

To the Graduate Council:

I am submitting herewith a dissertation written by Terry Norman Tiegs entitled "Microstructure Development, Compositional/Physical Gradient Formation and Related Mechanical Properties of Gas-Pressure-Sintered Silicon Nitride Ceramics." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Metallurgical Engineering.

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MICROSTRUCTURE DEVELOPMENT, COMPOSITIONAL/PHYSICAL
GRADIENT FORMATION AND RELATED MECHANICAL
PROPERTIES OF GAS-PRESSURE-SINTERED SILICON NITRIDE
CERAMICS

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Abstract

Three inter-related aspects in the fabrication of silicon nitride ceramics were performed for the thesis work. The topics included: (1) an analysis of the composition and physical gradients in bulk silicon nitride, (2) the effect of sintering parameters on microstructure development during the high-temperature sintering stage and the resulting mechanical properties, and (3) an investigation of β - Si_3N_4 nucleation and initial stage microstructure development.

The composition and physical gradients in bulk silicon nitride are due to the furnace conditions and the environment adjacent to the samples. Loss of SiO from the exposed surfaces results in the formation of nitrogen-rich phases, such as melilite on the as-sintered surfaces. The high nitrogen concentration in the near-surface region promotes β - Si_3N_4 grain growth. Along with the compositional gradients, mechanical property differences also exist between the as-sintered surfaces and the bulk materials. For example, the strengths of as-sintered surfaces of Si_3N_4 - Y_2O_3 - Al_2O_3 were observed to be reduced by more than 30% compared to the bulk material.

Gas-pressure sintering (GPS) was used to densify silicon nitride containing a wide variety of sintering additives: Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 and Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$. For both compositions a lower densification temperature (1900°C in the present experiments) was the most significant factor affecting the fracture toughness and promoting a bimodal grain structure. The low significance of the other process parameters implies the microstructure (and therefore properties) are essentially 'locked-in' during the densification stage and only minor changes can take place afterward. Thus, the microstructural development that occurs during the densification dictates the final properties.

The kinetics of the α -to- β Si_3N_4 transformation are dependent on several characteristics of the starting silicon nitride powder. Most importantly, are the silicon nitride powder surface area and initial β - Si_3N_4 content which both tend to increase the transformation rate. Other factors, such as lattice oxygen or carbon contents, appear to contribute to decreasing the transformation rate. In addition, the glass phase from the sintering additives also affects the transformation rate with higher viscosity and more refractory additives resulting in a decrease in the transformation rate. Larger volumes of the glass phase were observed to decrease the transformation rate.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Physical Properties of Silicon Nitride

Silicon nitride-based materials have long been the focus of considerable research for potential high-temperature structural ceramics because of their overall excellent combination of mechanical and physical properties.¹ As a result, several books, conferences and symposiums have been devoted exclusively to these types of ceramics.²⁻⁹ Materials can be made that possess high strength, fracture toughness, wear properties, fatigue resistance and elevated temperature creep resistance. Consequently, these materials are of interest in numerous applications for such diverse items as cutting tools, rotors and stator vanes for advanced gas turbines, valves and cam roller followers for gasoline and diesel engines, and radomes on missiles to name a few.¹⁰⁻¹⁴ Because of the broad interest, a considerable database has been generated over the years in processing and fabrication of silicon nitride ceramics.

Silicon in silicon nitride (Si_3N_4) is tetrahedrally coordinated with four nitrogen atoms due to the hybridized sp^3 configuration of the valence orbital electrons. This is a similar arrangement to the SiO_4 tetrahedra of silicate materials. The bonding between the Si and the N is approximately 70% covalent. Silicon nitride has primarily two crystallographic modifications.⁵ Both forms consist of silicon atoms surrounded by four irregular tetrahedrally oriented nitrogen atoms and each nitrogen is part of three tetrahedra as shown in Fig. 1.1. The tetrahedra join in a three dimensional network by sharing corners. The beta-phase ($\beta\text{-Si}_3\text{N}_4$) has a hexagonal unit cell with ABAB stacking sequence of Si-N layers along the c-axis. The Si_6N_8 unit cell is derived from the phenakit type (Be_2SiO_4)

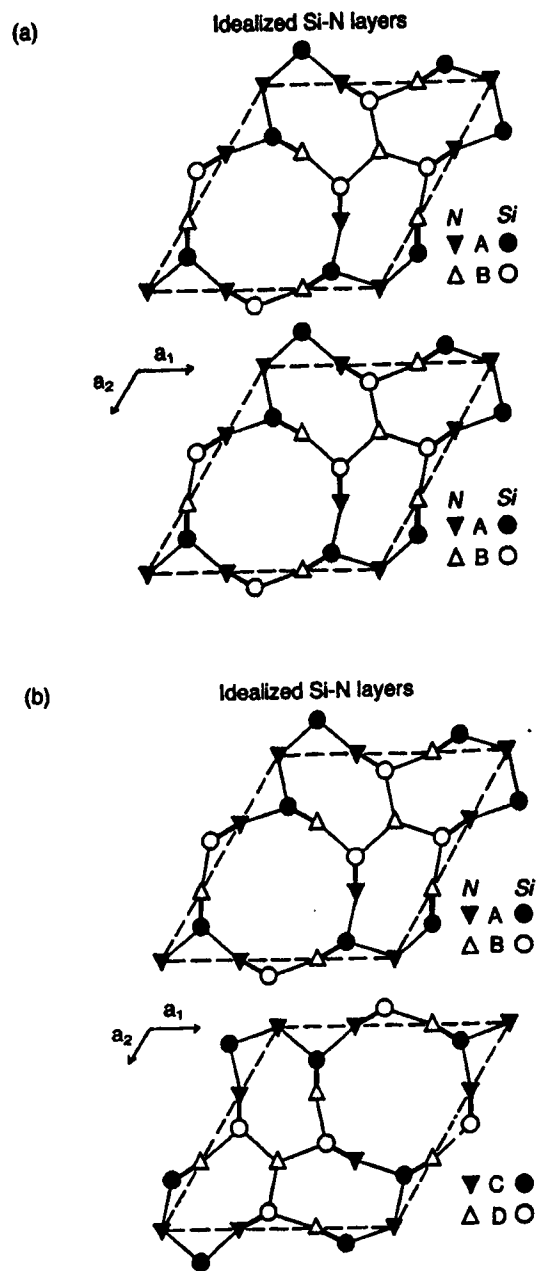


Fig. 1.1. (a) The AB layers in the β - Si_3N_4 crystal structure and (b) the AB and CD layers in the α - Si_3N_4 crystal structure. From Hampshire, 1983, Ref. 17.

with the Be atoms being replaced by Si and the O atoms by N.^{6,7} It is regarded as the high temperature stable phase. The alpha-phase (α -Si₃N₄) is also hexagonal in crystal structure, but the stacking sequence of Si-N layers is ABCDABCD in the c-direction. The AB layer is the same for both polymorphs and the CD layers are related to the AB layers by a 180° rotation relative to the AB layers. The differences in stacking sequences is illustrated in Fig. 1.2.¹⁸ The difference in stacking of the Si₁₂N₆ unit cell dimensions in the [001] direction results in a c-spacing of the α -phase of approximately twice that of the β -phase. The increase in the unit cell dimensions for the α -phase results in a increased Burger's vector which is believed to be the reason for the high hardness exhibited by the α -phase as compared to the β -phase. The stacking in the β -phase results in long continuous channels or tunnels in the crystallographic c-direction as shown in Fig. 1.3.¹⁹ In the α -phase, the stacking shift of the CD layers produces closed interstitial voids that are able to accommodate relatively large cations that can stabilize the α -phase even at high temperatures.

Early researchers had believed that the α -phase was stabilized with oxygen partially replacing nitrogen along with silicon vacancies to provide charge compensation. However, the current opinion is that the α -phase is a higher energy, metastable form.²⁰ The crystal structure of pure α -phase is believed to contain low levels of oxygen impurity substitution for the nitrogen depending on the fabrication route. It is important to recognize between the structural oxygen located in the crystal lattice, as just discussed, and the surface oxygen resulting from surface oxidation that occurs with all current Si₃N₄ powders. This is an important distinction that will become apparent in the analysis of results. The physical properties of silicon nitride are given in Table 1.1.

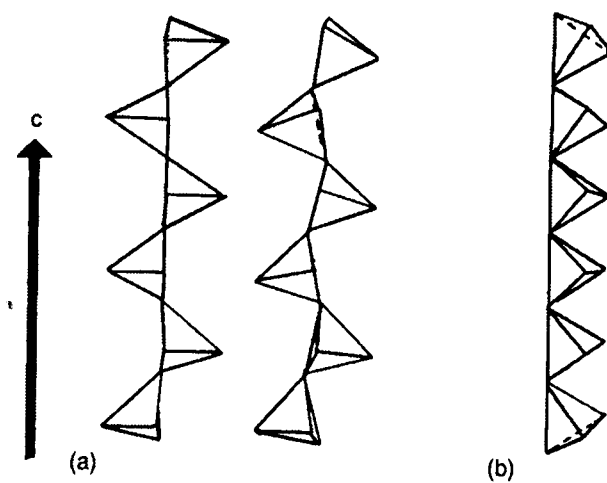


Fig. 1.2. (a) The two tetrahedra sequences of the α - Si_3N_4 along the c -axis and (b) the one tetrahedra sequence of the β - Si_3N_4 along the c -axis. from Grun, 1979, Ref. 18.

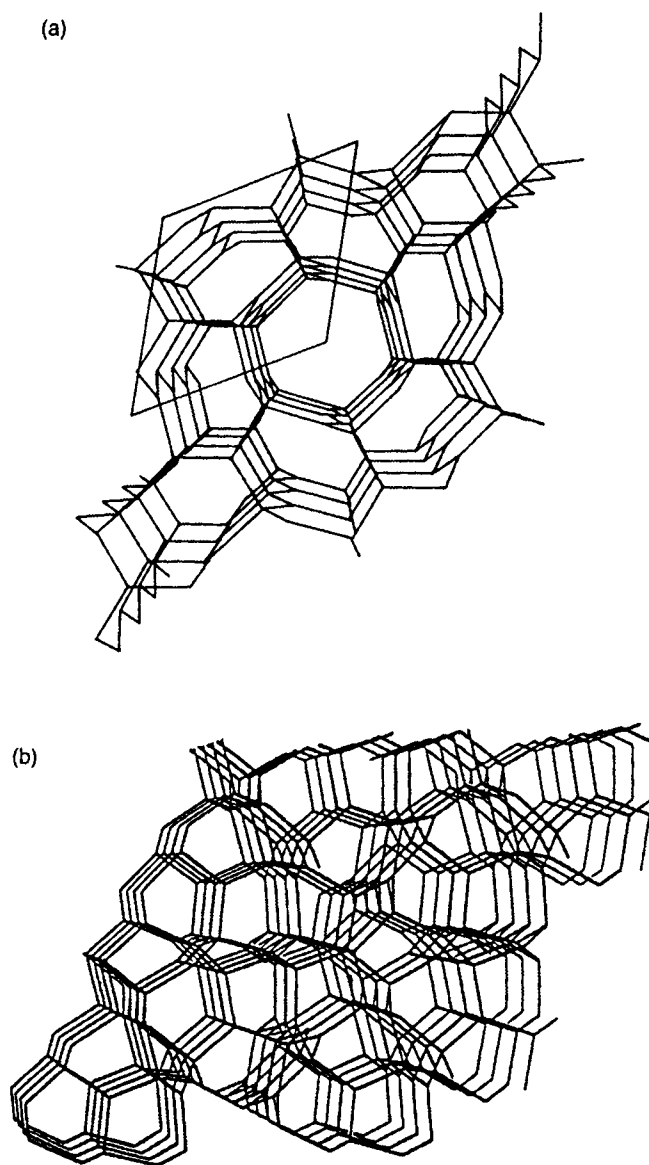


Fig. 1.3. (a) the ABAB layers of β - Si_3N_4 sketched close to the c-axis showing the continuous channels and (b) the ABCD stacking layers in α - Si_3N_4 showing the two closed interstices per unit cell. From Redington, 1989, Ref. 19.

Table 1.1. Physical properties of silicon nitride.

	β -Si ₃ N ₄ (hexagonal)	α -Si ₃ N ₄ (hexagonal)
a-axis (nm)	0.759-0.761	0.775-0.777
c-axis (nm)	0.271-0.292	0.516-0.569
c/a	~0.37	~0.70
Theoretical Density (g/cm ³)	3.19-3.202	3.168-3.188
Coef. Thermal Expan.	2.9-3.6X10 ⁻⁶ /°C	

Production of Silicon Nitride Powders

Silicon nitride does not occur naturally and hence must be synthesized. At the present time, several manufacturing processes are used to produce the powders commercially available.²¹⁻²³ In general, there are four different techniques employed: (1) direct nitridation of silicon in nitrogen or ammonia, (2) carbothermal reduction of silica, (3) formation and decomposition of silicon diimide, and (4) high temperature gas phase reaction of chlorosilanes and ammonia. These processes have been tailored to produce powders with controlled impurity and particle sizes, high α -phase content and low-cost. The overall reaction sequences and general powder characteristics are given in Table 1.2. Several other methods have been examined and speculated about for producing powders, but the ones listed are the ones most observed in the fabrication of sintered silicon nitride parts.

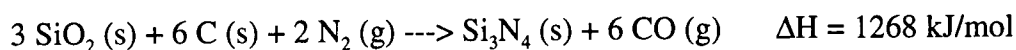
Numerous studies have shown that the silicon nitride powder used in fabrication is an extremely important variable in the microstructural development and final properties of the materials. Most of the early studies of silicon nitride powders were concerned only with either the densification behavior,²⁴⁻³⁵ the final mechanical properties or the high temperature

Table 1.2 Reaction sequences for the production of silicon nitride powders.

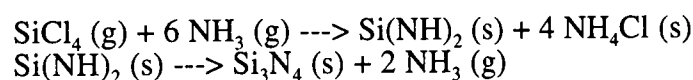
Nitridation of Silicon



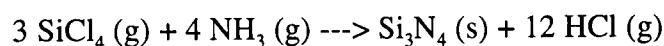
Carbothermic Reduction of Silica



Diimide Formation and Decomposition



Vapor Phase Reaction



properties³⁶⁻⁴² produced by the various grades of powders available. None of the studies have done a comparative assessment of the effects of the raw materials on the microstructural development from a fundamental standpoint. Generally, the previous work found that high starting α - Si_3N_4 contents in the powders are preferable for densification and final material mechanical properties.^{43,44} However, β -phase starting powders have also been used to produce materials with good mechanical properties.⁴⁵

Direct Nitridation of Silicon

The direct nitridation of silicon in nitrogen or ammonia is used commercially to produce large quantities of silicon nitride powders.⁴⁶ The reaction as shown in Table 1.2 is exothermic and must be controlled to prevent any runaway thermal excursions. In

production, silicon powders are heated to temperatures above $\sim 1250^{\circ}\text{C}$ (but below the melting point of silicon, 1410°C) under nitrogen, ammonia or mixtures of the two. The reaction is controlled to limit the temperature to below that of the silicon melting point. After synthesis, the reaction product is treated by a combination of grinding and acid leaching processes to both reduce the particle agglomeration that occurred during synthesis and for purification to remove impurities.

Carbothermal Reduction of Silica

A second method for synthesizing silicon nitride powders is by carbothermal reduction of silica.⁴⁷ The reaction is shown in Table 1.2. In the reaction, a powder mixture of carbon and silica is heated into the temperature range of $1300\text{--}1450^{\circ}\text{C}$. Typically, excess carbon is added and it is necessary to remove it at the end of the process. The kinetics and powder characteristics have been studied extensively on a laboratory scale for several years. Recently, Dow Chemical Company has been upscaling the process to commercial quantities after some early attempts at large scale production by other companies had been abandoned.⁴⁸

Formation and Decomposition of Silicon Diimide

Another commercially viable technique for producing silicon nitride is by formation and decomposition of silicon diimide. The process is comprised of three major steps: (1) diimide formation, (2) diimide thermal decomposition and (3) crystallization of amorphous silicon nitride. In the imide synthesis step, silicon tetrachloride (SiCl_4) and ammonia (NH_3) are reacted in either the liquid or vapor phase to form the silicon diimide ($\text{Si}(\text{NH})_2$) and ammonium chloride (NH_4Cl).⁴⁹⁻⁵¹ The reaction is exothermic and in the commercial

process it is controlled by implementing a liquid interface reaction between liquid ammonia and an organic solvent containing the SiCl_4 . The products are then washed and filtered to remove the NH_4Cl . Next, the silicon diimide is treated at $\sim 1000^\circ\text{C}$ to produce an amorphous product of silicon nitride. The amorphous product is finally treated at $1300\text{--}1500^\circ\text{C}$ to crystallize the powder into the α -phase.

