO: 2 Al_2O_3: 5 SiO_2 \) sintering aids

Silicon nitride samples with 5, 10 and 15 volume % of four different sintering aids were prepared. The sintering aids were combinations of the commonly used sintering aids cordierite (\( Mg_2Al_4Si_5O_18 \)) and YAG (\( Y_3Al_5O_12 \)). The compositions of the sintering aids are shown in Table 4.1.

The powders were attrition milled with silicon nitride for four hours. A three step firing schedule was used for the samples which contained 15 volume % sintering aid, as shown in Table 4.2. The samples were densified at 1640°C for 3 hours, then held at higher temperature to grow the grains, and then held at 1640 °C for two hours to re-equilibrate the grain boundary phase.

To determine the effect of the volume fraction of grain boundary phase on the fracture toughness of silicon nitride, a set of samples with 5, 10 and 15 volume % of the four different additives was sintered at 1640°C for three hours.
The samples were cooled rapidly by turning off the power to the furnace. X-ray diffraction was used to determine the phases present, which were β-Si3N4 and glass. Some samples underwent further heat treatment for 15 hours at 1250°C-1350°C to crystallize the grain boundary phase. X-ray diffraction was used to determine the phases present. The densities of the samples were measured using Archimedes method.

The compositions of the grain boundary glasses were determined by the lever rule from the volume fraction of glass present in SEM photos of the microstructure and knowledge of the overall compositions of the sample and of the silicon nitride grains. The compositions calculated using the lever rule were compared to the compositions determined from the bulk glasses in section 4.3.3.

The fracture toughness was measured by the indentation method with loads of 10 kg. The fracture toughness was calculated using the equation of Anstis et al.:

\[ K_c = 0.016 \left( \frac{E}{H} \right)^{\frac{3}{2}} \left( \frac{P}{c^2} \right) \]  

(8)

where \( K_c \) is the fracture toughness, \( E \) is the Young's modulus, \( H \) is the hardness, \( P \) is the peak load on the Vicker's indenter and \( c \) is the crack length from the center of the indent to one tip of the crack.

The microstructures and crack paths were examined using the SEM. When the elemental contrast in the SEM was insufficient to reveal the microstructure, the samples were etched in a molten salt solution for 15 to 30 seconds. The distance between bridging grains was measured from the SEM photographs from 5 indentation cracks for each sample. The cracks were photographed in segments of approximately 10 μ. The portions of the crack which showed space between the faces were examined for evidence of bridging grains. Grains which remained intact across the crack face were immediately identified as bridging grains. Grains which had fractured at a distance from the crack...
plane and which showed evidence of being pulled out from their sockets were also considered to have been grain bridges.

The mean angle of crack deflection and the maximum angle of crack deflection were measured from the SEM micrographs. The entire lengths of five indentation cracks per sample were used to determine the angles of crack deflection. The cracks were divided into segments roughly 10 µ in length. When the crack was deflected along a grain boundary, the angle between the macroscopic direction of the crack and the direction of the deflected segment was measured.

The grain size of the samples were measured by the disintegration method. The samples were disintegrated in a molten salt bath of KOH: NaOH in 1:1 molar ratio. To remove the surface grains, the samples were etched for three minutes, rinsed in water, and placed in water in an ultrasonic cleaner for five minutes. The sample was then etched again for an additional three minutes, rinsed in water and placed in water in the ultrasonic cleaner again for five minutes. The loose grains from the second etching step were collected from the water by vacuum filtration. SEM photos of the collected grains were used to determine the average length and width of the grains. At least one hundred grains were measured to determine the length and width values.

4.3.2 Silicon nitride with MgO, CaO and BaO Aluminosilicate Sintering Aids

Silicon nitride samples with 15 volume % of three different sintering aids were prepared. The sintering aids were 2 XO: 2 Al2O3 : 5 SiO2, where X was Mg, Ca or Ba. Samples were also made with 10, 15, 20 and 25 volume % of the 2 BaO: 2 Al2O3 : 5 SiO2 sintering aid. The oxide powders were attrition milled with silicon nitride for four hours. The samples which contained 15 volume % sintering aid were densified at 1640°C, then held at 1840°C for 3 hours to grow the grains, and then at 1640 °C for two hours to re-equilibrate the grain boundary phase. A set of samples which contained 10
volume %, 15 volume %, 20 volume % and 25 volume % sintering aid were densified for three hours at 1640 °C, then held at 1940°C for three hours. The samples were cooled rapidly by turning off the power to the furnace. X ray diffraction was used to determine the phases present. The densities of the samples were measured using Archimedes method.

The compositions of the grain boundary phases in the Ca, Al, Si/O,N and Ba, Al,Si/O,N samples were estimated from the volume fraction of glass present in SEM photographs using the lever rule. The overall compositions of the samples and of the silicon nitride grains were verified by EPMA. The compositions calculated using the lever rule were compared to the compositions determined from bulk glasses. In some samples, the grain boundary compositions could be verified by EPMA analysis inside large glass pockets.

The fracture toughness was measured by the indentation method with loads of 10 kg. The microstructures and crack paths were examined using the SEM.

4.3.3 Composition and Thermal Expansion Coefficients of Grain Boundary Phases

Glass compositions with the same ratios of oxide powders as in the sintering aids were prepared. Silicon nitride additions of 5, 10 and 15 wt % were added to the oxide powders. The MgO, Y2O3, Al2O3, SiO2, CaO, BaO and Si3N4 powders were mixed by hand. The powders were melted under 10 atmospheres nitrogen pressure at 1650°C - 1700°C for three hours. The maximum solubility of silicon nitride was determined using x-ray diffraction. Electron probe micro-analysis indicated that the cation ratios had not changed during melting. The weight losses were < 1 weight %. The thermal expansion coefficients of the glass were measured using an alumina rod dilatometer calibrated with a fused silica standard, as described in Chapter 3.
Some of the glasses in the Y, Mg, Si, Al/O, N system were crystallized at 1250°C-1350°C for 15 hours. The thermal expansion coefficient of the devitrified samples were measured using an alumina rod dilatometer calibrated with a fused silica standard.

The thermal expansion coefficients $\alpha$ of the Mg, Al, Si/O, N, Ca, Al, Si/O, N and Ba, Al, Si/O, N samples were also calculated from the compositions using the equation 32:

$$\alpha = \sum \alpha_i X_i$$  \hspace{1cm} (9)

where $X_i$ is the mole fraction of the constituent $i$ in the glass and $\alpha_i$ is the thermal expansion prefactor of the constituent. The prefactors are listed in Table 4.3.