High Temperature Gas Phase Reaction of Chloro-silanes and Ammonia

In the high temperature gas phase reaction of chloro-silanes and ammonia, the silane is diluted with nitrogen and then mixed with gaseous ammonia prior to reaction at $\sim 1400^\circ\text{C}$.^{52,53} The reaction product is amorphous and consequently, must be heat treated to obtain α -phase powder. This method is used to produce only small quantities of powders at the present time.

Overview of Microstructure Development and Densification Processes in Silicon Nitride

Unlike other advanced ceramic materials, such as Al_2O_3 and SiC , Si_3N_4 cannot be easily sintered by solid state diffusion processes although a few reports have reported solid state sintering.^{54,55} The use liquid phase sintering techniques is the most widespread method of obtaining dense materials with good properties.⁵⁶ Well before temperatures high enough for diffusion of N and Si to be significant, decomposition of the Si_3N_4 into the gas phase occurs. Thermodynamic stability calculations shown in Fig. 1.4 indicate that Si_3N_4 readily decomposes under 0.1 MPa (1 atmosphere) of nitrogen at temperatures $>1825^\circ\text{C}$.^{1,57-1,59} However, experimentally, the temperatures where appreciable weight losses are observed are significantly lower as shown in Fig. 1.5.⁶⁰ These lower temperatures are the result of

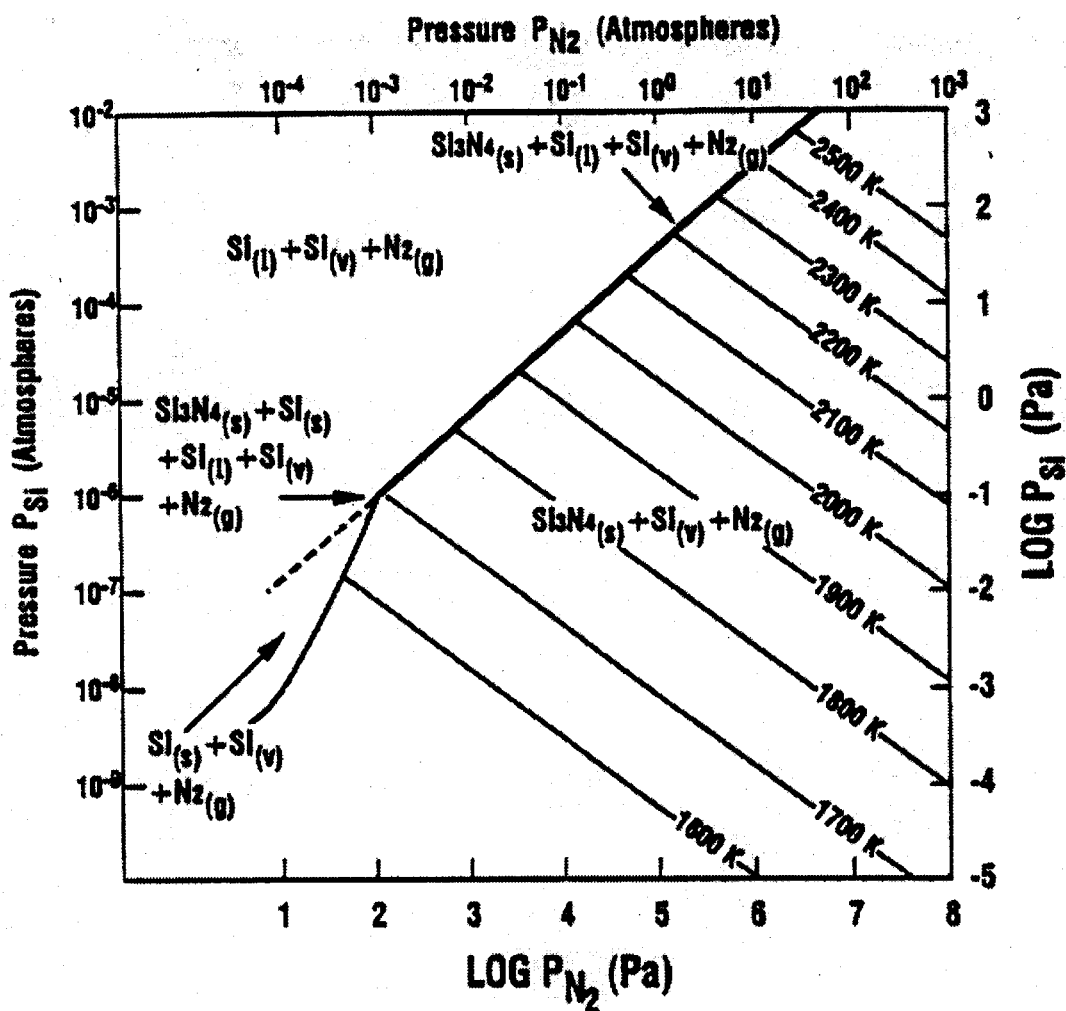


Fig. 1.4. Thermodynamic stability diagram for silicon nitride as a function of nitrogen pressure, silicon vapor pressure and temperature. From Greskovich and Prochazka, Ref. 197.

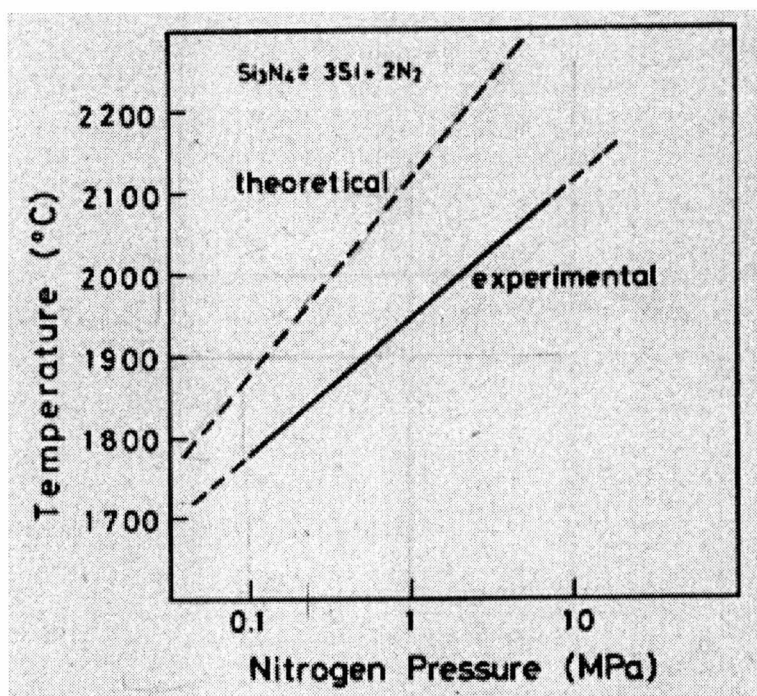


Fig. 1.5. Experimentally derived stability diagram of silicon nitride as a function of temperature. From Hattori et al, Ref. 60.

reactions associated with the oxide-rich grain boundary phases which will be discussed in later sections. Consequently, because of this, silicon nitride alone will not densify and additives are typically utilized to create liquid phases to aid in densification. Typical additives include Y_2O_3 , Al_2O_3 , AlN , MgO and several rare earth oxides. To suppress the decomposition of Si_3N_4 , nitrogen gas over-pressures can be used.^{57,58} Materials can be densified in this manner with pressures of 1-10 MPa (10-100 atmospheres) usually required, however, liquid phase sintering additives are still needed. The technique using high nitrogen pressures is referred to as gas pressure sintering (GPS).

Microstructural development and densification in silicon nitride ceramics occurs by a classical liquid phase sintering (LPS) mechanism which to the coexistence of liquid and solid phases during shrinkage. In general, three requirements are necessary for liquid phase sintering: (1) a liquid phase must be present at the sintering temperature, (2) wetting of the solid by the liquid must occur and (3) there must be some solubility of the solid in the liquid.⁶¹ The wetting that must occur between the liquid and solid phases is governed by the surface energies under equilibrium between the phases as shown in Fig. 1.6. This is classically described by the following relationship:

$$\gamma_{LV} = \frac{\gamma_{SV} - \gamma_{SL}}{\cos \theta} \quad [Eq. 1.1]$$

where γ_{LV} , γ_{SV} and γ_{SL} are the surface energies of the liquid-vapor, solid-vapor and solid-liquid, respectively. The contact angle between the liquid and the solid is θ .

LPS not only limited to silicon nitride sintering, but is used to sinter powder compacts of both metal and ceramic systems.^{62,63} Early work showed, the LPS process can be divided

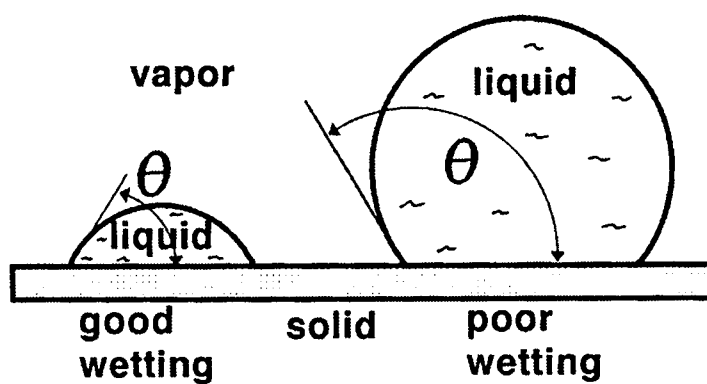


Fig. 1.6. Geometric representations of the solid-liquid-vapor equilibrium conditions for good wetting and poor wetting conditions. The equilibrium relation between the contact angle and the three interfacial energies is defined by a vector balance. From German, Ref. 152.

into three different stages: (1) liquid formation and particle rearrangement, (2) solution, β -phase nucleation and reprecipitation, and (3) grain growth and final pore removal. These stages are distinguished from one another by three different densification rates and rate controlling mechanisms as shown in Fig. 1.7.

Initially upon heating of a silicon nitride powder compact, the additives react with the surface SiO_2 on the starting Si_3N_4 particles to form a liquid phase.^{64,65} The temperature for these reactions varies with the types of additives. For example, in the Y_2O_3 - SiO_2 - Al_2O_3 system the eutectic liquid forms at about 1300°C compared to the Y_2O_3 - SiO_2 system with a eutectic of 1660°C . Table 1.3 shows some values for the temperatures for the various compositions.

After the initial liquid formation, dissolution of the α - and β - Si_3N_4 phases takes place. The substitution of nitrogen from the Si_3N_4 reaction for small to moderate amounts of oxygen lowers the liquid forming temperature (e.g. Y-Si-O-N is at approximately 1500°C), increases the liquid viscosity and inhibits nucleation of pure silicate phases by the formation of $\text{Si}(\text{O,N})_4$ tetrahedra in the melt. This liquid phase, in turn, reacts further with the Si_3N_4 particles and there is an increase in the total liquid phase content. After formation of the liquid phase, rearrangement of the particles can occur by capillary pressure at this stage. The various stages are schematically shown in Fig. 1.8.

Drew and coworkers have shown that up to 15 a/o nitrogen can be accommodated into oxynitride glasses containing Al, Mg, Ca, Y, and Nd with all the M-Si-O-N compositions able to accommodate similar nitrogen contents.^{66,67} Elements such as Mg and Ca are glass modifiers in oxide systems, but are glass formers in oxynitride systems. Therefore glass formation is initially enhanced as nitrogen is incorporated into the M-Si-O glass. However,

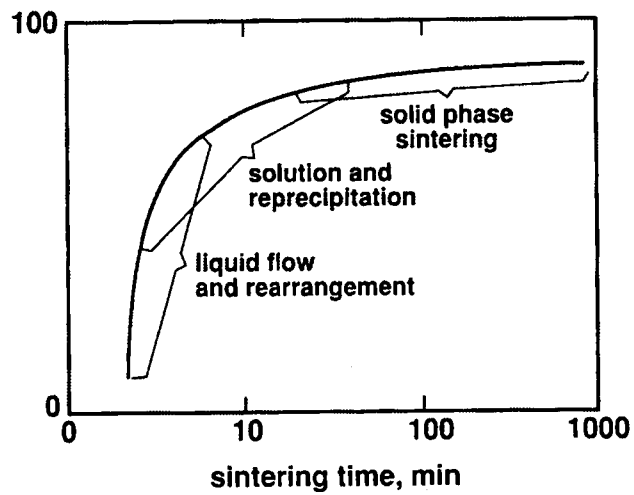


Fig. 1.7. Different stages of liquid phase sintering with an approximate time scale and densification profile. From German, Ref. 152.

Table 1.3 - Eutectic temperatures for M-Si-O and M-Si-O-N systems

Eutectic Temperatures (°C)		
M (Metal Atom)	M-Si-O (M _x O _y -SiO ₂)	M-Si-O-N
Mg	1540	1390
Ca	1485	1440
Al	1595	1470
Y	1640	1500

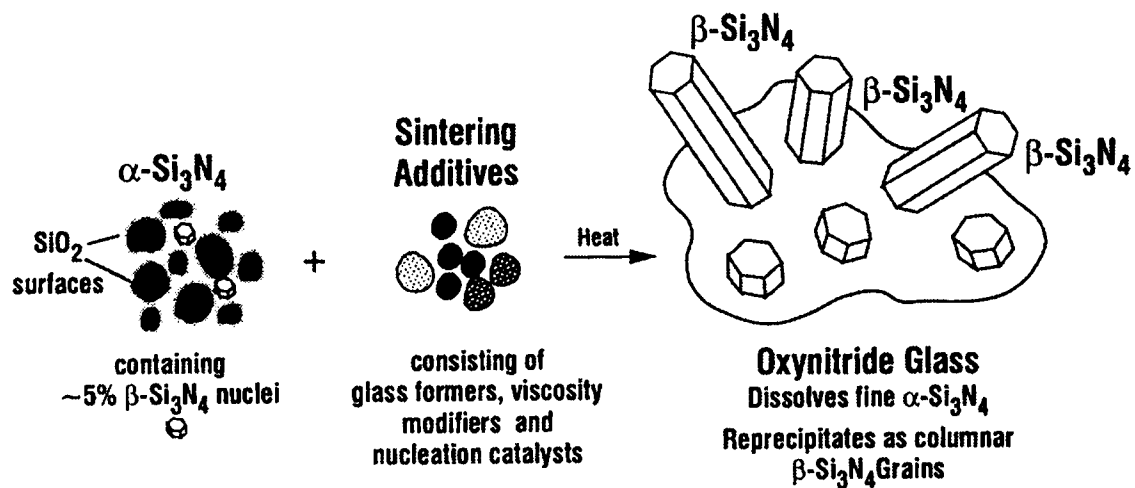


Fig. 1.8. Schematic diagram of microstructural development sequence for silicon nitride ceramics. Fine $\alpha\text{-Si}_3\text{N}_4$ particles are dissolved into the liquid glass phase, from which acicular $\beta\text{-Si}_3\text{N}_4$ grains grow. From Pyzik and Carroll, Ref. 124.

with increasing nitrogen, the interatomic bonding becomes more covalent and directional so that glass formation reaches a maximum and then decreases. Additions of Al into the M-Si-O-N system extends the glass forming region. So the chemistry of the intergranular phases does not greatly influence the amount of α - Si_3N_4 dissolution that occurs prior to β - Si_3N_4 nucleation.

Nucleation and growth of β - Si_3N_4 grains from the liquid phase occurs on existing crystals. Early work suggested that the β -phase could be nucleated heterogeneously in the M-Si-O-N liquid, however it is now recognized that precipitation occurs on both pre-existing α and β -particles.⁶⁸⁻⁷⁰ The α -to- β transformation is not a displacive one, but a reconstructive transformation where breaking of the atomic bonds is necessary. Thus, it is facilitated by the formation of the liquid. However, the transformation can also occur through the gas phase where the bonds are broken. In general, ceramic materials that undergo reconstructive transformations (e.g. Al_2O_3 and TiO_2) by nucleation and growth have high activation energies.⁷¹

Because of differences in growth rates on different crystallographic planes, the β - Si_3N_4 grains grow with acicular or elongated morphologies with preferential grain growth in the [001] or c-axis direction as compared to the [210] or a-axis. The acicular nature of the β - Si_3N_4 growth has been reported for many years.^{72,73} The growth characteristics, such as rate constants and activation energies, in these orthogonal axial directions were found to be different.⁷⁴⁻⁷⁶ Growth rates in the c-axis or [001] direction were observed to be about two orders of magnitude higher than in the a-axis or [210] direction. This growth anisotropy was attributed to the contrast in the solid-liquid interface structures between the two axes and localized differences in solute concentration and diffusivity. It was found that the solid-liquid interface in the [001] direction was hemispherical and contained numerous

atomic steps as shown in Fig. 1.9.⁷⁴⁻⁷⁶ In contrast, the solid-liquid interface in the [210] direction was basically flat. Other materials systems have shown enhanced axial growth rates for rough surfaces as compared to smooth surfaces.⁷⁷ This earlier work also suggested that until impingement of the growing grains, the [001] growth consumes α - Si_3N_4 grains which dissolve into the liquid phase. As the aspect ratio of the β - Si_3N_4 grains increases, diffusion paths for nitrogen and silicon become larger and consequently, growth in the [210] direction is limited by solute deficiency.