4.4 Results

4.4.1 Compositions and Thermal Expansion Coefficients of Glasses

The compositions and thermal expansion coefficients (as determined from the model glasses) of the grain boundary glasses are shown in Table 4.4. The crystalline phases and their thermal expansion coefficients are listed in Table 4.5. The thermal expansion coefficient of the cordierite-rich glasses decreases on crystallization. The thermal expansion coefficient of the YAG-rich glasses increases on crystallization.

4.4.2 Effect of Thermal Expansion Coefficient of the Grain Boundary Phase on Crack Propagation in Silicon Nitride

All the sintered samples were at least 99% dense and contained $\beta$-Si$_3$N$_4$ and glass after sintering. The microstructures produced using the different sintering aids in the Y, Mg, Si, Al/O, N were very similar, as shown in Figure 4.4 for samples sintered at 1640°C.
for 3 hours, followed by 1880°C for 3 hours and 1640°C for an additional 2 hours. The average length and width of the silicon nitride grains are shown as a function of the amount of YAG in the sintering aids in Figures 4.3a and 4.5b. Note that the effect of sintering aid chemistry on grain morphology was negligible in this particular case, primarily because the grain growth temperature was very low and the volume fractions of liquid were the same. Therefore, any changes in fracture toughness for samples treated at the same temperature were not due to changes in grain shape or size. However, the crack paths are very different when different sintering aids are used, as shown in Figure 4.4. The sample sintered with cordierite alone shows a nearly straight crack path with almost no bridging grains. In contrast, the sample sintered with YAG shows crack deflection and bridging grains.

When the alkaline earth aluminosilicate sintering aids were used, the substitution of Ca or Ba for Mg did not produce any noticeable change in microstructure, as shown in Figure 4.6. Similarly, examination of the crack paths in Figure 4.6 shows that the amount of crack bridging and crack deflection increases when Ca is substituted for Mg, and increases more when Ba is substituted for Mg.

The fracture toughness would be expected to increase as the distance between bridging grains decreased and as the amount of crack deflection increased. As expected from the photos of the crack paths, the fracture toughness increased as the thermal expansion coefficient of the grain boundary phase increased, as shown in Figures 4.7 and 4.8. In some cases, the fracture toughness varied between different samples with the same composition, as shown in Table 4.6. The difference in fracture toughness between samples of the same composition was used to establish the error bars.

The distance between bridging grains was measured from the SEM photographs. The distance between grains decreased as the thermal expansion coefficient of the grain boundary phase increased, as shown in Figure 4.9.
The mean and maximum angles of crack deflection were determined from the SEM micrographs. The grain size of the sample had only a small effect on the crack deflection angles, as shown in Figure 4.10. The angles increased as the thermal expansion coefficient of the grain boundary phase increased, as shown in Figures 4.10 and 11 for the samples sintered with Y,Mg,Al,O sintering aids. The angles increased slightly as the grain size of the sample increased. The range of mean crack deflection angles is the same as the range reported for Si\textsubscript{3}N\textsubscript{4} samples of similar toughness by Faber and Evans.\textsuperscript{33} The maximum crack deflection angles also increased as the thermal expansion coefficient of the grain boundary for the samples sintered with the rare earth aluminosilicate sintering aids, as shown in Figure 4.12.

The crystallization treatments produced N phase in the Mg,Si,Al,O,N samples, YAG in the Y, Al, Si,O,N samples and combinations of N phase and YAG in the Y, Mg,Al, Si,O, N samples. The effect of crystallization on fracture toughness is shown in Figure 4.13. When the thermal expansion coefficient of the grain boundary phase increased on crystallization, the fracture toughness increased upon crystallization. When the thermal expansion coefficient of the grain boundary phase decreased on crystallization, so did the fracture toughness.

Some of the change in fracture toughness on crystallization may be due to the stresses or porosity arising from volume changes which occur on crystallization. The density of the grain boundary phase in the Mg, Si,Al/O,N samples increased from the density of the glass at 2.6 g/cm\textsuperscript{3} to the density of N-phase, which is 2.9 g/cm\textsuperscript{3}, an increase of 11\%.\textsuperscript{34} The density of the grain boundary phase in the Y, Si,Al/O,N samples increased from the density of the glass, at 3.9 g/cm\textsuperscript{3} to the density of Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}, at 4.55 g/cm\textsuperscript{3}, an increase in density of almost 17 \%. The volume changes can be accomodated by the development of pores in the grain boundary phase, by viscous flow of the grain boundary phase during crystallization, or by solution/precipitation of the silicon nitride grains during crystallization.\textsuperscript{35} Nunn reported that small shrinkage pores appeared in the
grain boundary phase after crystallization in samples of β'-SiAlON sintered with cordierite additives. Shrinkage pores have also been reported in the corners of the grain boundary triple points following crystallization treatments in samples of β-Si3N4 sintered with yttria and strontia. SEM examination of the samples in this study did not reveal any pores in the grain boundary pockets.

4.4.4. Effect of Volume Fraction of Sintering Aid on Silicon Nitride

When small amounts of sintering aid were used, the grain length increased slightly as the amount of sintering aid increased, as shown in Figure 4.14 for silicon nitride sintered with cordierite. When large amounts of sintering aid were used, no noticeable change in grain size resulted from the difference in sintering aid content, as shown in Figure 4.15. This suggests that the grain growth may be hindered by impingement between growing grains when less than 15 volume % of sintering liquid is present. The fracture toughness of the silicon nitride did not change when different volume fractions of magnesium aluminosilicate sintering aid were used. The fracture toughness increased slightly with increasing volume fraction of YAG, as shown in Figure 4.16. The fracture toughness also increased slightly with increasing volume fraction of barium aluminosilicate, as shown in Figure 4.17.

4.5. Discussion

The material properties used in the calculations in this section are listed in Table 4.7. Using modified version of Eshelby's inclusion method discussed earlier, the residual stress in the silicon nitride and in the grain boundary phase can be calculated from equations 5 and 6, as shown in Figure 4.18 for 15 volume % of sintering aid. When the thermal expansion coefficient of the grain boundary phase is greater than that
of the silicon nitride, both the tensile stress in the grain boundary and the compressive stress in the silicon nitride grains increase as the thermal expansion coefficient of the grain boundary phase increases. The residual stress in both phases can also be calculated as a function of the volume fraction of sintering aid, as shown in Figure 4.19.