Diffusion through the liquid phase affects the densification behavior, the resulting grain sizes, the aspect ratio of the β - Si_3N_4 grains and the kinetics of the α -to- β conversion.⁷⁸ Several studies have examined grain growth kinetics during densification and all have been done at one atmosphere on nitrogen pressure. Lee et al studied materials in the Y_2O_3 - SiO_2 - Al_2O_3 system and determined that the grain growth mechanism was controlled by reaction at the grain interface and not diffusion through the liquid.⁷⁹ Hoffmann looked at the effect of different rare earth cations on grain growth in a SiO_2 - Al_2O_3 system and found that the growth controlling step can change from interface controlled for larger cations (such as La and Y) to diffusion controlled for smaller cations (such as Yb).⁸⁰ No accepted explanation for this behavior has been put forward.

During gas pressure sintering (GPS) at elevated temperatures, silicon nitride materials exhibit elongated grain growth resulting in a microstructure as shown in Figs. 1.10 and 1.11. Such a microstructure produces materials with high fracture resistance or toughness. All of the available literature on high toughness materials fabricated by GPS showed that all of those materials were processed at temperatures $\geq 1900^\circ\text{C}$ to grow the large grains.⁸¹⁻⁸⁶ At the high temperatures used in GPS, the grain growth kinetics are accelerated and this results in the development of a duplex structure composed of large elongated β - Si_3N_4

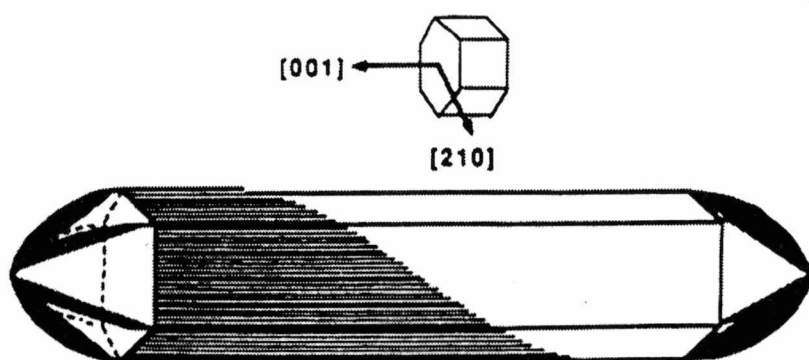


Fig. 1.9. Schematic diagram of a β - Si_3N_4 grain showing the solid-liquid interface structures in the $[001]$ and $[210]$ directions during anisotropic growth. From Hwang and Tien, Ref. 75.

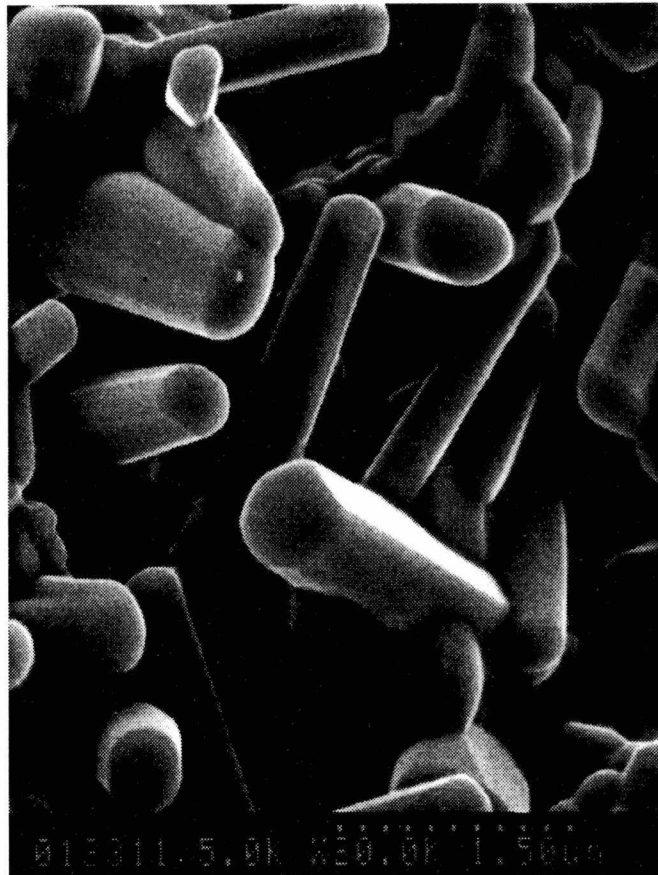


Fig. 1.10. Interlocking grain morphology of β - Si_3N_4 grains.

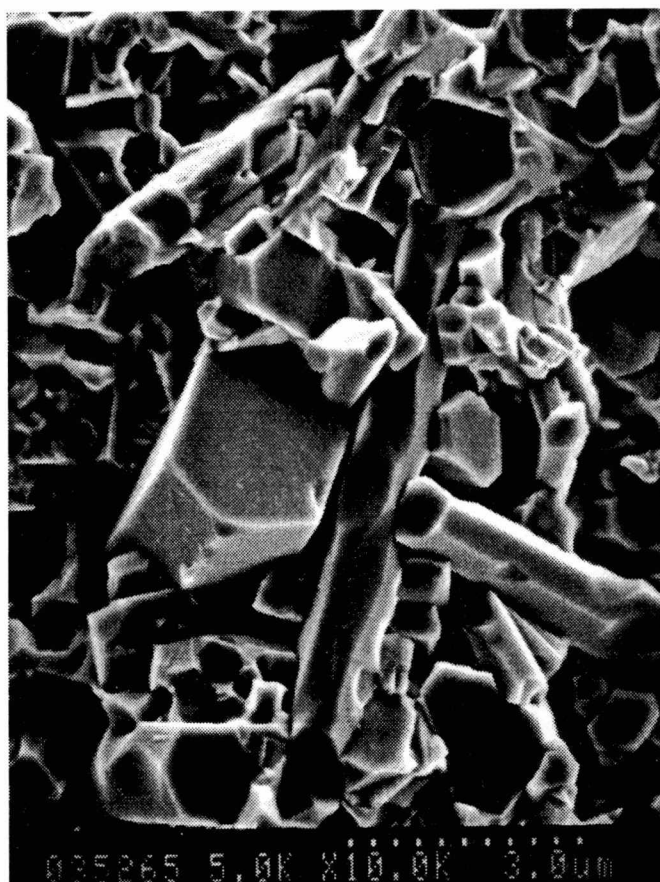


Fig. 1.11. Fracture surface of a silicon nitride showing different orientations of β - Si_3N_4 grains.

grains interspersed with smaller, lower aspect ratio β -grains. High temperatures are preferred for several reasons. The higher temperatures lead to more liquid phase which improves densification due to particle rearrangement and allows more acicular growth of the β - Si_3N_4 grains prior to impingement. Also the growth rates in the [001] direction will be enhanced because of the activation energy differences for growth in the two orthogonal directions. Approximate activation energies are ~ 700 kJ/mol in the [210] direction and 850 kJ/mol in the [001] direction. These studies suggest that the nature of the liquid phase, temperature and time all play key roles in determining the growth of β - Si_3N_4 grains.

Other reactions occur during GPS at elevated temperatures where the silicon nitride materials exhibit weight losses due to decomposition and loss of Si, N and SiO .^{87,88} Early work found that to minimize weight loss and suppress the decomposition reactions, specimens could be embedded in a protective powder where the composition of the powder is tailored to the composition of the specimen.⁸⁹ The purpose of the powder was to create a protective atmosphere around the specimens. At temperatures $>1825^\circ\text{C}$, nitrogen gas overpressures can also be used, in addition to packing powders, to suppress the decomposition of Si_3N_4 so that materials can be densified. Pressures of 0.2-10 MPa (2-100 atmospheres) are usually required.

The decomposition of the silicon nitride leads to a reaction layer at the surface of the fired parts and is a normal occurrence. The thickness of the reaction zone can be quite variable with visible differences up to 2 mm from the surface common. Gradients of this type have been reported in the literature and are reported to be minimized by the use of two-stage gas-sintering techniques.⁹⁰ The reaction layer is believed to form due to the interdiffusion of elements contained in the silicon nitride sample (including the sintering aids) and those present in the furnace atmosphere surrounding the samples. This may result from the

decomposition of silicon nitride during sintering, from loss of volatile sintering aid constituents, and, during gas-pressure sintering, from increased solubility of nitrogen in the sintering aid phase.

The α -to- β transformation continues to proceed until all of the α -phase is gone. β - Si_3N_4 grain growth takes place with further heating, however, steric hindrance by impingement of adjacent grains decreases the overall grain growth rate. If the materials are held at elevated temperatures after completion of the α -to- β conversion, diffusion continues in the intergranular liquids resulting in grain growth and coarsening of the microstructure.⁹¹ These further changes in grain size are driven by the reduction in surface energy associated with grain boundaries. Growth of large β - Si_3N_4 grains in both the c-axis and a-axis directions occurs at the expense of smaller grains. However, once impingement of the grains occurs, enhanced growth in the c-axis direction is highly restricted. The effect of grain impingement on the morphology of the β - Si_3N_4 grains is shown in Figs. 1.12 and 1.13. Continued grain growth results in an overall decrease in the aspect ratio of the β - Si_3N_4 grains.

The final microstructure consists of β - Si_3N_4 grains surrounded by a grain boundary phase with a composition based on the initial sintering additives used. Most of the intergranular phase is contained in pockets at triple-point junctions, however, a thin intergranular film is present at grain-grain junction.^{92,93}

Because the microstructure is developed by nucleation and growth mechanisms, it is amenable to seeding of the structure. Seeding of microstructures has been performed extensively in glass ceramics for commercial products, such as Corning Ware.⁹⁴ It has also been applied to the formation of α - Al_2O_3 from amorphous structures.⁹⁵

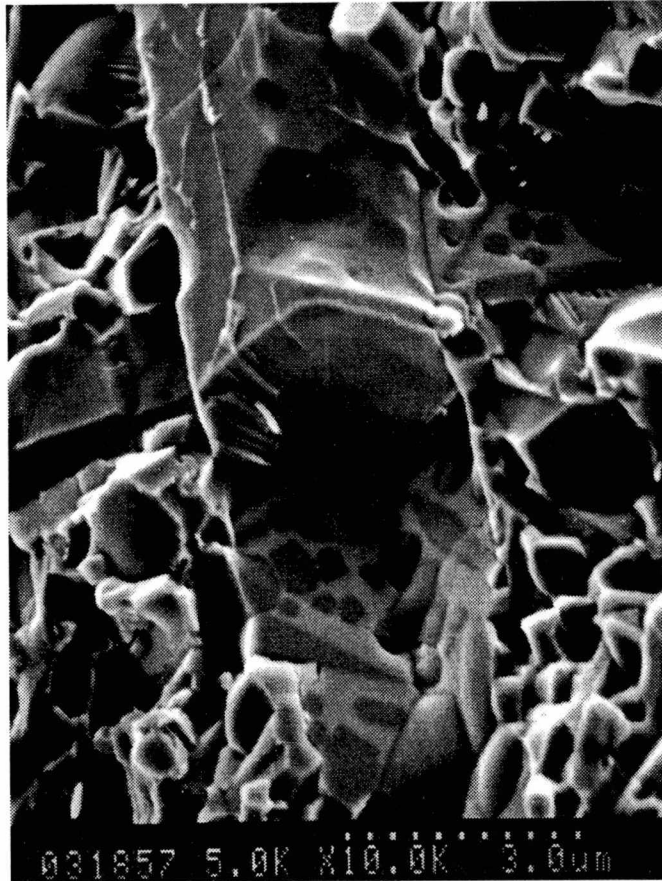


Fig. 1.12. Fracture surface of a silicon nitride showing different orientations of β - Si_3N_4 grains. Also the effect of grain impingement on the morphology can be seen.

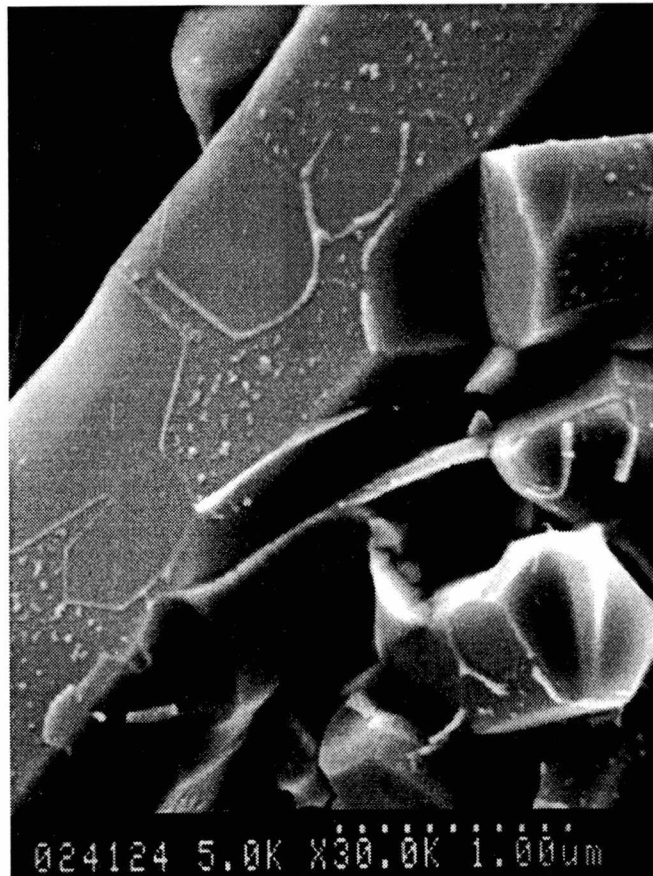


Fig. 1.13. Fracture surface of a silicon nitride showing different orientations of β - Si_3N_4 grains. Also the effect of grain impingement on the morphology can be seen.

Several studies have examined the nature of the β -nuclei present in the starting powders and found that they do influence the final microstructure.⁹⁶⁻¹⁰³ Seeding of the starting Si_3N_4 powders with β -phase particles has been done by several groups to dictate the nucleation step and control the final properties. It was determined that the β -seeds needed to have a large enough size that they would survive in the initial liquid formation and would not be dissolved. Most of the early studies did not address the shape of the seeds, however, it was found that the morphology of the seeds was important in generating β -grains with high aspect ratios and therefore high fracture toughness. All of these studies examined the effect of β -seeds in silicon nitride with $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ as the liquid phase. Recent work has been done in orienting the β -seeds by tape-casting methods to produce materials with anisotropic properties and very high fracture toughness in the direction perpendicular to the tape-casting direction.

After the densification and grain growth processes have been completed, the materials are typically cooled to ambient temperature. During cooling, the intergranular phase that was liquid at the high temperatures solidifies. Because of the glassy nature of the constituents, the intergranular phase can be retained in the amorphous state. Depending on the cooling rate and any additional heat treatments that are given to the materials, the intergranular phase can also be crystallized to stable silicate structures.¹⁰⁴⁻¹⁰⁶

Silicon Nitride as a Structural Material

In spite of the excellent properties of silicon nitride ceramics achieved to date, the use of these materials for many applications is still limited because of their brittle nature and potential for catastrophic failure. Therefore, a major goal for many years has been to make

structural ceramics more reliable. In general, ceramics are sensitive to flaws or other stress concentrators and follow the Griffith relationship¹⁰⁷ for brittle fracture:

$$\sigma_f = AK_{Ic}c^{-0.5} \quad [1.1]$$

, where σ_f = fracture strength

A = geometric constant

K_{Ic} = fracture toughness

c = flaw size

A typical fracture surface of a brittle silicon nitride showing the presence of a critical flaw is shown in Fig. 1.14. To reduce the damage and flaw sensitivity, a significant amount of effort has been expended in developing methods to increase the fracture toughness of the ceramics and hence the reliability. Most monolithic ceramics, such as alumina and silicon carbide, have fracture toughness values in the range of K_{Ic} =2-5 MPa√m. As mentioned, silicon nitride ceramics have long been recognized as having excellent mechanical properties and typical fracture toughness values for silicon nitride are K_{Ic} =5-7 MPa√m. The explanation for much of this behavior is the acicular grain structure of the β -phase and the interlocking morphology of these grains in the densified materials as shown in Fig. 1.15. This behavior has been well known since the 1970's.¹⁰⁸⁻¹¹⁰

Initial attempts at further increasing the fracture toughness of silicon nitride was by SiC whisker reinforcement.¹¹¹⁻¹¹³ The addition of SiC whiskers to silicon nitride matrices resulted in only moderate increases in the fracture toughness as compared to monolithic materials. Fracture strengths of the composite materials showed increases in some cases

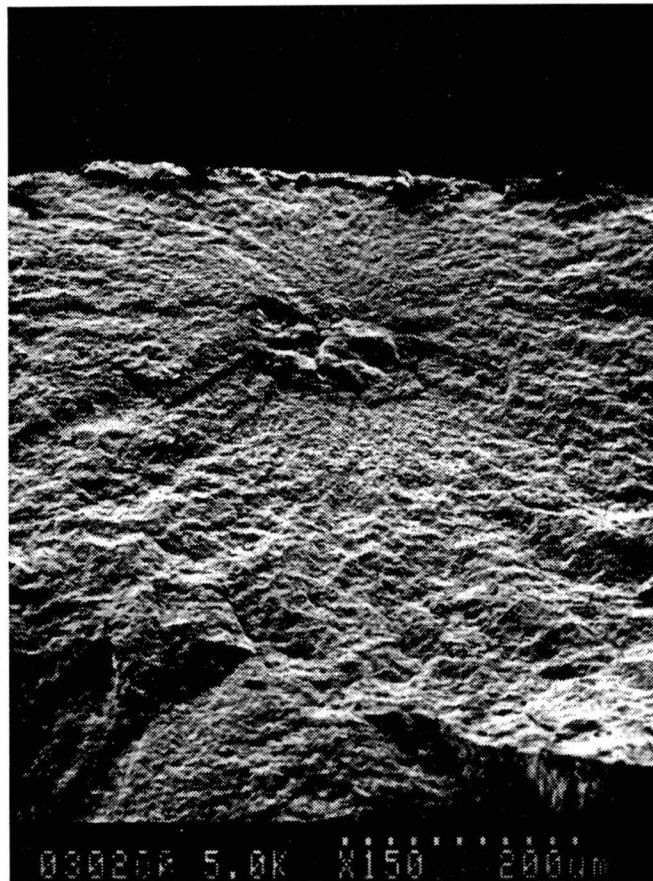


Fig. 1.14. Fracture surface of silicon nitride material showing brittle fracture and the critical flaw which initiated fracture is visible.

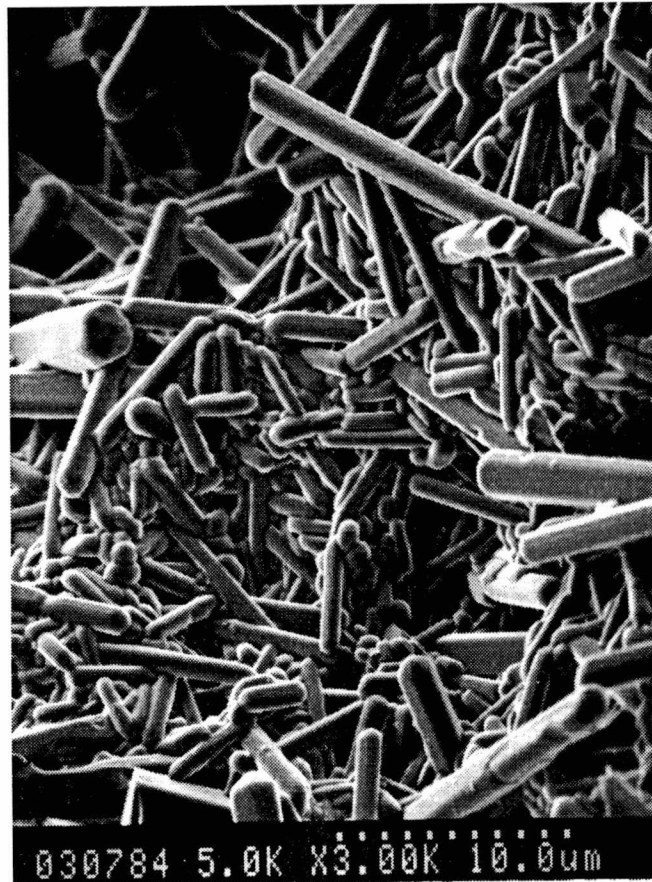


Fig. 1.15. Fracture surface showing interlocking of elongated grains of silicon nitride.

and slight decreases in others. The less than originally expected increases in toughness are attributable to inhibition of acicular growth of the β - Si_3N_4 grains that normally occurs in conventional fabrication of silicon nitride. This results in a lower matrix toughness and so the contribution from the whisker reinforcement is diminished. A similar effect is also observed in particulate additions to silicon nitride.¹¹⁴ The differences in strength are mainly a result of the degree and quality of whisker dispersion in the composites.

An alternative method that has shown good results for achieving increased toughening of silicon nitride is by the use of microstructure control. Recent work has emphasized the production of Si_3N_4 ceramics with grains having large diameters and high aspect ratios for improved fracture toughness.¹¹⁵⁻¹²² These studies have shown that the grain growth can be manipulated to produce materials with very high fracture toughness values (K_{IC}) in the range of 8-11 $\text{MPa}\sqrt{\text{m}}$. These materials also exhibit high strength with low standard deviation and high Weibull modulus.¹¹⁵ For the most part, the studies have taken an empirical approach for producing materials with superior properties. Only a few studies have examined the fundamentals of the mechanisms and kinetics of densification, phase transformation and grain growth. Surprisingly, early researchers believed these large acicular grains would be strength limiting flaws and consequently, their formation was discouraged.

In the case of silicon nitride, the in-situ growth of the acicular grains results in a microstructure in which several toughening mechanisms are operable in the wake region of the propagating crack. The microstructure simulates ones like those observed in whisker-toughened ceramic composites where similar toughening mechanisms are operable.¹²³ However, the use of in-situ reinforcement has several other significant advantages compared to whisker reinforcement in the areas of lower cost of raw materials, improved

ease of fabricability and no health concerns like those associated with the SiC whisker morphology.¹²⁴

The toughening mechanisms operable in the wake region of a propagating crack include crack-bridging by elongated grains, grain rotation and grain pullout. Crack bridging is believed to be the dominant mechanism for toughening in silicon nitride. As a crack approaches an acicular Si_3N_4 grain, the crack is tilted out of its normal propagation plane at an angle corresponding to the grain orientation. The crack front will twist when adjacent grains force the crack path to tilt in an opposite direction. Consequently, the deflected crack is subjected to mixed-mode loading requiring an increase in energy necessary for further crack propagation. An example of how the propagating crack is deflected around the grain structure is illustrated in Figs. 1.16 and 1.17.

The fracture toughness of silicon nitride can be described as the sum of contributions from the several crack bridging mechanisms according to the following:^{123,125}

$$K = \sqrt{[E_c(\Delta J_m + \Delta J_{cb})]} \quad [1.2]$$

where, K is the fracture resistance for the silicon nitride

E_c is the Young's modulus for the silicon nitride

ΔJ_m is the energy dissipated by crack extension in the absence of crack wake

toughening mechanisms

ΔJ_{cb} is the sum of the energy dissipated by each of the crack wake toughening

mechanisms

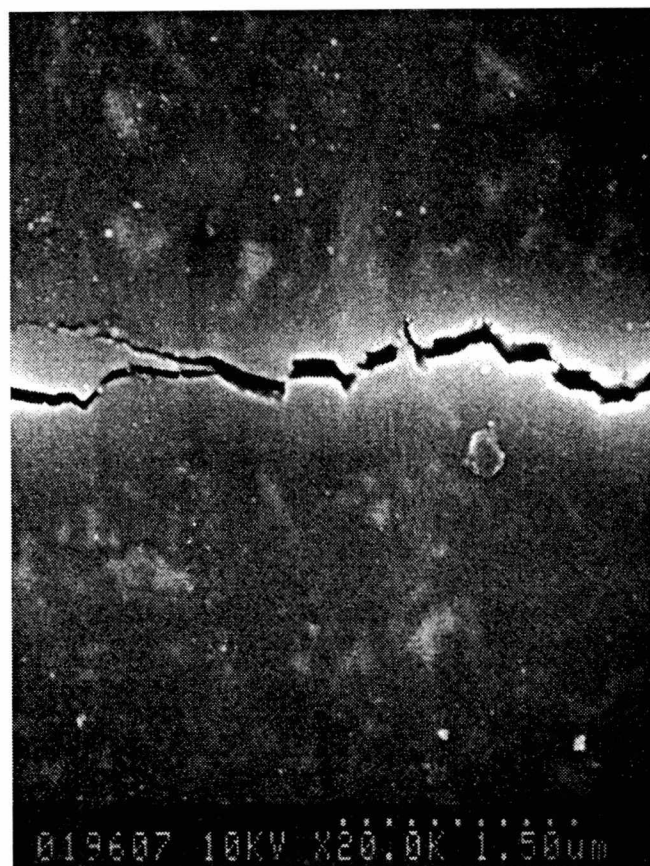


Fig. 1.16. Crack propagation in a silicon nitride showing crack bridging, deflection and branching mechanisms of toughening.

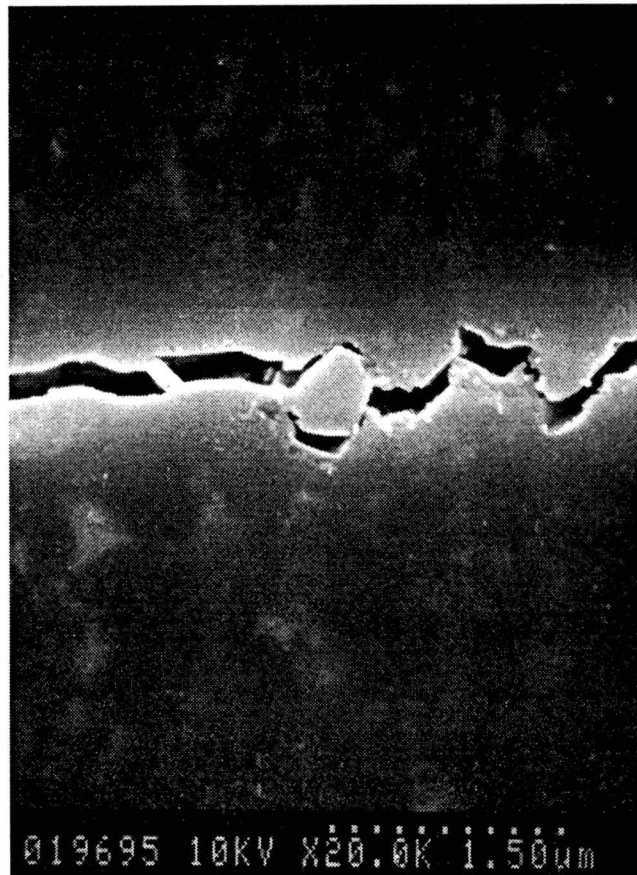


Fig. 1.17. Crack propagation in a silicon nitride showing crack bridging, deflection and grain rotation mechanisms of toughening.

The crack bridging term is described by:

$$\Delta J_{cb} = \Delta J_{fb} + \Delta J_{gr} + \Delta J_{po} \quad [1.3]$$

,where ΔJ_{fb} is the contribution from grain bridging

ΔJ_{gr} is the contribution from grain rotation

ΔJ_{po} is the contribution from grain pullout

The energy dissipated by fiber bridging and involving frictional motion along the interface until grain failure is described by:

$$\Delta J_{fb} = \left[\frac{A_r(\sigma_f r)3}{12E_r\tau_i} \right] d = \frac{A_r(\sigma_f r)^2 l_{db}}{3E_r} = \frac{d[A_r(\sigma_f r)^2 \frac{\gamma_r}{\gamma_i}]}{36E_r} \quad [1.4]$$

,where A_r is the areal fraction of the reinforcing phase

E_r is the Young's modulus of the reinforcing phase

d is the diameter of the reinforcing phase

σ_f^r is tensile strength of the reinforcing phase

γ_r is fracture energy of the reinforcing phase

τ_i is the interfacial shear resistance

γ_i is debonding energy

The contribution from grain rotation follows the relationship:

$$\Delta J_{gr} = \left[\frac{\pi A_{gr} \mu \sigma_f^r}{2} \right] d \quad [1.5]$$

,where A_{gr} is the areal fraction of the reinforcing phase

The friction pullout is described by:

$$\Delta J_{po} = \left[\frac{A_{po} (\sigma_f^r)^2}{8 \tau_i} \right] d \quad [1.6]$$

,where A_{po} is the areal fraction of the reinforcing phase

For these toughening mechanisms to operate, debonding along the elongated grain interfaces must occur. The debonding term (γ_i) shows up in the contribution for fiber bridging. The β - Si_3N_4 grain-intergranular phase boundaries are normally regions of low strength and is where debonding typically occurs. A fracture surface photomicrograph shows the debonding that occurs between the β - Si_3N_4 grains and the intergranular phase (Fig. 1.12). However, when there is strong bonding and high interfacial strength, debonding does not occur and low toughness is observed. In this situation, the crack plane is relatively flat and in that case, no toughening mechanisms in the wake region are possible.

Phase Relationships

As discussed, the bonding in Si_3N_4 is highly covalent and consequently, the diffusion is low and the materials do not densify without additives. The types of additives are mainly oxides and are restricted by their stability in oxynitride liquids. Thus, the metal ions that are possible include: Li, Ce, Mg, Al, Ba, Zr, La, Nd, Ca, Be, Sc, and Y. Because of the multitude of additives used, only a few of the more important ones that are pertinent to this research study will be discussed. Reviews of the phase equilibria can be found in the literature.¹²⁶

Most of the phase diagrams for silicon nitride materials employ the use of equivalent % instead of atom %. This is because the compounds involved usually involve two oxides and two nitrides and this can be represented by a tetrahedron. However, if the atoms have only one valence state, then the tetrahedron representing these four compounds becomes an irregular quadrangle when using atom %. Transforming the atom % to equivalent % transforms the irregular quadrangle into a square. This method of representing silicon nitride phase diagrams has been used for many years.¹²⁷

The Si-Al-O-N system is one of the earliest ones used and also the most extensively studied.¹²⁸ The quaternary system is shown in Fig. 1.18.

The Si-Y-O-N system is probably the next most studied system with silicon nitride.¹²⁹ Si_3N_4 , SiO_2 and Y_2O_3 form many intermediate compounds as indicated in Fig. 1.19. The compounds in the Si_3N_4 - Y_2O_3 -YN part of the phase diagram have not been examined because of the low interest for practical applications because of the oxidation of YN.