Tensile stress at the grain boundary and compressive stress in the silicon nitride grains promote crack deflection and the formation of bridging grains. The expected Ti/Tf ratio was estimated (roughly) as a function of residual stress using equation 4 and the material properties listed in Table 4.8.

Since the residual stresses arose from thermal expansion mismatch between the silicon nitride grains and the grain boundary phase, the residual stress distribution was expected to vary over the same dimensions as the microstructure. Therefore, the distance over which stress was exerted was interpreted as the average grain diameter of the silicon nitride grains. The initial toughness value of the aluminosilicate glass was taken as 0.9 MPa-m$^{0.5}$. The initial toughness of silicon nitride was taken as the single crystal value of 2.0 MPa-m$^{0.5}$. The distance over which stress was exerted was interpreted as the average diameter of the silicon nitride grain. Since the maximum angle of crack deflection occurs when $T_j/T_f = G_j/G_f$, the predicted maximum angles of deflection can be found from the calculated Ti/Tf ratios and the calculated Dundar's parameter, $\alpha_{\text{Dundar}}$. The value of $\alpha_{\text{Dundar}}$ was calculated as 0.5. The critical angle of deflection was found from the graphs in He and Hutchinson's paper. The calculated critical angle of deflection is compared to the measured critical angle of deflection in Figure 4.20.

The fraction of grains which become bridges depends on the fraction of grains which intersect the crack at an angle favorable for crack deflection. The linear fraction of the crack which was bridged is $l/d$, where $l$ is the grain diameter and $d$ is the distance between bridging grains. The linear fraction of the crack which was bridged increased linearly as the fraction of grains expected to intersect the crack at an angle less than the
critical angle increased, as shown in Figure 4.21 for silicon nitride sintered with combinations of cordierite and YAG.

The area fraction of bridging grains, $A_{gb}$, can be estimated from the grain diameter and the distance between bridging grains $^{29}$:

$$ A_{gb} = \frac{l^2}{2d^2} $$

If a sample was broken in half and the fracture surface was examined, the fraction of the fracture surface which consisted of broken grain bridges would be the area fraction of bridging grains. In the samples in this study, the area fraction is just a mathematical convenience, since only the portion of the crack which lies on the surface of the sample can be measured. Figure 4.22 shows the linear increase in fracture toughness with the area fraction of bridging grains, in agreement with Shum's theory. $^{30}$ For modeling purposes, it should be possible to predict the area fraction of bridging grains from the predicted maximum deflection angle and the grain diameter.

The changes which occur in fracture toughness after crystallization of the grain boundary phase can't be attributed entirely to changes in the thermal expansion coefficient of the grain boundary phase. Some of the change in fracture toughness after crystallization may be due to the stresses or porosity arising from volume changes which occur on crystallization. The density of the grain boundary phase in the Mg, Si,Al/O,N samples increased from the density of the glass at 2.6 g/cm$^3$ to the density of N-phase, which is 2.9 g/cm$^3$, an increase of 11%. $^{34}$ The density of the grain boundary phase in the Y, Si,Al/O,N samples increased from the density of the glass, at 3.9 g/cm$^3$ to the density of $Y_3Al_5O_{12}$, at 4.55 g/cm$^3$, an increase in density of almost 17%.

The volume changes can be accomodated by viscous flow of the grain boundary phase during crystallization, by solution/precipitation of the silicon nitride grains during crystallization or by the development of pores in the grain boundary phase. $^{35}$ Extensive
crystallization would not have been possible unless most of the stresses produced during crystallization were relieved.\textsuperscript{35} Nunn reported that small shrinkage pores appeared in the grain boundary phase after crystallization in samples of $\beta'$-SiAlON sintered with cordierite additives.\textsuperscript{34} Shrinkage pores have also been reported in the corners of the grain boundary triple points following crystallization treatments in samples of $\beta$-Si$_3$N$_4$ sintered with yttria and strontia.\textsuperscript{36} SEM examination of the samples in this study did not reveal any pores in the grain boundary pockets. In any case, the data in Figure 4.12 suggests that the change in fracture toughness on crystallization is influenced by the change in thermal expansion coefficient of the grain boundary phase.

\section*{4.5. Conclusions}

Thermal expansion mismatch between the grain boundary glass and the silicon nitride has been shown to influence the fracture toughness of silicon nitride. The thermal expansion mismatch causes residual stresses in the material, which interact with the advancing crack. Residual tensile stress at the grain boundary has been shown to increase the number of bridging grains and increase the fracture toughness. Although the thermal expansion coefficient of the grain boundary phase is not the only factor which affects the fracture behavior of silicon nitride ceramics, it has a large and predictable effect. Further studies on the effect of the chemistry of the sintering aid on microstructural development of the silicon nitride/glass interfaces and on the bond strengths between the silicon nitride and the glass would further improve understanding of the effect of the grain boundary phase on the fracture toughness of silicon nitride.
REFERENCES


Table 4.1 Compositions of Sintering Aids

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cordierite</th>
<th>YAG</th>
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</thead>
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<tr>
<td>C</td>
<td>100</td>
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</tr>
<tr>
<td>80C/20Y</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>60C/40Y</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Y</td>
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Table 4.2 Sintering and Crystallization Schedules

<table>
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<th>STEP 3</th>
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<td>1640°C 3 hrs</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1640°C 3 hrs</td>
<td>1800°C 3 hrs</td>
<td>1640°C 2 hrs</td>
</tr>
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<td>1640°C 2 hrs</td>
</tr>
<tr>
<td>1840 (6)</td>
<td>1640°C 3 hrs</td>
<td>1840°C 6 hrs</td>
<td>1640°C 2 hrs</td>
</tr>
<tr>
<td>1880 (3)</td>
<td>1640°C 3 hrs</td>
<td>1880°C 3 hrs</td>
<td>1640°C 2 hrs</td>
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Table 4.3 Thermal Expansion Prefactors for Oxynitride Glasses

<table>
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<tr>
<td>SiO₂</td>
<td>3.8 (^A)</td>
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<tr>
<td>Al₂O₃</td>
<td>3.1 (^T)</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>-7.5 (^*)</td>
</tr>
<tr>
<td>MgO</td>
<td>6.0 (^A)</td>
</tr>
<tr>
<td>CaO</td>
<td>13.0 (^A)</td>
</tr>
<tr>
<td>BaO</td>
<td>20.0 (^A)</td>
</tr>
</tbody>
</table>