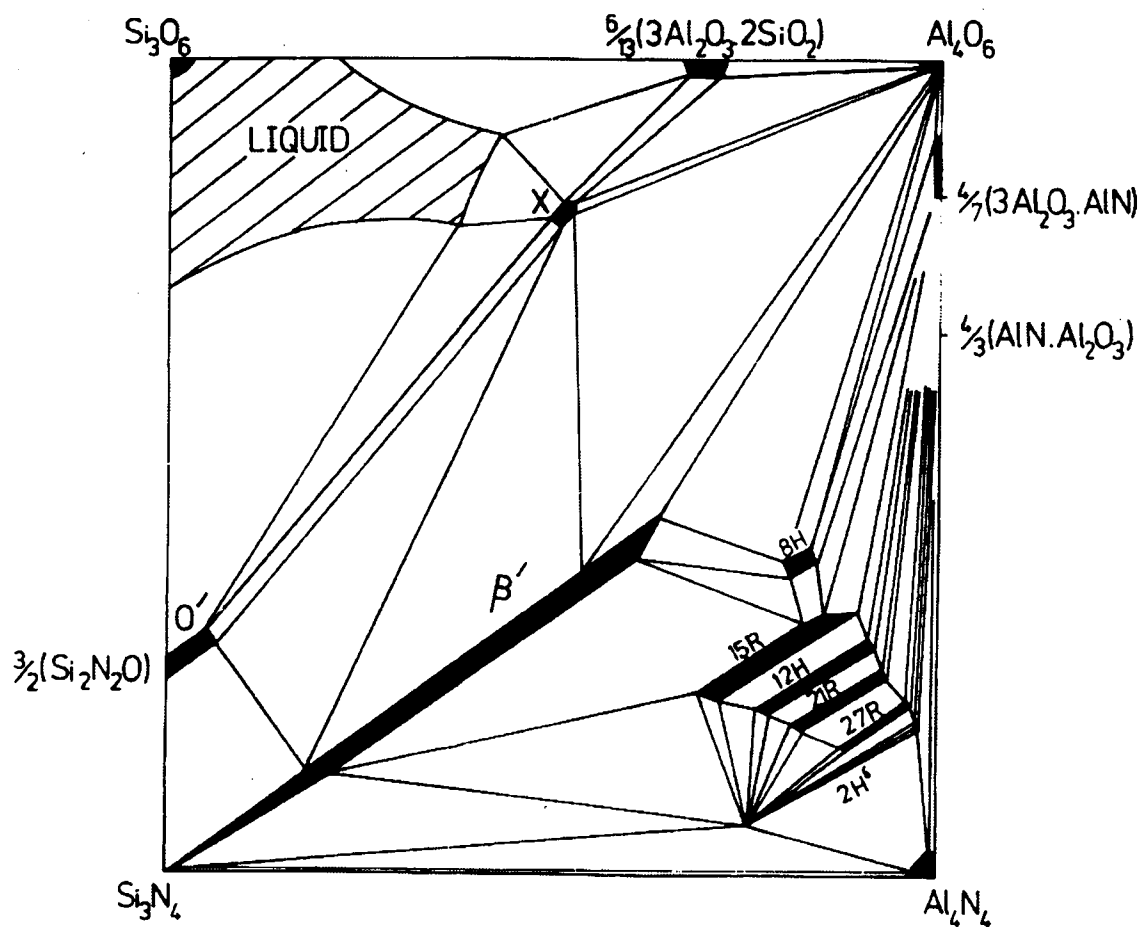


Fig. 1.18. Phase diagram in Si_3N_4 - SiO_2 - AlN - Al_2O_3 system showing tentative intermediate crystallization compounds. From Jack, Ref. 128.

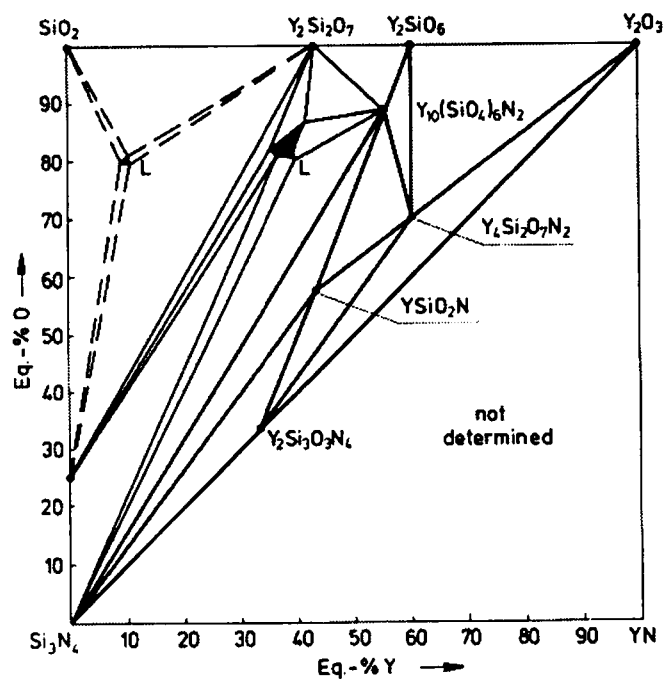


Fig. 1.19. Phase diagram of Si_3N_4 - SiO_2 - YN - Y_2O_3 system at 1550°C . From Lange, et al, Ref. 129.

The Si-Al-Y-O-N system is represented by a Jancke prism as shown in Fig. 1.20 (also using equivalent %).¹³⁰ It does not exhibit any phases other than the Si-Al-O-N and Si-Y-O-N compounds on the oxygen-rich side of the diagram.

The Si-Yb-O-N system is shown in Fig. 1.21. The small cation radius of the ytterbium prevents the crystallization of other compounds, which are found with the other rare earth oxides and yttrium.^{131,132}

Engineering Interest in Silicon Nitride Structural Ceramics

The subject of engineering has been defined in several ways. One definition states it is the “application of scientific principles to practical purposes, as the design, construction and operation of efficient and economical structures, equipment and systems.”¹³³ It is also defined as the “application of science and mathematics by which the properties of matter and the sources of energy in nature are made useful to people in structures, machines, products systems and processes.”¹³⁴ The goal of much of the research on silicon nitride structural ceramics has been to develop materials for use in commercial applications. As stated previously, silicon nitride-based materials have the best overall combination of properties and consequently are the leading candidates for use as high-temperature structural ceramics. Thus, there is a great deal of engineering interest in their development. In fact, significant progress has been made in recent years in producing materials with superior strength, fracture toughness, wear behavior, and creep resistance. However, this progress was driven by property optimization with the economics of the fabrication a minor consideration. Consequently, these materials tend to be very expensive and are not competitive with metal parts on a replacement basis in many applications. Reduction of

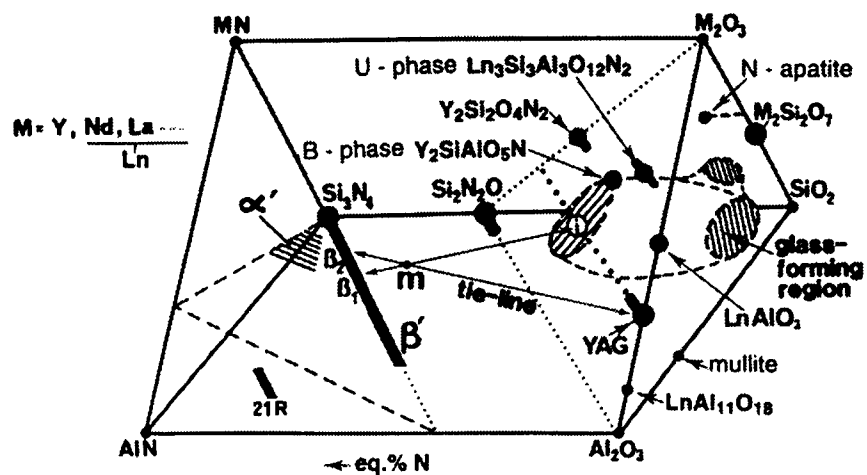


Fig. 1.20. Janecke prism representation of M-Si-Al-O-N systems showing the relation between major ceramic phases and potential intergranular crystalline phases. From Lewis, Ref. 130.

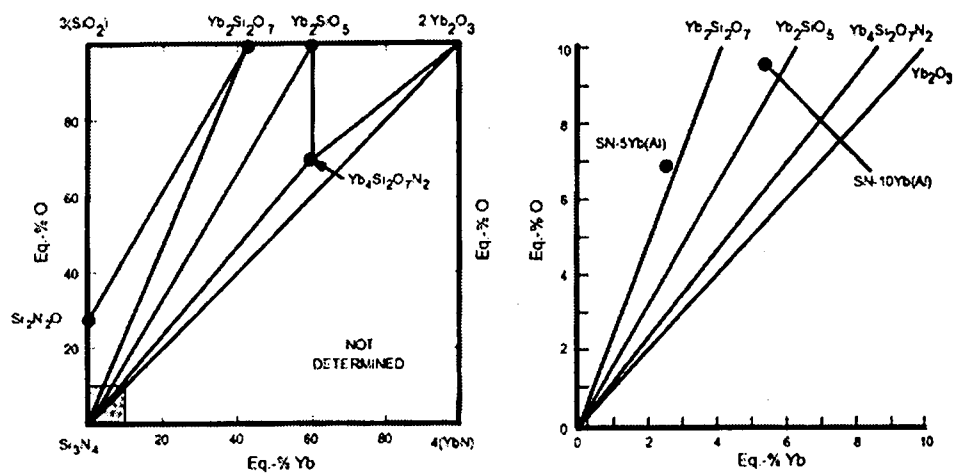


Fig. 1.21. Phase diagram in Si_3N_4 - SiO_2 - YbN - Yb_2O_3 system showing tentative intermediate crystallization compounds. From Hoffmann, Ref. 131.

costs has been recognized as a major factor for the introduction of advanced ceramics into the marketplace, especially for silicon nitride.¹³⁵⁻¹³⁹

Examination of the expenses associated with production of silicon nitride parts shows that the greatest cost reduction impacts are in the areas of raw materials, sintering and machining. For example, a recent study concluded that with a cam roller follower, raw materials account for ~37%, labor and machining ~44% and capital charges ~11% of the total cost.¹⁴⁰ Another study for a engine valve component, showed the cost breakdown to be: 44% for machining, 23% for sintering, 23% for raw materials, 6% for shaping and 4% miscellaneous.¹⁴¹ Such a cost breakdown is illustrated in Fig. 1.22.

Major reductions in the cost of silicon nitride parts would be realized by cheaper raw materials, improvements in sintering techniques and reductions in machining requirements. Thus some of the issues to be examined and studied in this proposal are based on the idea that they will improve the cost-effectiveness of the final materials.

Specific Thesis Topics

As shown in the introduction, microstructure development and therefore, the final properties of silicon nitride are controlled by three basic variables:

1. the starting raw silicon nitride powder
2. the type and quantity of sintering additives
3. the densification conditions

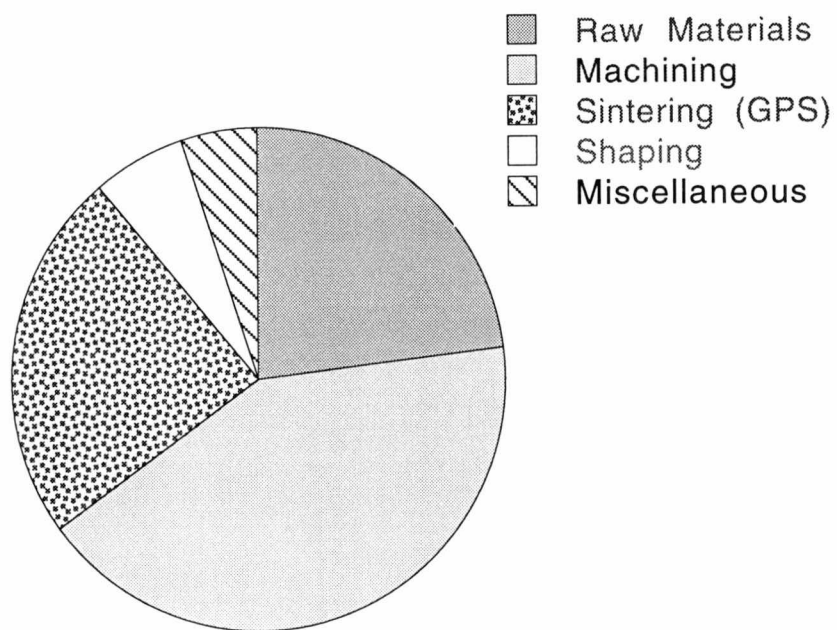


Fig. 1.22. Cost breakdown for fabrication of a silicon nitride engine valve.

Thus, any study of the microstructure development of silicon nitride needs to be concerned with the parameters associated with these variables.

Three inter-related aspects in the fabrication of silicon nitride ceramics were performed for the thesis work. The topics included: (1) an analysis of the effect of the densification conditions on composition and physical gradients in bulk silicon nitride, (2) the effect of sintering parameters on microstructure development during the high-temperature sintering stage and resulting mechanical properties, and (3) an investigation of β - Si_3N_4 nucleation and initial stage microstructure development. The mechanical properties that accompany the microstructure development and the composition/physical gradients were determined.

Analysis of the Composition and Physical Gradients in Bulk Silicon Nitride

By nature of the process, the high temperature sintering conditions result in the decomposition of the silicon nitride. The decomposition of the silicon nitride leads to the formation of a composition/microstructure/property gradient (or reaction layer) extending from the exposed surface of the parts into the bulk of the material. The thickness of the reaction zone can be quite variable with visible differences up to 2 mm from the surface common. For optimum mechanical properties, these reaction layers are machined off. It is well established that machining represents a major portion of the cost of silicon nitride parts and efforts are underway to reduce its impact on the economics of these materials for engine applications. Consequently, it is desirable to minimize the reaction layers and thereby minimize the machining necessary. The ultimate goal would be to eliminate the reaction zone completely and use as-fabricated surfaces. However, that goal is not anticipated to be fulfilled in the near-term.

There is also a scientific interest in the formation of the composition gradients. Understanding of the processes involved may elucidate some aspects of the sintering process not recognized by the analysis of the bulk microstructures and properties. In addition, differences in properties caused by the gradients may explain many of the discrepancies in published data on the same materials systems. In other words, the environmental sintering conditions may be the major cause for many of the discrepancies.

At the present time, no extensive work has been done on the formation, effect on mechanical properties and characterization of these physical and compositional gradients. Only a few published papers on the topic were found and the work presented here is some of the first.¹⁴²⁻¹⁴⁵ It is uncertain what sintering parameters and environmental conditions affect the formation of the gradients and to what extent. The analysis of the composition and physical gradients in silicon nitride had several objectives that will be addressed: (1) identification of the important processing parameters concerned with the gradient formation, (2) determination of the mechanisms by which gradient formation takes place, (3) characterization of the gradients as to their composition and phase assemblage, and (4) assessment of the mechanical property gradients of the materials as they correspond to the changes in chemistry and microstructure.

Effect of Sintering Parameters on Microstructure Development During the High-Temperature Sintering Stage

Obviously, the sintering conditions of temperature, time and heating rates influence the microstructure development and mechanical properties. The kinetics and growth mechanisms of β -Si₃N₄ grains in oxynitride liquids and the resulting properties have been studied extensively. Almost exclusively, however, the grain growth studies have used

$\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ as the sintering additives, densification temperatures $\leq 1800^\circ\text{C}$ and ambient nitrogen pressures (~ 1 ATM). Previous GPS studies have not examined the relationships between the various parameters. It is recognized that the understanding of the microstructure development during high temperature ($\geq 1900^\circ\text{C}$) abnormal grain growth is limited.¹⁴⁶ It was the purpose of the present research to examine the microstructure development under GPS conditions of high temperature ($\geq 1900^\circ\text{C}$), high nitrogen pressure (≥ 1 ATM) and with alternate sintering additives (other than $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$). Additionally, the microstructure development would be related to the resultant mechanical properties. The goal was to identify the important sintering parameters related to the development of the interlocked elongated grain microstructure that are important for obtaining superior mechanical properties.

The experimentation involved with the effect of sintering parameters on microstructure development during the high-temperature sintering stage initially identified the important sintering parameters related to the development of the elongated grain microstructure of silicon nitride. Additional work examined the effect of the $\beta\text{-Si}_3\text{N}_4$ nucleation conditions on the microstructure development during high-temperature sintering and correlated this to the final material properties. The nucleation conditions were determined to be the critical element in microstructure development during some preliminary studies to support this thesis work.

$\beta\text{-Si}_3\text{N}_4$ Nucleation and Initial Stage Microstructure Development

It is just being recognized how important the β -phase nucleation and initial growth stage of microstructure development is to the final properties of the silicon nitride.⁹⁶⁻¹⁰³ In fact, the β -phase nucleation and initial growth could be the key step to producing materials with high

fracture toughness. The microstructure development is directly related to the kinetics and morphology changes that occur during β -phase nucleation and initial growth. Consequently, understanding of the process variables in the initial stage of sintering and their control is essential for obtaining materials with high reliability and superior mechanical properties. Thus, the basic premise of this research topic is to determine the relationships between the characteristics of the raw silicon nitride powders, the sintering additives as the liquid phase forms, β -phase nucleation and the kinetics of the α -to- β transformation. This is an area where there is a large body of fragmented data and observations, however, there is no systematic examination of the system. The present work examined the effects of the silicon nitride powders, the type of sintering additive and the effect of β - Si_3N_4 seeds on the initial microstructure development.

CHAPTER II

EXPERIMENTAL PROCEDURES AND TECHNIQUES

The various experimental procedures, techniques and calculations used in performing the work are described below. Several of the more detailed experimental conditions used, such as time and temperature, are given in the sections pertaining to those particular samples.

Composition Nomenclature

The compositions in these studies are typically listed by weight percent of each component. Another convenient method that has been frequently used to describe silicon nitride ceramics is to use equivalent percent of the constituent atomic species (eq. %).¹²⁷ This method takes into account the different valence states between the anions in silicon nitride materials. The eq. % oxygen is calculated as follows:

$$\text{eq. \% O} = \left[\frac{\text{atom.\% O} \cdot 2}{\{\text{atom.\% O} \cdot 2\} + \{\text{atom.\% N} \cdot 3\}} \right] \times 100 \quad [\text{Eq. 2.1}]$$

Similar calculations can be done for the nitrogen.

Powder Batching

For each of the compositions studied in this work, powder batching consisted of weighing out of the constituent powders. For the ball milling procedure, the powders were all added together in 500 ml high density polyethylene (HDPE) bottles. For the turbomilling

operation, the constituent powders were added individually to the slurry during initial start-up of the milling procedure.

Powder Mixing and Milling

Because of the high surface area of the advanced ceramic powders commonly used, the individual particles are typically agglomerated together due to van der Waals forces. Milling of the powders with dense ceramic milling media effectively breaks up these 'soft' agglomerates.

Several methods were utilized for mixing of the component powders together. The first method consisted of conventional ball milling. This type of mixing is well known in ceramic processing and was used mainly for the β -nucleation studies where the mechanical properties of the final samples were not tested.¹⁴⁷ For samples where the mechanical properties were determined, a second method referred to as turbomilling was employed.¹⁴⁸ Turbomilling has been shown to improve the mixing of ceramic powders and increase the mechanical properties obtained.^{149,150} It is much more effective than ball milling in breaking up the agglomerates and mixing the constituent powders together. In both cases, milling was done in a liquid medium (either water or isopropanol, IPA) using commercial silicon nitride balls (~3 mm in diameter). Specific experimental conditions for each set of samples is given in the appropriate section for those samples.

Organic binders were always added to the powder mixtures during processing to give the compacted powders samples strength during subsequent handling operations. This is a standard practice in the ceramic field. Polyvinylpyrrolidone (PVP) was typically added

because of its excellent environmental safety, good bond strength, its ability to act as a dispersant of the powders and its low ash content after binder burnout.

After milling, the slurries were passed through a 40 mesh screen (Tyler Equivalent Size) to separate the media from the mixed powders. The slurries were then placed in 60°C ovens and dried. After drying, the mixtures were broken up and screened through a 100 mesh screen (Tyler Equivalent Size) to yield a powder with a particulate size less than 150 μm .

Fabrication of $\beta\text{-Si}_3\text{N}_4$ Seed Particles

$\beta\text{-Si}_3\text{N}_4$ seed was produced by heating various combinations of Si_3N_4 powders and Y_2O_3 . This is similar to previous work on β -phase formation.¹⁰¹ Y_2O_3 was used because it has been found to produce β -grains with the highest aspect ratios. The powders were milled together in isopropanol and then fired at 1700°C for 4 hours to produce the β - phase materials.

Powder Compaction

After sizing the powder mixtures were fabricated into disc samples by conventional pressing technology using both uniaxial and isostatic methods. For uniaxial (or unidirectional) pressing, the procedure involved weighing out an appropriate amount of loose powder which was poured into a circular steel die. The walls and punch faces were coated with stearic acid to aid in lubrication of the powders at the die walls. Several die sizes were employed (1.125-3 in. diameter) and the particular sizes are given in the sections detailing the procedures for the different sample types. Axial pressing pressures were 69-103 MPa (10-15 ksi).

For some sample types, the uniaxial pressing was followed by a cold isostatic pressing using conventional wet-bag pressing procedures.¹⁵¹⁻¹⁵⁴ This procedure slightly increases the green density of the samples and was used on the samples where the mechanical properties of the materials was determined. The technique consists of taking the sample from the uniaxial pressing, bagging it in latex rubber bags and vacuum sealing the bag. The samples were then placed into a hydraulic pressing chamber containing a water-hydraulic fluid mixture and the chamber sealed. The hydraulic pressure was then increased to 345 MPa (50 ksi). The chamber was then depressurized and the samples removed.

Binder Removal

As mentioned before, the samples contained organic binders that needed to be removed prior to being fired under nitrogen. If the binders are decomposed under vacuum or inert gas, they do not decompose well and the ash content or residual carbon is higher. All of the samples in the present study were subjected to a binder removal procedure. This consisted of slowly heating the compacted samples from ambient temperature to 600°C by the following schedule:

1. Room temperature to 300°C at 1°C/min.
2. Hold at 300°C for 4 hours.
3. 300°C to 600°C at 1°C/min.
4. Hold at 600°C for 1 hour.
5. Cool to room temperature at approximately 10°C/min.

The hold at 300°C was intended to decompose most of the binders. Thermal gravimetric analysis had shown that both the PVP and PEG binders used in the studies exhibit the

majority of their weight loss (>90 %) at 275-300°C. The slow heating rates and hold time allow the decomposition gases from the binders to be released slowly without damaging the samples. The final heating to 600°C is to oxidize any residual carbon due to the binders.

Determination of Green Density

The green density of the samples was determined by geometrical means. Because the sample shapes were simple discs, the diameters and thickness were measured and the volume calculated. Using the weight of the samples, the green densities were calculated by the following equation:

$$D = \frac{W}{\pi r^2 t} \times 100 \quad [\text{Eq. 2.2}]$$

where D = green density (g/cm³)

W = sample weight (g)

r = sample radius (cm)

t = sample thickness (cm)

Fabrication of Packing Powders

As part of the experimentation on the physical and composition gradients, several different types of packing powders were fabricated. These are summarized below:

Mixture - This consisted of as-received powders mixed together by oblique blending for 4 hours. It contained 75 wt. % Si_3N_4 (Starck S1), 20 wt. % BN (Union Carbide HP) and 5 wt. % Y_2O_3 (Molycorp 5600).

Low Oxygen - Si_3N_4 (Starck S1) powder was heated to 1800°C for 2 hours under 1 ATM nitrogen in a graphite furnace. Weight loss was ~ 0.7 wt. % during the heat-treatment. The powder was then mixed with 20 wt. % BN (Union Carbide HP). The BN was employed to prevent sintering of the packing powder during the high temperature exposures.

Oxidized - Si_3N_4 (Starck S1) powder was heated to 1000°C for 1 hour in air. Weight gain was ~ 1 wt. % during the heat-treatment. This weight gain is similar to previous work on oxidation of powders and would result in a SiO_2 surface on the particles.¹⁵⁵ The powder was then mixed with 20 wt. % BN (Union Carbide HP). The BN was employed to prevent sintering of the packing powder during the high temperature exposures.

BN - This powder consisted of 100% BN (Union Carbide HP).

High Temperature Firing Techniques

Sintering was performed in a non-industrial graphite element high temperature furnace with gas overpressure capability (≤ 2 MPa, 300 psi). A generic heating schedule is shown below:

1. Room temperature to 1000°C at $20^\circ\text{C}/\text{min}$ under vacuum.
2. At 1000°C , add nitrogen to 1 ATM.

3. Continue heating from 1000°C to 1800°C at predetermined rate (usually 10°C/min).
4. At 1800°C, increase nitrogen pressure to predetermined level based on initial hold temperature.
5. Continue heating from 1800°C to initial hold temperature at predetermined rate (usually 10°C/min).

Specific experimental details are given in the following chapters. In all cases, the heating from ambient temperature to 1000°C was done at 20°C/min under vacuum. During sintering, the samples were contained in a crucible with an arrangement similar to that shown in Fig. 2.1.

Density Measurements

After densification, the Archimedes technique was used to determine the densities of the samples after sintering using the following formula:¹⁵²⁻¹⁵⁴

$$\rho = \frac{W_d \rho_w}{[W_i + W_w - W_s]} \quad [\text{Eq. 2.3}]$$

where ρ is the density of the sample

W_d is the dry weight of the sample

ρ_w is the density of the liquid (temperature dependence is taken into account)

W_i is the wet weight of the sample impregnated with the liquid

W_w is the suspension wire weight

W_s is the suspended weight of the sample

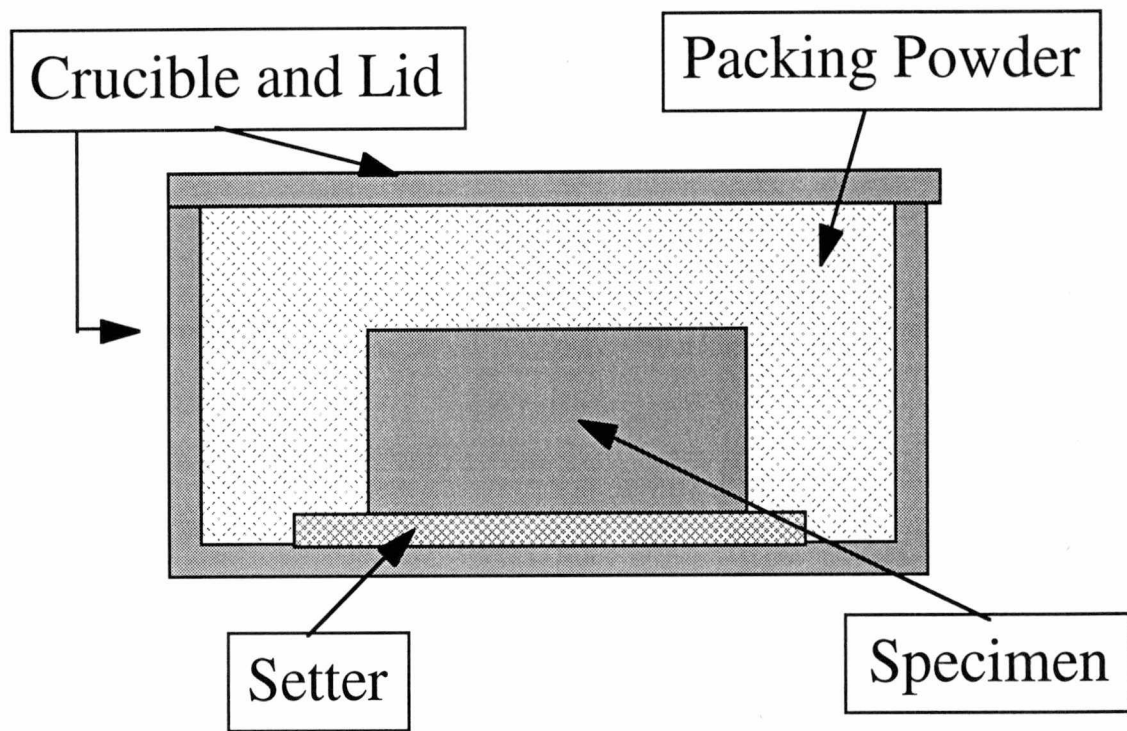


Fig. 2.1. Schematic diagram of firing arrangement.

Fractional Factorial Experiments

Because of the number of variables to be studied, statistical experimental design is appropriate to assess the impact of each of the variables on the microstructure development and mechanical properties of silicon nitride. The Taguchi method was selected for this work it is a good technique for identifying the important processing parameters affecting microstructure development and the mechanical properties.^{156,157} Taguchi analysis of engineering problems has made significant contributions to the accomplishment of designed experiments.¹⁵⁸ The method was employed as a research tool in the present work, much like a scanning electron microscope, and the details of the statistical analysis will only be described briefly here.

Taguchi methods are statistical designed experiments that use fractional factorial orthogonal arrays.¹⁵⁶⁻¹⁵⁸ The arrays are designed to distribute the variables in such a manner that variance analysis of the data (ANOVA) allows one to determine the effect of any one variable on a property compared to the others. These arrays have been shown to be an excellent method to identify important processing parameters in materials development and have been successfully applied to several materials systems where there were so many variables that a full factorial experiment was impossible.¹⁵⁸⁻¹⁶²

A Taguchi analysis follows a series of steps as outlined below:¹⁵⁸

1. Identification of the important variables in the process
2. Select range of variables
3. Determine the parameters to be evaluated.
4. Select a suitable orthogonal array for the test

5. Conduct the experiment
6. Perform the data analysis

In the ANOVA data analysis, several calculations are performed from which the decisions about the impact of the variables on the process and their levels are made. The calculations are as follows:

$$\text{Grand Average} = \frac{\text{Sum of All Individual Observations}}{\text{Total Number of All Observations}} \quad [\text{Eq. 2.4}]$$

$$\text{Level Mean} = \frac{\Sigma \text{All Observations at Level } i}{\text{Number of Observations at Level } i} \quad [\text{Eq. 2.5}]$$

$$\text{Level Effect} = \text{Level Mean} - \text{Grand Average} \quad [\text{Eq. 2.6}]$$

$$\begin{aligned} \text{Sum of Squares Total} = \\ (\text{Difference Between Individual Observations and Grand Average})^2 \quad [\text{Eq. 2.7}] \end{aligned}$$

$$\begin{aligned} \text{Sum of Squares for Factors} = \\ \Sigma (\text{Level Effect})^2 \times (\text{Number of Observations at Each Level}) \quad [\text{Eq. 2.8}] \end{aligned}$$

$$\text{Mean Squares} = \frac{\text{Sum of Squares}}{\text{Degrees of Freedom}} \quad [\text{Eq. 2.9}]$$

$$F = \frac{\text{Mean Squares for Factors}}{\text{Mean Squares for Error}} \quad [\text{Eq. 2.10}]$$

$$\text{Pure Sum of Squares} = [\text{Sum of the Squares}] - [\text{Mean Squares for Error} * \text{Degrees of Freedom}] \quad [\text{Eq. 2.11}]$$

$$\% \text{ Contribution} = \frac{\text{Pure Sum of Squares}}{\text{Total Sum of Squares}} \times 100 \quad [\text{Eq. 2.12}]$$

The F-test is a statistical tool that can provide a decision at some confidence level as to whether the estimates are significantly different. It was named after Sir Ronald Fisher, who originally developed the ANOVA method for data analysis.¹⁵⁷ The F-test is basically a simple ratio of the sample variances. When the ratio is large, the sample variances are believed to be unequal at some confidence level (usually 90, 95 or 99%). These required F-test values significantly depend on the degrees of freedom associated with the sample variance in the numerator (usually the variable) and the denominator (usually the error). These values can be found in tables provided in statistical analysis books. Each combination of confidence level, degrees of freedom in the numerator, and degrees of freedom in the denominator has a F-test value associated with it.

The portion of the total variation observed in an experiment attributed to each factor is reflected in the percent contribution calculation. It indicates the relative power of a variable to reduce variation of the parameter being tested. If the variable is controlled precisely, then the percent contribution is low. If the observed range of variation is small, then the indication is that the factor is unimportant to the variation, the factor which really causes variation has been left out of the test or that the levels chosen for the test were too narrow.

For situations when the Sum of Squares, Mean Squares and % Contribution for the error is large, the indications is that there may be other significant contributors to the variation that were not considered in the experiment or attributable to common cause variation. In general, for a percent contribution for the error in the range of 15% or less, it is assumed that no important variables affecting the parameter were omitted from the experiment. However, if the percent contribution for the error is high, >50%, this indicates one or more of several possibilities: (1) that some important factors were omitted, (2) the experimental conditions were not controlled well, (3) the experimental conditions were not significantly different from one another, or (3) measurement error was excessive.¹⁵⁷

Fabrication of Mechanical Test Specimens

Selected samples of high density were machined by a commercial vendor using diamond grinding wheels into bend bar specimens with nominal dimensions of 3 mm x 4 mm x 50 mm. The grinding procedure followed the standard presently used in testing of most advanced ceramic materials in the United States at the present time.¹⁶³

Flexural Strength Testing

The strength of ceramics is typically characterized by flexure testing and is commonly referred to as modulus of rupture (MOR).¹⁶⁴ The test specimens can have a circular, or rectangular cross-section, however, a standard test procedure has been developed and accepted as an ASTM standard for ceramics.¹⁶⁵ The test uses a rectangular cross-section bar that is fractured in four-point bending. In this configuration, the general stress formula is:

$$S = \frac{Mc}{I} \quad [\text{Eq. 2.13}]$$

where S = flexural strength

M = moment

c = distance from the neutral axis to the tensile surface ($c=d/2$)

I = moment of inertia ($I=bd^3/12$)

b = specimen thickness

d = specimen width

For the four point bending situation, the equation for the flexural strength or modulus of rupture (MOR) is:

$$MOR = \frac{3Pa}{bd^2} \quad [\text{Eq. 2.14}]$$

where P = fracture load

a = distance difference between the inner and outer spans/2

For the present work, the flexural strength testing was done in four point bending with inner and outer spans of 20 mm and 40 mm, respectively.

Determination of Fracture Toughness

Several methods have been used to determine fracture toughness of silicon nitride materials.^{166,167} These include both indentation and indentation-strength techniques.

For the indentation method, a diamond Vickers indentation is made into the polished surface of the ceramic material. The cracks that are generated from the indent corners are measured and the fracture toughness can be calculated. There has been several studies examining the different ways to interpret these cracks and each has its own set of assumptions associated with it. One of the more popular methods developed by Evans and Charles uses the following equation:¹⁶⁸

$$K_{Ic} = 0.113HD^{0.5}\left[1 + \frac{C_L}{2D}\right]^{-3/2} \quad [\text{Eq. 2.15}]$$

where K_{Ic} is the fracture toughness (MPa $\sqrt{\text{m}}$).