\(^*\) Measured in Chapter 3
\(^A\) A.A. Appen, *Silikatechn.* 3, 113 (1953)
Table 4.4a Grain Boundary Glass Compositions and Thermal Expansion Coefficients

Y, Mg, Al, Si/ O₂N Grain Boundary Phases

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>Y₂O₃</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Si₃N₄</th>
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<td>0.20</td>
<td>0</td>
<td>0.21</td>
<td>0.51</td>
<td>0.08</td>
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<td>0.08</td>
<td>0.25</td>
<td>4.6</td>
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Thermal expansion of coefficient of β-Si₃N₄: 3.0 x 10⁻⁶/°C

Table 4.4b Grain Boundary Glass Compositions (in Mole Fractions) and Thermal Expansion Coefficients

Alkaline Earth Aluminosilicate Oxynitride Grain Boundary Phases

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>CaO</th>
<th>BaO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Si₃N₄</th>
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</thead>
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<tr>
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<tr>
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<td>0.2</td>
<td>0.21</td>
<td>0.51</td>
<td>0.08</td>
<td>5.7</td>
<td>6.0</td>
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Table 4.5 Thermal Expansion Coefficients of Crystalline Grain Boundary Phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\alpha \times 10^6$/$^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAG ($Y_3Al_5O_{12}$)</td>
<td>8.0</td>
</tr>
<tr>
<td>N-phase ($MgAl_2Si_4O_6N_4$)</td>
<td>2.3 *</td>
</tr>
</tbody>
</table>

* The thermal expansion coefficient of N phase was measured by Nunn. 20

Table 4.6 Variability in Fracture Toughness Measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fracture Toughness (MPa-m$^{0.5}$)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>6.6</td>
</tr>
<tr>
<td>2</td>
<td>7.0</td>
</tr>
<tr>
<td>3</td>
<td>6.9</td>
</tr>
<tr>
<td>4</td>
<td>6.5</td>
</tr>
</tbody>
</table>

The composition of all four samples in this table was:
85 volume % $Si_3N_4$/ 15 volume % of $2 BaO$: $2 Al_2O_3$: 5 $SiO_2$.

The samples were sintered at 1640°C for three hours and then at 1940°C for three hours.

Table 4.7 Elastic Properties Used in Calculations

<table>
<thead>
<tr>
<th></th>
<th>Silicon Nitride</th>
<th>Glass</th>
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<tr>
<td>$E$, GPa</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>$v$</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>$K_0$, MPa-m$^{1/2}$</td>
<td>2.0</td>
<td>0.9</td>
</tr>
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</table>
Figure 4.1. Solid/Liquid Phase Equilibria in the Mg, Al, Si/O,N System (After Ref. 7)
Figure 4.2. Solid/Liquid Phase Equilibria in the Y, Si, Al, O, N System (After Ref. 9)
Figure 4.3. Comparison of liquidus regions in a. CaO-Si3N4-AlN at 1700°C and b. MgO-Al2O3-AlN at 1750°C (After Ref. 10)

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Figure 4.4a. Microstructure and crack path in silicon nitride sintered with 100% cordierite

Figure 4.4b. Microstructure and crack path in silicon nitride sintered with 60% cordierite/40% YAG
Figure 4.5a. Effect of sintering aid composition on length of grains

Figure 4.5b. Effect of sintering aid composition on width of grains
Figure 4.6. Microstructure and crack path of Si$_3$N$_4$ sintered with 2 XO: 2 Al$_2$O$_3$: 5 SiO$_2$ where a. $X = \text{Mg}$  b. $X = \text{Ca}$  c. $X = \text{Ba}$
Figure 4.7. Effect of thermal expansion coefficient of grain boundary phase on fracture toughness of silicon nitride sintered with $Y_2O_3$-$Al_2O_3$-$MgO$-$SiO_2$ additives
Figure 4.8. Effect of thermal expansion coefficient of grain boundary phase on fracture toughness of silicon nitride sintered with alkaline earth aluminosilicate additives.
Figure 4.9. Effect of thermal expansion coefficient on distance between bridging grains
Figure 4.10. Effect of sintering temperature and thermal expansion coefficient on mean crack deflection angle
Figure 4.11. Effect of thermal expansion coefficient on maximum crack deflection angle
(Sintering step 2 at 1840°C for 3 hours.)

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Figure 4.12. Effect of thermal expansion coefficient on maximum crack deflection angle, alkaline earth aluminosilicate additives (Sintering step 2 at 1840°C for 3 hours)
Figure 4.13. Effect of crystallization on fracture toughness
Figure 4.14. Effect of small volume fractions of cordierite additive on length of Si$_3$N$_4$ grains

Figure 4.15. Effect of increasing the volume fraction of barium aluminosilicate additive on microstructure of Si$_3$N$_4$ a. 15 volume % additive b. 25 volume % additive

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Figure 4.16. Effect of the volume fraction of cordierite and YAG additives on the fracture toughness of silicon nitride.

Figure 4.17. Effect of volume fraction barium aluminosilicate additive on fracture toughness of silicon nitride.
Figure 4.18. Residual stress as a function of thermal expansion coefficient of the grain boundary phase at 15 volume % grain boundary phase.
Figure 4.19. Residual stress as a function of the volume fraction of grain boundary phase

Thermal expansion coefficient of the grain boundary phase = $6 \times 10^{-6/°C}$
Figure 4.20. Measured maximum deflection angles and calculated deflection angles
Figure 4.21. Linear fraction of crack which is bridged increases as the fraction of grains oriented favorably for deflection increases (Sintering step 2 at 1840°C for 3 hrs)
Figure 4.22. Fracture toughness increases linearly as the area fraction of bridging grains increases.
5.1 Introduction

X-ray and neutron diffraction were used to measure the residual stresses in silicon nitride sintered with different sintering aids. The thermal expansion mismatch between the grain boundary phase and the β-silicon nitride resulted in compressive residual stresses as large as 600 MPa. The amount of residual stress increased as the amount of the grain boundary phase increased. The stress also increased as the difference in thermal expansion coefficients between the silicon nitride and the grain boundary phase increased. The measured residual stresses were compared with theoretical calculations based on Eshelby's inclusion theory.

Sintered silicon nitride can be treated as a composite material consisting of elongated grains and a grain boundary phase. As in other composite materials, residual stresses arise due to the difference in thermal expansion coefficients between the two phases. These residual stresses cause strains in the silicon nitride lattice, which can be measured using x-ray and neutron diffraction. In this study, the residual stresses in silicon nitride caused by thermal expansion mismatch were studied using both x-ray and neutron diffraction. Both x-ray and neutron diffraction are widely used to study residual stresses.1,2
Two types of stresses are studied using diffraction techniques: macrostresses and microstresses. Macrostresses vary over dimensions which are large compared to the dimensions of the microstructure of the material. Welding stresses are an example of this type of stress. In contrast, microstresses vary over distances on the scale of the microstructure. In a composite material, one is mainly concerned with the residual microstresses arising from differences in thermal expansion between various constituents of the composite.

Both x-ray and neutron diffraction techniques measure the shift in the positions of the diffraction peaks caused by distortion in a crystalline lattice. For example, if the lattice is under compression, the interplanar lattice spacing will decrease, which will shift the peak position to higher angles.

X-rays usually penetrate a few microns into a sample. The short penetration depth of x-rays makes x-ray diffraction the preferred choice for mapping surface stresses. In addition, the x-ray beam has high intensity, which allows the use of small beam sizes. The small beam allows mapping of macrostress distributions.

Neutrons penetrate more deeply into a sample, typically a few centimeters. As a result, the residual stresses obtained with neutron diffraction are representative of the bulk. Moreover, if the entire sample is illuminated in the neutron beam, then the macrostresses in the sample cancel out to zero, allowing better resolution of the microstresses. The major disadvantage of neutron diffraction is the low intensity of the neutron beam. A large neutron beam and large samples must be used. In addition, because of the limited number of neutron sources, instrument time is not always readily available.

The major goal of this study was to compare the residual stresses in Si₃N₄ ceramics containing different amounts and compositions of a grain boundary phase. A second goal was to compare the values of residual stress measured by x-ray and neutron
diffraction techniques, in order to determine which technique is more suitable for studies involving larger numbers of ceramic samples.

5.2 Literature Review

5.2.1 Residual stress determination from diffraction data

Residual stresses are determined from the difference in lattice spacing between an unstressed (reference) sample and a stressed sample. The strain, \( \varepsilon \), in any particular crystallographic direction \([h k l]\) can be determined from the lattice spacing \( d \):

\[
\varepsilon = \frac{d - d_0}{d_0}
\]  

(1)

where \( d \) is the lattice spacing along \([h k l]\) and \( d_0 \) is the lattice spacing in the unstressed samples.

If the stress in the sample is hydrostatic, as expected for the samples in this study, the residual stresses \( \sigma \) can be determined from the measured strains using:

\[
\sigma = \frac{E}{(1-2\nu)} \varepsilon
\]  

(2)

where \( E \) is the elastic constant and \( \varepsilon \) is the measured strain.

5.2.2 Calculation of residual stresses using Eshelby's inclusion theory

There are many theories in the literature to evaluate residual stresses in composite materials. One widely used theory is based on Eshelby's inclusion theory\(^4\) as arranged by Hsueh et al\(^5\) and Taya et al\(^6\):
where \( \sigma \) is the stress, \( \alpha \) is the thermal expansion coefficient, \( f \) is the volume fraction, \( v \) is the Poisson's ratio, and \( E \) is the Young's modulus. The subscripts \( sn \) and \( g \) denote the silicon nitride and glass phases respectively. \( \Delta T \) is the difference in temperature over which the stresses are locked in. \( \Delta T \) was taken as the difference between the glass transition temperature of the glass and room temperature, which was approximately 1000°C. The material properties used in the calculations in this section are listed in Table 5.1.

Using modified version of Eshelby's inclusion method discussed earlier, the residual stress in the silicon nitride can be calculated from equation 5, as shown in Figure 5.1 for silicon nitride containing 20 volume % of sintering aid. The glass was assumed to be the continuous phase and the particles to be Si\(_3\)N\(_4\). This assumption is physically correct, but strays from the situation envisioned by the authors of the model. The modified version of Eshelby's inclusion method assumes that the phase which is present in the higher volume fraction is the phase which is physically continuous. In the silicon nitride samples, the phase which is present in higher volume fraction (the silicon nitride grains) is physically discontinuous.

When the thermal expansion coefficient of the grain boundary phase is greater than that of the silicon nitride, both the tensile stress in the grain boundary and the compressive stress in the silicon nitride grains increase as the thermal expansion coefficient of the grain boundary phase increases. The residual stress in both phases can also be calculated as a function of the volume fraction of sintering aid. The residual stress
in the silicon nitride is shown in Figure 5.2 for grain boundary phases with two different thermal expansion coefficients.

5.3 Experimental Procedures

5.3.1 Processing and Preliminary Characterization of Silicon Nitride

Silicon nitride samples with different volume percentages of two different sintering aids were prepared, as shown in Table 5.2. The sintering aids were two different alkaline earth aluminosilicate compositions: 2 MgO: 2 Al₂O₃: 5 SiC> 2 and 2 BaO: 2 Al₂O₃: 5 SiO₂.

The oxide powders were attrition milled with silicon nitride for four hours. The sintering schedules are shown in Table 5.3. The samples were all densified by gas pressure sintering under 10 atmospheres of nitrogen. The samples were quenched by turning off the power to the furnace. The sample containing 10 volume % BaO- was sintered at a higher temperature than the others to avoid the crystallization of its refractory grain boundary phase. The sample containing 25 volume % barium aluminosilicate underwent further heat treatment to crystallize the grain boundary phase, as shown in Table 5.3. The samples were polished to 0.1 μm. After polishing, the samples were annealed at 1500°C for one hour to remove the polishing stresses. X-ray diffraction was used to verify the phases present. The densities of the samples were determined using Archimedes method.

The compositions and linear thermal expansion coefficients of the glass grain boundary phases were determined in Chapter 3. The compositions were confirmed in the samples used in this study by SEM examination of the volume fractions of glass and silicon nitride present in the samples. The thermal expansion coefficient of the crystalline
barium aluminosilicate was measured by Bandyopadhyay et al. 8 (The thermal expansion coefficient of Si3N4 is 3.0 x 10^{-6}/°C.)