H is indent hardness (GN/m²).

C_L is the total crack length (μm).

D is the diagonal length (μm)

Another frequently used method developed by Anstis et al is similar in format but makes some other assumptions as shown below:¹⁶⁹

$$K_{Ic} = A\left[\frac{E}{H}\right]^n \frac{P}{c^{3/2}} \quad [\text{Eq. 2.16}]$$

where A is a constant determined empirically.

E is the elastic modulus (GPa).

H is the Vickers hardness (GPa).

n is a constant determined empirically.

The most widely used indentation-strength measurement technique for fracture toughness determinations was derived by Chantikul et al.¹⁷⁰ It uses the following equation:

$$K_c = \frac{\chi_r P}{c_o^{1.5}} = \xi_V^R \left(\frac{E}{H} \right)^{0.5} \left(\frac{P}{c_o^{1.5}} \right) \quad [\text{Eq. 2.17}]$$

where K_c is the fracture toughness

χ_r is a calibration constant calculated to be 0.016 ± 0.004

E is the elastic modulus of the sample

H is the hardness of the sample

P is the indent load used in the test

c_o is the crack dimension

Determination of Hardness

The hardness of advanced ceramics is measured by Vickers indentation. The size of the indentation can be used to calculate the hardness according to the following:^{171,172}

$$H_v = \frac{1.8544L}{d^2} \quad [\text{Eq. 2.18}]$$

where H_v is the hardness (GPa)

L is the indenter load

d is the diagonal of the indent.

The hardness is a function of the grain size, composition of the intergranular phase, amount of intergranular phase and density. As indicated, the load used to determine the hardness is

a parameter in the calculations. The hardness at low loads (<1 kg) can result in unusually high values of hardness. The measurements performed in the present work were all done at loads of 10 kg to eliminate any discrepancies due to low loads.

Plasma Etching of Microstructure

It has been discovered that the microstructure of silicon nitride ceramics can be revealed very well by reactive gas etching of polished surfaces.¹⁷³⁻¹⁷⁵ The technique uses a mixture of CF_4 and O_2 at low pressure. A plasma is formed by microwave energy which selectively reacts with the $\beta\text{-Si}_3\text{N}_4$ grains to form gaseous SiF_4 and N_2 . The results is that the intergranular phase remains relatively intact and the grain structure is clearly observed. Commercial units are presently on the market and are similar to those used in the semiconductor industry.

Examination of Microstructure

The microstructures of the specimens were examined using a scanning electron microscope (SEM) model Hitachi 800. The specimens included fracture surfaces which show the virgin surfaces exposed during crack propagation, as well as, polished surfaces that were plasma etched (described in previous section). In addition, individual grains were examined where the grains were retrieved by dissolution of the intergranular phase (as described in the following section). In all cases, the surfaces were coated with a carbon film to provide electrical conduction to prevent charging of the specimens under the electron beam in the SEM. this is a standard procedure for SEM examination of non-conductive materials such as ceramics. The magnification and accelerating voltages used are indicated

on the photomicrographs. For example, in Fig. 1.11 the magnification is 10000X and the accelerating voltage is 5.0 kev. The bar marker indicates a scale of 3 μm .

Quantitative Analysis of $\beta\text{-Si}_3\text{N}_4$ Grain Size

The acicular nature of the $\beta\text{-Si}_3\text{N}_4$ grain morphology and their interlocking growth makes quantitative evaluation of the grain sizes extremely difficult. Most quantitative analysis of microstructures rely on the use of metallographic polished cross-sections of the materials and a two-dimensional representation of the planar cross-section. Because of the random orientation of the of the c-axis preferential growth direction, a plane cross-section intersects the grains at all orientations. Thus, to determine the length and aspect ratio of the acicular grains from polished specimens, several studies made assumptions on orientation frequencies to determine the grain size distribution.¹⁷⁶⁻¹⁷⁸

An alternative method developed in recent years, chemically dissolves the intergranular phase, the collects the $\beta\text{-Si}_3\text{N}_4$ grains and the directly measures the grains using a scanning electron microscope (SEM).¹⁷⁹ The intergranular phase is dissolved by reaction with NaOH to produce sodium silicates that are soluble in water. After dissolution, the $\beta\text{-Si}_3\text{N}_4$ grains are free from the matrix and can be collected. This method eliminates the errors associated with mathematical assumptions. However, the technique does require careful handling to insure all of the grains are properly retrieved during dissolution of the samples. It was the technique used in the present study.

The procedure for dissolution of the intergranular phase and collection of the $\beta\text{-Si}_3\text{N}_4$ grains is as follows:

1. Select clean surface of sample to be chemically dissolved.
2. Place small quantity (~0.1 g) on surface.
3. Place sample in furnace at 350°C for 30 minutes to melt NaOH and reaction.
4. Remove sample and place it in a clean test tube filled with warm water (~50°C).
5. Put test tube into ultrasonic bath for 1 minute.
6. Repeat steps 2 through 5 for a total of 5 times.
7. Remove bulk sample from the test tube and centrifuge test tube for 10 minutes.
8. Pour off excess liquid from test tube and collect sample of grains from bottom.

X-Ray Diffraction Analysis

The samples, both densified materials and powders, were examined by x-ray diffraction. To determine the respective α and β Si_3N_4 contents, an experimentally derived relationship was employed. It uses selected peak intensities in the following relationship¹⁸⁰

$$X_{\alpha} = \frac{I_{\alpha}[102] + I_{\alpha}[210]}{0.647(I_{\beta}[101] + I_{\beta}[210] + I_{\alpha}[102] + I_{\alpha}[210])} \quad [\text{Eq. 2.19}]$$

CHAPTER III

ANALYSIS OF COMPOSITION/PHYSICAL GRADIENTS IN BULK SILICON NITRIDE

The decomposition of the silicon nitride leads to a reaction layer at the surface of the parts. The thickness of the reaction zone can be quite variable with visible differences up to 2 mm from the surface common. An example of a reaction layer is shown in Fig. 3.1. For optimum mechanical properties, these reaction layers are machined off. It is well established that machining represents a major portion of the cost of silicon nitride parts and efforts are underway to reduce its impact on the economics of these materials for engine applications. Consequently, it is desirable to minimize the reaction layers and thereby minimize the machining necessary. The ultimate goal would be to eliminate the reaction zone completely and use as-fabricated surfaces.

There is also a scientific interest in the formation of the composition gradients. Understanding of the processes involved may elucidate some aspects of the sintering process not recognized by the analysis of the bulk microstructures and properties. In addition, differences in properties caused by the gradients may explain many of the discrepancies in published data on the same materials systems. In other words, the environmental sintering conditions may be the root cause for many of the discrepancies.

At the present time, no extensive work has been done on the formation, effect on mechanical properties and characterization of these physical and compositional gradients. It is unknown what sintering parameters and environmental conditions affect the formation of the gradients and to what extent. The purpose of the work was to: (1) identify the

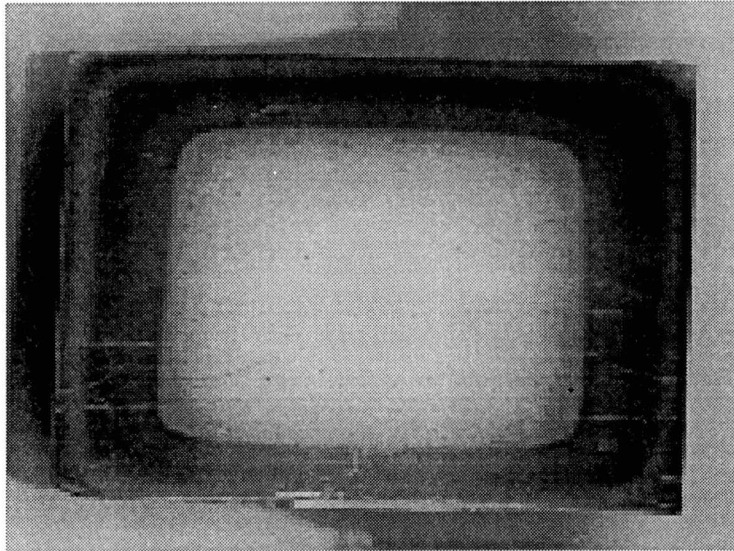
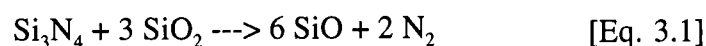


Fig. 3.1. Optical photograph of cross-section through a GPS silicon nitride showing the formation of the reaction layers near the exposed surfaces.

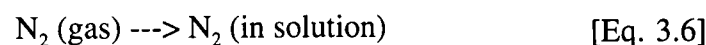
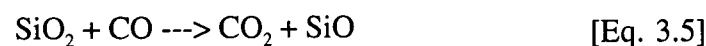
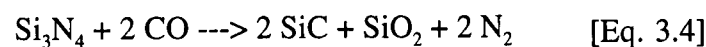
important processing parameters concerned with the gradient formation, (2) determine the mechanisms occurring during gradient formation, (3) characterize the gradients as to their composition and phase assemblage, and (4) assess the mechanical property gradients of the materials as they correspond to the changes in chemistry and microstructure.

Observed weight changes occurring during sintering can be associated with numerous possible reactions as shown below:

Sample Decomposition:



Reaction (Sample and environment):



Reaction (Crucible or furnace heating elements and environment):



To examine the effects of GPS processing parameters on the formation of these reaction zones during the densification and grain growth of silicon nitride several types of tests were

performed. A review of the processing sequence indicated that the important parameters affecting the reaction layers include the packing powder composition, crucible type, sintering temperature, nitrogen pressure, sintering time, use of barrier/protective coatings, and setter type.

Experimental Design and Conditions

Fractional Factorial Experiments (Taguchi Orthogonal Arrays)

The factors to be examined were packing powder composition, crucible type, sintering temperature, nitrogen pressure, sintering time, use of barrier/protective coatings, and setter type. With this many variables a Taguchi experimental array was formulated to assess the impact of each of the variables on a two-step gas-pressure sintering process (Table 3.1). The design used was a $L_{18}(6^1 \times 3^6)$ with temperature, nitrogen pressure, time and coating dummy-loaded to two variables. The dummy treatment accommodates two-level factors by using only two of the possible three levels in the orthogonal array. The indicated third level is simply a repeat of one of the other factors. Any one of the factors can be chosen and it is typically the one that is either the best choice (based on the experimenters knowledge), the easiest or the most cost-effective.¹⁵⁷

For each of the conditions listed in Table 3.1, three compositions of silicon nitride with different intergranular phases were tested. These compositions are Si_3N_4 -6 wt.% Y_2O_3 -2 wt.% Al_2O_3 , Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ (at 5 equivalent % oxygen) and Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

Table 3.1. Taguchi experimental design array for examination of reaction layers on the surface of silicon nitride ceramics. The design is a L_{18} ($6^1 \times 3^6$) with temperature, nitrogen pressure, time and coating dummy-loaded to two variables.

Test No.	Packing Powder ^a	Crucible Material	Sintering Temperature (°C/°C)	Nitrogen Pressure (MPa)	Time (h/h)	Coating	Setter
1	Mixture	Graphite	1850/1900	0.3/0.6	2/1	No	BN
2	Mixture	BN	1900/1950	0.6/3.5	2/2	No	None
3	Mixture	RBSN	1900/1950	0.6/3.5	2/2	Yes	SiC
4	Low Ox.	Graphite	1850/1900	0.3/3.5	2/2	Yes	SiC
5	Low Ox.	BN	1900/1950	0.6/3.5	2/2	No	BN
6	Low Ox.	RBSN	1900/1950	0.6/1.0	2/1	No	None
7	Oxidized	Graphite	1900/1950	0.6/1.0	2/2	No	SiC
8	Oxidized	BN	1900/1950	0.6/3.5	2/1	Yes	BN
9	Oxidized	RBSN	1850/1900	0.3/3.5	2/2	No	None
10	BN	Graphite	1900/1950	0.6/3.5	2/2	No	BN
11	BN	BN	1850/1900	0.3/0.6	2/2	Yes	None
12	BN	RBSN	1900/1950	0.6/3.5	2/1	No	SiC
13	None	Graphite	1900/1950	0.6/3.5	2/1	Yes	None
14	None	BN	1900/1950	0.6/1.0	2/2	No	SiC
15	None	RBSN	1850/1900	0.3/3.5	2/2	No	BN
16	Mix*	Graphite	1900/1950	0.6/3.5	2/2	No	None
17	Mix*	BN	1850/1900	0.3/3.5	2/1	No	SiC
18	Mix*	RBSN	1900/1950	0.6/1.0	2/2	Yes	BN

^a Mixture- Si₃N₄-20% BN-5% Y₂O₃; Low Ox.- Si₃N₄ fired in nitrogen to 1800°C for 2 h; Oxidized- Si₃N₄ fired in air to 1000°C for 1 h; BN- 100% BN; Mix*- Layer of Si₃N₄-20% BN-5% Y₂O₃ on bottom of crucible (No contact with samples).

The $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system is one that has been studied extensively and has been used for most of the basic studies on grain growth and densification behavior. It is included here as a defacto standard for comparison with other studies. The $\text{Y}_2\text{Si}_2\text{O}_7$ composition represents a very refractory grain boundary phase.¹⁸¹⁻¹⁸⁷ The SiO_2 additions will be used to control the intergranular phases and maintain the composition in an appropriate phase compatibility area, so oxidation problems are not encountered. If the rare earth contents are too high without the SiO_2 additions, phases, such as melilite, can be obtained that undergo dramatic volume expansions during oxidation.^{188,189} Lewis and co-workers have demonstrated good mechanical properties for these types of compositions.^{183,184}

The $\text{Sr}_2\text{La}_4\text{Yb}_4[\text{SiO}_4]_6\text{O}_2$ composition was included in the present study to examine a system with a very complex intergranular glass phase. Such alternate grain boundary phases are being examined because they can aid in densification, but be of a transient nature and crystallize into a refractory grain boundary phase. Some possible grain boundary phases include the rare earth-oxide and nitride apatites as discussed by Thompson.¹⁹⁰ These include a wide range of stable apatites of composition $\text{A}_2\text{B}_8(\text{SiO}_4)_6\text{O}_2$ where A is a divalent cation (typically Mg, Mn, Pb, Ca, Sr, Ba) and B is a trivalent cation (typically Y, La, Ce, Nd). An advantage of the nitrogen apatite is that it can oxidize without a large volume expansion. The $\text{Sr}_2\text{La}_4\text{Yb}_4[\text{SiO}_4]_6\text{O}_2$ composition meets the requirements for the formation of the nitrogen apatite as the grain boundary phase.

The differences in the packing powders allowed an assessment of the roles of Si, N, and SiO in the formation of the reaction layers. Packing powders act as sacrificial materials that preferentially decompose to 'create' a protective atmosphere or environment surrounding the specimens. Thus, their composition and behavior during high-temperature firing directly affect the nature of the surface reactions that can take place.

The 'Mixture' packing powder was a combination of Si_3N_4 , Y_2O_3 and BN that is commonly found in use in the literature and serves as a baseline for comparison purposes. The 'Oxidized' packing powder allowed the investigation of the effect of high SiO vapor pressure on the sintering behavior. Likewise, the 'Low Oxygen' packing powder was used to determine the effect of low SiO, but normal Si vapor pressure. The choice of 'BN' packing powder was intended to result in low SiO and N vapor pressures, but provide a physical barrier to any reactions with the crucible. In addition, the 'BN' powder would help retain any protective atmosphere around the specimens that was generated by decomposition of the specimens themselves. The 'Mixed*' packing powder used excess powder (with the same composition used in the 'Mixture') in the crucible to aid in generating a protective atmosphere surrounding the specimens, but would not be in direct contact with them. The 'None' packing powder is self-explanatory, in that no packing powder was surrounding the specimens and the only protective atmosphere would be generated by the specimens themselves. A schematic diagram of the packing arrangement is shown in Fig. 2.1.

The various crucible types examined the typical varieties currently used to determine if there is any impact. Crucibles are an integral part of the processing system and the choice impacts the economics as well as the final properties of the materials. The ones chosen in these experiments are the most commonly used materials found in the literature.