The overall compositions of the samples and the compositions of the silicon nitride grains were measured using EPMA. The composition of the silicon nitride grains was important because Al2O3 from the sintering aid can enter into solid solution inside β-Si3N4 lattice, which causes the β-Si3N4 lattice to expand, as shown in Figure 5.3. 9

The amount of Al which enter into the lattice can be expressed in equivalent percent:

\[ \text{Eq. % Al} = \frac{3X_{Al}}{3X_{Al} + 4X_{Si}} \]  

(5)

where \(X_{Al}\) and \(X_{Si}\) are the mole fractions of Al and Si respectively. The equivalent percent of Al is a measure of what fraction of the positive charges in a mole of β'SiAlON solid solution are provided by Al^{3+}.

The compositions of this study were chosen to avoid the formation of the solid solutions. The compositions of the silicon nitride grains were determined using Electron Probe Micro-Analysis. To minimize differences in lattice parameter caused by the solid solution of undetectable amounts of Al2O3, the sample which contained 5 volume % sintering aid was used instead of pure β-Si3N4 powder as the reference sample.

5.3.2. Diffraction

In silicon nitride, the (233)/(323) peak and the ((413)/(143) & (720)/(270) ) peaks were used for the neutron diffraction measurements of strain. The wavelength was 1.4178 angstroms. The pattern from 80°<2θ<150° was also obtained for each sample.

For the x-ray measurements of strain, the (233)/(323) peak was used. The wavelength was CuKα at 1.5406 angstroms. Tilt angles of 0°, 45° and 90° did not detect
any significant macrostresses. The pattern from $130^\circ < 2\theta < 155^\circ$ was also obtained for each sample.

5.4 Results

The reference sample contained about 5 volume % porosity. The other samples were greater than 99% of theoretical density. X-ray diffraction measurements showed only $\beta$-Si$_3$N$_4$ present for samples which did not undergo the crystallization treatment. In the crystallized sample, $\beta$-Si$_3$N$_4$ and hexacelsian barium aluminosilicate were present. EPMA measurements on the silicon nitride samples showed a maximum of 3 equivalent % Al present in solid solution in the silicon nitride grains. The actual value may have been even smaller, if some of the Al detected came from the grain boundary phase instead of from the grain. Therefore, differences in lattice parameter between the samples was not caused by changes in grain chemistry.

The diffraction peaks from x-ray and neutron diffraction measurements were narrow and Gaussian in shape. Figure 5.4 shows the excellent Gaussian fit for a typical neutron diffraction peak. The points are the data. The line represents the calculated Gaussian shape. Large peak shifts were evident in both x-ray and neutron scattering. Figure 5.5 shows the peak shifts evident from the x-ray measurement. As shown in Figure 5.5a as the amount of barium aluminosilicate in the sample increased, the silicon nitride peak shifted to higher angle, indicating an increase in the compressive stress present in the silicon nitride. As shown in Figure 5.5b, as the amount of magnesium aluminosilicate in the sample increased, the silicon nitride peaks also shifted to higher angle.

The lattice strains are listed in Tables 5.4a and 5.4b, along with the standard deviation ($\pm \sigma$) of the measurement. The strains along the a and c axes obtained using Rietveld refinement of the neutron scattering data are also listed. The Rietveld
refinement was performed using RIETAN, a structure refinement program developed by F. Izumi. 3, 10

5.5. Discussion

The stresses were calculated from the measured strains using x-ray elastic constants measured by Tanaka et al. 11 The Young's moduli and Poisson's ratio for the [323] direction are \( E_{323} = 305 \text{ GPa} \) and \( \nu = 0.26.9 \) The thermal expansion coefficients of the grain boundary phases used for the stress calculations are shown in Table 5.5. The stresses calculated from the measured strains and the stresses calculated from Eshelby's inclusion theory are shown in Table 5.6.

The stresses found from the x-ray data are about 100 MPa smaller than those found from the neutron data. The lower stress values found by x-ray diffraction probably indicate surface relaxation.

The stresses found from both diffraction techniques are much higher than the calculated stresses. There are two possible sources for this discrepancy. The discrepancy could be caused by the difference between the physical situation and the assumptions in the model, or by the presence of stresses which are not due to the thermal expansion mismatch between the grain boundary phase and the silicon nitride.

The physical arrangement of the silicon nitride and glass contradicts the assumptions made in the model. The Eshelby inclusion model assumes that the phase present in the largest amount is the continuous phase; in silicon nitride the glass phase (present in small volume fractions) is the continuous phase. The silicon nitride grains are close enough together for their stress fields to interact, and impose additional constraints on the deformation of the glass, which contradicts the model's assumption that there is no interaction between particles. The shape of the particles also changes the magnitude of the residual stresses. 4 The particles in the model are spherical, but the silicon nitride
particles are elongated hexagonal prisms. The interaction between particles and the shape of the particles were not considered in the calculations. As a result, the calculated stress would be expected to underestimate the actual stress present in the sample. Unfortunately, there is not a simple model available which is appropriate for calculations of residual stress fields from thermal expansion mismatch between anisotropic grains and a grain boundary phase.

The discrepancy between the measured stresses and the calculated stresses could reflect the presence of stresses which do not arise from thermal expansion mismatch between the grain boundary phase and the silicon nitride. One source of these stresses is the thermal expansion anisotropy between the a and c directions in silicon nitride. The thermal expansion coefficients are $3.1 \times 10^{-6} \degree \text{C}$ and $2.0 \times 10^{-6} \degree \text{C}$ in the a and c directions, respectively. The overall hydrostatic stress due to the thermal expansion anisotropy of the silicon nitride grains would be zero. The stresses would be relaxed by the flow of the grain boundary phase. Therefore, the contribution of these stresses would be greatest when the amount of grain boundary phase was very small. The presence of stresses due to anisotropic thermal expansion can be assessed by examining the strains in the a and c directions when the amount of the grain boundary phase increases from 5 to 15 volume %. Rietveld analysis found a strain of $-3.0 \times 10^{-4}$ in the a direction and $-5.5 \times 10^{-4}$ in the c direction. As expected, the compressive strain in the c direction is larger.

Without the anisotropic contribution, the measured strain would be approximately halfway between the strains measured in the a and c direction, or approximately $-4.25 \times 10^{-4}$. The strain measured on the (233)/(323) peak is $-4.5 \times 10^{-4}$, so the anisotropic contributions do not affect the strains measured on this peak. Therefore, the anisotropic thermal expansion of the silicon nitride does not contribute significantly to the stresses calculated from the shifts of the (233)/(323) peak.

Differences in porosity and microstructure could also change the magnitude of stresses in the material. The difference in stress between the reference sample, which
contains 5 volume % magnesium aluminosilicate and the sample which contains 15 volume % magnesium aluminosilicate is particularly surprising. About 5 volume % porosity was present in the reference sample, while the other samples had densities greater that 99% theoretical. The porosity indicates that the reference sample behaved as if it contained unsinterable agglomerates. Models indicate that samples which contain agglomerates can develop tensile stresses during sintering. Therefore, some of the large difference in peak position between the sample containing 5 volume % sintering aid and the rest of the samples could be the result of unrelieved tensile stresses caused by an insufficient amount of sintering aid or of stresses introduced during processing which were not relieved because of an insufficient amount of sintering aid. If the 5 volume % sample is left out of the analysis, a new comparison between stresses in the other samples can be made, as shown in Table 5.7. The differences in stress between the dense samples is much closer to the expected values.

Stresses can develop during crystallization of the grain boundary phase if the densities of the glass and crystalline phases are not the same. During crystallization of the barium aluminosilicate grain boundary phase, compressive stresses may have developed in the silicon nitride.

5.6 Conclusions

The strains in the silicon nitride lattice caused by the presence of different grain boundary phases were measured using both x-ray and neutron diffraction. The stresses in the silicon nitride were calculated from the measured strains. The effect of thermal expansion coefficient and volume fraction of the grain boundary phase was calculated using Eshelby's inclusion theory. As expected from theory, the compressive stress in the silicon nitride increased as the thermal expansion coefficient of the grain boundary phase increased. However, the measured stresses were much larger than the calculated stresses,
indicating that other sources of stress were present. Further work would be needed to develop a predictive model for the effect of the thermal expansion coefficient and the volume fraction of the grain boundary phase on the residual stresses in silicon nitride.
REFERENCES


Table 5.1 Material Properties Used in Calculations of Residual Stress Using Eshelby's Inclusion Theory

<table>
<thead>
<tr>
<th></th>
<th>Silicon Nitride</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus</td>
<td>300 GPa</td>
<td>100 GPa</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.26</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 5.2 Sintering Aids

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering Aid</th>
<th>Volume % Sintering Aid</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 MgAlSi</td>
<td>2 MgO: 2 Al₂O₃: 5 SiO₂</td>
<td>5</td>
</tr>
<tr>
<td>15 MgAlSi</td>
<td>2 MgO: 2 Al₂O₃: 5 SiO₂</td>
<td>15</td>
</tr>
<tr>
<td>10 BaAlSi</td>
<td>2 BaO: 2 Al₂O₃: 5 SiO₂</td>
<td>10</td>
</tr>
<tr>
<td>25 BaAlSi (crystallized)</td>
<td>2 BaO: 2 Al₂O₃: 5 SiO₂</td>
<td>25</td>
</tr>
</tbody>
</table>
Table 5.3 Sintering Schedules: Multi-Step Sintering and Annealing

<table>
<thead>
<tr>
<th>Sample</th>
<th>STEP 1</th>
<th>STEP 2</th>
<th>STEP 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 MgAlSi</td>
<td>1640°C (3 hrs)</td>
<td>1840°C (3 hrs)</td>
<td>1640°C (2 hrs)</td>
</tr>
<tr>
<td>15 MgAlSi</td>
<td>1640°C (3 hrs)</td>
<td>1840°C (3 hrs)</td>
<td>1640°C (2 hrs)</td>
</tr>
<tr>
<td>10 BaAlSi</td>
<td>1640°C (3 hrs)</td>
<td>1940°C (3 hrs)</td>
<td></td>
</tr>
<tr>
<td>25 BaAlSi</td>
<td>1640°C (3 hrs)</td>
<td>1840°C (3 hrs)</td>
<td>1640°C (2 hrs)</td>
</tr>
</tbody>
</table>

Crystallization Treatment

| 25 BaAlSi | 1450°C (6 hrs) |

Annealing

| 5 MgAlSi   | 1500°C (1 hr)  |
| 15 MgAlSi  | 1500°C (1 hr)  |
| 10 BaAlSi  | 1500°C (1 hr)  |
| 25 BaAlSi  | 1500°C (1 hr)  |
Table 5.4a Lattice Strains Measured by X-Ray and Neutron Diffraction

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain boundary</th>
<th>X-ray</th>
<th>Neutron*</th>
<th>Neutron (Rtvlid)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ε (+σ)</td>
<td>ε (+σ)</td>
<td>εa, εc</td>
</tr>
<tr>
<td>5 MgAlSi</td>
<td>Glass</td>
<td>0 (standard)</td>
<td>0 (standard)</td>
<td>0, 0 (standard)</td>
</tr>
<tr>
<td>15 MgAlSi</td>
<td>Glass</td>
<td>-2.96 x 10^{-4}</td>
<td>-4.50 x 10^{-4}</td>
<td>εa = -3.0 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(±0.04 x 10^{-4})</td>
<td>(±0.11 x 10^{-4})</td>
<td>εc = -5.5 x 10^{-4}</td>
</tr>
<tr>
<td>10 BaAlSi</td>
<td>Glass</td>
<td>-5.0 x 10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(±0.04 x 10^{-4})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 BaAlSi</td>
<td>Crystalline</td>
<td>-8.4 x 10^{-4}</td>
<td>-9.2 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(±0.05 x 10^{-4})</td>
<td>(±0.11 x 10^{-4})</td>
<td></td>
</tr>
</tbody>
</table>

* (323)/(233) peak

Table 5.4b Comparison of Strains Measured From (233)/(323) Peak and Strains From (413)/(143)&(270/720) Peaks by Neutron Diffraction

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain Boundary</th>
<th>Neutron (233)/(323)</th>
<th>Neutron (413)/(143)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ε (+σ)</td>
<td>ε (+σ)</td>
</tr>
<tr>
<td>5 MgAlSi</td>
<td>Glass</td>
<td>0 (Standard)</td>
<td>0 (Standard)</td>
</tr>
<tr>
<td>15 MgAlSi</td>
<td>Glass</td>
<td>-4.5 x 10^{-4}</td>
<td>-4.2 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(±0.11 x 10^{-4})</td>
<td>(±0.11 x 10^{-4})</td>
</tr>
<tr>
<td>25 BaAlSi</td>
<td>Crystalline</td>
<td>-9.2 x 10^{-4}</td>
<td>-8.1 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(±0.11 x 10^{-4})</td>
<td>(±0.11 x 10^{-4})</td>
</tr>
</tbody>
</table>

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Table 5.5 Linear Thermal Expansion Coefficients and Compositions of Grain Boundary Phases

Glass Grain Boundary Phases

<table>
<thead>
<tr>
<th>MgO</th>
<th>BaO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Si₃N₄</th>
<th>α x 10⁶°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mole %)</td>
<td>(mole %)</td>
<td>(mole %)</td>
<td>(mole %)</td>
<td>(mole %)</td>
<td>(mole %)</td>
</tr>
<tr>
<td>0.20</td>
<td>0</td>
<td>0.21</td>
<td>0.51</td>
<td>0.08</td>
<td>3.4</td>
</tr>
<tr>
<td>0</td>
<td>0.20</td>
<td>0.21</td>
<td>0.51</td>
<td>0.08</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Crystalline Grain Boundary Phases: BaAl₂Si₂O₈ (Hexacelsian) : α = 8 x 10⁻⁶°C

Table 5.6 Stresses in Silicon Nitride

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain Boundary</th>
<th>Calculated Stress (MPa)</th>
<th>Measured Stress Neutron (MPa)</th>
<th>Measured Stress X-Ray (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 MgAlSi</td>
<td>Glass</td>
<td>0 (standard)</td>
<td>0 (standard)</td>
<td>0 (standard)</td>
</tr>
<tr>
<td>15 MgAlSi</td>
<td>Glass</td>
<td>-3</td>
<td>-284</td>
<td>-187</td>
</tr>
<tr>
<td>10 BaAlSi</td>
<td>Glass</td>
<td>-33</td>
<td>-580</td>
<td>-532</td>
</tr>
<tr>
<td>25 BaAlSi</td>
<td>Crystalline</td>
<td>-197</td>
<td>-580</td>
<td>-532</td>
</tr>
</tbody>
</table>
Table 5.7 Comparison of Residual Stresses in Dense Samples

<table>
<thead>
<tr>
<th></th>
<th>Calculated Stress (MPa)</th>
<th>Measured Stress Neutron (MPa)</th>
<th>Measured Stress X-Ray (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 MgAlSi</td>
<td>0 (standard)</td>
<td>0 (standard)</td>
<td>0 (standard)</td>
</tr>
<tr>
<td>10 BaAlSi</td>
<td>-30</td>
<td></td>
<td>-126</td>
</tr>
<tr>
<td>25 BaAlSi</td>
<td>-194</td>
<td>-296</td>
<td>-348</td>
</tr>
</tbody>
</table>
Figure 5.1. Calculated residual stress in the silicon nitride increases as the thermal expansion coefficient ($\alpha$) of the grain boundary phase increases (Calculated for a grain boundary phase volume of 20%)
Figure 5.2. The calculated stress in the silicon nitride grains increases as the amount of grain boundary phase increases. The increase is larger for additives with higher thermal expansion coefficients.
Figure 5.3. Effect of solid solution formation on the lattice parameter of $\beta'$-SiAlON  
(After Ref. 9)
Figure 5.4. Neutron peak (323) and Gaussian fit
Figure 5.5a. X-ray peak shifts to higher angle as amount of magnesium aluminosilicate grain boundary phase increases.
Figure 5.5b. X-ray peak shifts to higher angle as amount of barium aluminosilicate grain boundary phase increases
CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The fracture toughness of silicon nitride ceramics depends on the shape of the crack paths in the silicon nitride. Fracture toughness is enhanced by crack deflection and the formation of bridging grains.

The crack path in the material is strongly influenced by the presence of residual stresses. One source of residual stress is the difference in thermal expansion coefficient between the silicon nitride and the grain boundary phase. When the thermal expansion coefficient of the grain boundary phase is larger than the thermal expansion coefficient of the silicon nitride grains, residual tensile stresses develop in the grain boundary phase on cooling. Compressive stresses develop in the silicon nitride grains. This stress distribution enhances crack deflection, and allows the crack to detour around intact grains, which leads to the bridging grains in the crack wake. The effect of the residual stresses on crack propagation and fracture toughness were demonstrated in this thesis. The residual stresses in the silicon nitride grains can be several hundred MPa in magnitude, and can be measured using x-ray and neutron diffraction. The magnitude of the residual stresses can be designed by altering the thermal expansion coefficient of the grain boundary phase.

The thermal expansion coefficient of an oxynitride grain boundary phase can be predicted from the constituents present in the glass. Relationships between the field strengths of the cations in the glass and the thermal expansion coefficient can be used to design grain boundary compositions with appropriate thermal expansion coefficients. The agreement between thermal expansion coefficients calculated from the composition and measured values was demonstrated for several oxynitride glass compositions in this thesis.
Several unanswered questions about the development of residual stresses remain for future study. The relationship between the thermal expansion coefficient of the grain boundary phase and the residual stresses is explained only qualitatively by existing models. More measurements of these stresses as a function of the thermal expansion coefficient and volume fraction of the grain boundary phase could lead to a better model. Measurements of the change in stress as a function of temperature would also assist development of a predictive model.

This study identified residual stresses from thermal expansion mismatch as one important factor which affects the fracture toughness of silicon nitride. The residual stresses affect both the strength of the intergranular phase and of the silicon nitride/grain boundary interface. The strength of the interface is also affected by the chemistry of the grain boundary phase. Although some studies on the relationship between the chemistry of the grain boundary phase and the adhesion at the grain boundary/silicon nitride interface have been reported, further studies are needed. In addition, the effect of the sintering aid on the structure of the silicon nitride/glass interface is not understood. The structure of the interface could affect the fracture toughness. The structure of the silicon nitride/liquid interface could also influence grain growth during sintering.

The creep resistance of silicon nitride improves if the grain boundary phase is crystallized. Several crystalline grain boundary phases were produced as part of the work on this thesis, including N phase, YAG, and hexacelsian barium aluminosilicate. However, the crystallization process is not well understood. One factor which may effect crystallization of the grain boundary phase is the stress which develops during crystallization of the grain boundary phase as a result of the difference in density between the glass and crystalline phase. The development and relaxation of residual stresses during crystallization of the grain boundary phase have not been measured. A better
understanding of the role of stresses on the crystallization process would assist in the development of optimum crystallization treatments for the grain boundary phase.

The grain boundary phase may affect a wide variety of mechanical and chemical properties. The effect of the grain boundary phase on fracture strength, Weibull modulus and thermal shock resistance could be the subject of a future study. An understanding of the effect of the grain boundary phase on corrosion resistance would also have important implications on the design of desirable grain boundary phases.