Temperatures consisted of either a low or high two-stage thermal cycle. These have been used in previous studies and showed good densification results.^{191,192}

Nitrogen pressure is also an important factor in GPS. Higher pressures can increase the nitrogen solubility in the liquid phase and very high solubilities can be achieved using significant gas pressures.^{193, 194} For example, nitrogen saturation was increased by a factor of 3 using gas overpressures of ~200 MPa. The higher nitrogen pressures maintain elevated equilibrium concentrations of nitrogen within the liquid. Previous work had shown that the application of mechanical pressure in hot-pressing could actually increase the α -to- β transformation.¹⁹⁵ In the present study, different nitrogen pressures will be used only in the second stage of the sintering cycle. Because nitrogen is capable of being absorbed by the liquid phase at high temperature, the effect of gas pressure was determined. Early work indicated that high pressure during initial sintering inhibited densification by trapping high pressure gas bubbles in the sample interior prior to attaining closed porosity (~93 % T. D.). Consequently, during the early densification, only gas pressure appropriate to decrease Si_3N_4 decomposition was employed. The lowest pressure used in the second stage was the minimum pressure to prevent excessive decomposition from taking place at that temperature (either 1900 or 1950°C). This is based on theoretical calculations as well as experimental experience. In addition to decomposition, during gas-pressure sintering, nitrogen can be dissolved into the liquid phase, which also can contribute to the formation of a surface reaction layer. So a high pressure second stage was used to determine if excessive nitrogen pressure adversely affects the formation kinetics of surface reactions and the phases produced.

The time variable only examined the time at the higher temperature second stage of the sintering cycle. The second stage was the high pressure part of the cycle so the time under pressure was considered to be the most important.

The effect of a barrier/protective coating was assessed by painting layers of BN/Si₃N₄ (+ sintering aids) on the surfaces of the samples prior to sintering. The sintering additive combinations were the same ones used for each specimen composition. The coating chemistry is similar to those used in the glass encapsulated hot-isostatic-pressing (HIP) technology.¹⁹⁶ These coatings were sacrificial and were readily removed by simply rubbing with a wire brush.

Setters or other fixturing is commonly used during firing of ceramics to aid in handling operations and also to limit high-temperature deformation that can occur especially with LPS materials. The various setter types examined the typical varieties currently used to determine any effect with their use.

Experimental Conditions

The starting materials consisted of appropriate amounts of Si₃N₄, Al₂O₃, La₂O₃, Y₂O₃, Yb₂O₃, or SrO to form the desired intergranular phase.^a The oxygen content of the silicon nitride powders was taken into account in the calculation of the silica addition and milling was done in isopropanol to minimize any oxygen pickup during processing. The powders were turbomilled for ~2 h (1.3 wt.% PVP^b and 1 wt.% Darvan^c were added as dispersants) to fully deagglomerate and mix the various constituents. The mixtures were dried, screened to -200 mesh and isopressed at 207 MPa into discs approximately 7 cm in diameter and 2 cm thick. Binder burnout consisted of the heat-treatment to 600°C in air prior to sintering as discussed in Chapter 2.

^a Si₃N₄- Ube, Japan, E10; Al₂O₃- Reynolds, Malakoff, TX, RC-HP DBM; La₂O₃, Y₂O₃, Yb₂O₃- Molycorp, White Plains, NY; >99.9%; SrO as SrCO₃; Mallinckrodt, St. Louis, MO; Reagent Grade

^b GAF Chemicals, Wayne, NJ: Polyvinylpyrrolidone K-15 ^c R. T. Vanderbilt, Norwalk, CT, 821A,

Sintering was performed in a graphite element furnace with gas overpressure capability. A two-step firing procedure was used to minimize any density gradients across the cross-section of the samples, as this has been known to occur with one-step firing processes. All of the GPS runs had a 1 h hold at 1500°C after sintering with no applied nitrogen overpressure (0.1 MPa) for crystallization of the grain boundary phases.

As will be shown below, after the initial tests were performed, the optimum conditions for firing of the various compositions were determined based on a combination for maximizing the sintered density, minimizing the visible reaction layer or minimizing the weight loss. Samples to further determine the effects of the chemical and physical gradient on the mechanical properties were prepared using these optimum conditions.

Densities were measured by the Archimedes method. The reaction layer thickness was determined by diamond machining the sample in half and visually examining the cut surface that was adjacent to the setter material by optical microscopy. Selected samples of high density were machined into bend bar specimens with nominal dimensions of 3 mm x 4 mm x 50 mm. Flexural strength testing was done in four point bending with inner and outer spans of 20 mm and 40 mm, respectively.

Results and Discussion

Reaction Layer Thickness, Weight Losses and Density

The test results on the reaction layer study are given in Tables 3.2, 3.3, and 3.4 for the three different compositions. As shown, significant differences in visible reaction layer thickness, weight loss and sintered density were observed at the various conditions from

Table 3.2. Results for the gas-pressure sintered samples containing Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

Test Condition	Specimen Number	Weight Loss (%)	Density (g/cm^3)	Density (%TD)	Visible Reaction Layer Thickness (mm)	Number of Visible Reaction Layers
1	1	1.16	3.19	97.6	2.0	3
2	8	0.29	3.14	96.0	1.1	3
3	7	0.97	3.24	99.1	1.2	3
4	18	1.11	3.26	99.8	1.7	--
5	9	0.60	3.24	99.0	1.5	3
6	25	0.83	3.21	98.2	1.8	
7	11	1.85	3.23	98.8	1.2	2
8	4	0.98	3.12	95.4	3.0	1
9	19	-0.05	3.22	98.4	3.0	--
10	10	2.48	3.24	99.1	1.4	4
11	14	2.44	3.12	95.4	3.1	4
12	6	0.70	3.25	99.4	1.8	3
13	5	4.59	3.25	99.4	2.5	3
14	12	1.53	3.21	98.2	1.0	2
15	20	0.0	3.1	94.8	1.2	--
16	24	1.06	3.21	98.2	1.2	--
17	26	0.77	3.19	97.6	0.1	--
18	13	1.66	3.23	98.8	1.0	2
19	2	0.74	3.21	98.2	1.2	3
20	3	0.09	3.15	96.3	1.4	3

Table 3.3. Results for the gas-pressure sintered samples containing Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$.

Test Condition	Specimen Number	Weight Loss (%)	Density (g/cm^3)	Density (%TD)	Visible Reaction Layer Thickness (mm)	Number of Visible Reaction Layers
1	1	3.81	3.10	89.9	3.2	5
2	8	1.92	3.08	89.3	3.5	4
3	7	3.03	3.21	93.0	3.6	4
4	18	3.25	3.18	92.6	4.9	--
5	9	1.89	3.25	94.2	3.1	3
6	25	2.12	3.06	89.3	6.1	--
7	11	4.07	3.45	100	1.0	3
8	4	-0.90	3.30	95.7	3.2	4
9	19	0.98	3.10	90.5	2.5	--
10	10	4.75	3.40	98.6	5.8	5
11	14	3.86	3.32	96.2	1.8	4
12	6	2.90	3.20	92.8	3.3	3
13	5	8.57	3.30	96.2	2.1	1
14	12	3.62	3.44	99.7	1.2	2
15	20	0.53	3.02	88.1	1.0	--
16	24	3.35	3.10	90.5	3.6	--
17	26	1.99	3.03	88.3	2.0	--
18	13	3.90	3.45	100	1.1	2
19	2	3.37	3.10	89.9	1.7	3
20	3	0.98	3.07	89.0	4.5	6

Table 3.4. Results for the gas-pressure sintered samples containing $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$.

Test Condition	Specimen Number	Weight Loss (%)	Density (g/cm^3)	Density (%TD)	Visible Reaction Layer Thickness (mm)	Number of Visible Reaction Layers
1	1	3.75	3.05	91.6	1.8	4
2	8	1.40	3.05	91.6	2.3	5
3	7	2.27	3.24	97.3	4.5	8
4	18	2.88	3.22	96.7	4.1	--
5	9	2.25	3.25	97.6	1.8	3
6	25	2.24	2.99	89.7	1.7	--
7	11	3.66	3.21	96.4	2.8	5
8	4	-0.74	3.13	94.0	2.4	3
9	19	1.95	2.97	89.1	2.0	--
10	10	6.44	3.23	97.0	5.2	6
11	14	4.14	3.10	93.1	2.8	5
12	6	2.20	3.23	97.1	2.9	5
13	5	17.8	3.26	97.9	3.6	6
14	12	4.44	3.19	95.8	2.3	6
15	20	0.93	2.84	85.4	0.3	--
16	24	2.65	3.03	91.1	2.0	--
17	26	3.43	2.93	88.1	3.0	3
18	13	4.75	3.25	97.6	2.8	4
19	2	3.10	3.06	91.9	3.1	5
20	3	1.63	2.96	88.9	1.5	3

the orthogonal array. The Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition achieved high densities for all of the firing conditions used in the tests. On the other hand the other two compositions with more refractory grain boundary phases showed quite variable densification. The Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition exhibited densities from ~88 to >100% T. D. and the Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ composition had densities between 85-98 % T. D. depending of the conditions.

Summaries of the results for grand averages, variable mean level effects and the variable total effect of the orthogonal arrays are given in Tables 3.5, 3.6 and 3.7 for the three compositions tested. The summaries of the ANOVA results for the statistical parameters on the orthogonal arrays for the reaction layer thickness, weight losses and densities for the three different compositions are given in Tables 3. 8 through 3.16.

Specimens that attained $\geq 95\%$ T. D. were sectioned and polished. These include all of the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 samples and selected ones from the other two compositions. Indent hardness and fracture toughness were determined as a function of distance from the as-sintered surfaces. The results are summarized in Tables 3.17 through 3.19 for the three compositions. Because all of the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 samples achieved high densities they could be statistically analyzed by ANOVA to determine the effect of the sintering conditions. Those results are given in Tables 3.20 through 3.23.

In several cases, the associated error exhibited a large contribution which indicates one or more of several possibilities. It could be that some important factors were omitted, the experimental conditions were not controlled well, the experimental conditions were not significantly different from one another or measurement error was excessive. For the present set of experiments, a few possible experimental conditions could have contributed

Table 3.5. Summary of ANOVA results for grand averages, variable mean level effects and the variable total effect of the orthogonal arrays for the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition.

	Reaction Layer Thickness (mm)	Weight Loss (%)	Density (% T. D.)
Grand Average	1.66	1.28	97.96
Packing Powder			
Mixture	1.47	0.81	97.57
Low Oxygen	1.69	0.85	99.00
Oxidized	2.38	0.93	97.53
BN	2.10	1.87	97.97
None	1.58	2.04	97.47
Mix*	0.76	1.16	98.20
Total Effect	1.62	1.23	1.53
Crucible			
Graphite	1.66	2.04	98.82
BN	1.63	1.10	96.93
RBSN	1.69	0.68	98.12
Total Effect	0.06	1.36	1.88
Temperature			
1850/1900	1.85	0.91	97.27
1900/1950	1.57	1.46	98.30
Total Effect	0.28	0.56	1.03
Pressure			
Low	1.67	1.58	97.83
High	1.66	1.12	98.02
Total Effect	0.02	0.45	0.18
Time			
2/1	1.88	1.50	97.93
2/2	1.55	1.16	97.97
Total Effect	0.33	0.34	0.03
Coating			
Yes	2.09	1.96	97.98
No	1.45	0.93	97.94
Total Effect	0.65	1.02	0.04
Setter			
BN	1.68	1.15	97.45
None	2.13	1.53	97.60
SiC	1.18	1.15	98.82
Total Effect	0.95	0.37	1.37

Table 3.6. Summary of ANOVA results for grand averages, variable mean level effects and the variable total effect of the orthogonal arrays for the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition.

	Reaction Layer Thickness (mm)	Weight Loss (%)	Density (% T. D.)
Grand Average	2.93	2.98	93.94
Packing Powder			
Mixture	3.43	2.92	91.27
Low Oxygen	4.69	2.42	92.23
Oxidized	2.20	1.38	95.77
BN	3.61	3.84	96.40
None	1.42	4.24	94.87
Mix*	2.24	3.08	93.13
Total Effect	3.27	2.86	5.13
Crucible			
Graphite	3.41	4.63	94.90
BN	2.45	2.06	94.37
RBSN	2.94	2.24	92.57
Total Effect	0.96	2.57	2.33
Temperature			
1850/1900	2.56	2.40	91.12
1900/1950	3.12	3.27	95.36
Total Effect	0.56	0.86	4.24
Pressure			
Low	2.39	3.56	96.33
High	3.21	2.69	92.75
Total Effect	0.82	0.88	3.58
Time			
2/1	3.30	3.08	92.28
2/2	2.75	2.93	94.78
Total Effect	0.55	0.15	2.49
Coating			
Yes	2.78	3.62	96.00
No	3.01	2.66	92.92
Total Effect	0.23	0.96	3.08
Setter			
BN	2.88	2.33	94.87
None	3.26	3.47	92.18
SiC	2.65	3.14	94.78
Total Effect	0.61	1.14	2.68

Table 3.7. Summary of ANOVA results for grand averages, variable mean level effects and the variable total effect of the orthogonal arrays for the $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ composition.

	Reaction Layer Thickness (mm)	Weight Loss (%)	Density (% T. D.)
Grand Average	2.68	3.69	93.73
Packing Powder			
Mixture	2.86	2.47	93.50
Low Oxygen	2.52	2.46	94.67
Oxidized	2.39	1.63	93.17
BN	3.64	4.26	95.73
None	2.07	7.72	93.03
Mix*	2.59	3.61	92.27
Total Effect	1.57	6.10	3.47
Crucible			
Graphite	3.25	6.20	95.12
BN	2.41	2.49	93.37
RBSN	2.37	2.39	92.70
Total Effect	0.88	3.81	2.42
Temperature			
1850/1900	2.33	2.85	90.67
1900/1950	2.85	4.11	95.26
Total Effect	0.52	1.27	4.59
Pressure			
Low	2.36	3.83	94.03
High	2.84	3.62	93.58
Total Effect	0.48	0.21	0.46
Time			
2/1	2.57	4.78	93.07
2/2	2.73	3.15	94.06
Total Effect	0.17	1.63	0.99
Coating			
Yes	3.36	5.18	96.10
No	2.34	2.95	92.54
Total Effect	1.02	2.24	3.56
Setter			
BN	2.35	2.90	93.87
None	2.40	5.03	92.08
SiC	3.28	3.15	95.23
Total Effect	0.92	2.13	3.15

Table 3.8. Summary of results on ANOVA of Taguchi array on Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition for examination of the reaction layer thickness.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	4.67	0.93	14.05	2.2	2.8	4.3	4.34	39.4
Crucible Type	2	0.01	0.01	0.08	2.6	3.6	6	-0.12	0.0
Sintering Temperature	1	0.30	0.30	4.57	3	4.4	8.4	0.24	2.2
Nitrogen Pressure	1	0.00	0.00	0.02	3	4.4	8.4	-0.07	0.0
Sintering Time	1	0.42	0.42	6.37	3	4.4	8.4	0.36	3.2
Surface Coating	1	1.68	1.68	25.29	3	4.4	8.4	1.62	14.7
Setter Material	2	2.72	1.36	20.43	2.6	3.6	6	2.58	23.5
Error	18	1.20	0.07						17.0

Table 3.9. Summary of results on ANOVA of Taguchi array on Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition for examination of the weight loss.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	4.44	0.89	5.94	2.2	2.8	4.3	3.69	18.3
Crucible Type	2	5.80	2.90	19.42	2.6	3.6	6	5.50	27.2
Sintering Temperature	1	1.24	1.24	8.28	3	4.4	8.4	1.09	5.4
Nitrogen Pressure	1	0.82	0.82	5.52	3	4.4	8.4	0.68	3.3
Sintering Time	1	0.47	0.47	3.13	3	4.4	8.4	0.32	1.6
Surface Coating	1	4.19	4.19	28.05	3	4.4	8.4	4.04	20.0
Setter Material	2	0.56	0.28	1.89	2.6	3.6	6	0.27	1.3
Error	18	2.69	0.15						22.9

Table 3.10. Summary of results on ANOVA of Taguchi array on Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition for examination of the density.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	5.16	1.03	1.43	2.2	2.8	4.3	1.55	3.9
Crucible Type	2	10.87	5.44	7.53	2.6	3.6	6	9.43	23.5
Sintering Temperature	1	4.27	4.27	5.92	3	4.4	8.4	3.55	8.8
Nitrogen Pressure	1	0.13	0.13	0.19	3	4.4	8.4	-0.59	0.0
Sintering Time	1	0.00	0.00	0.01	3	4.4	8.4	-0.72	0.0
Surface Coating	1	0.01	0.01	0.01	3	4.4	8.4	-0.71	0.0
Setter Material	2	6.74	3.37	4.67	2.6	3.6	6	5.30	13.2
Error	18	12.99	0.72						50.7

Table 3.11. Summary of results on ANOVA of Taguchi array on $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition for examination of the reaction layer thickness.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	21.34	4.27	7.76	2.2	2.8	4.3	18.59	45.9
Crucible Type	2	2.79	1.39	2.53	2.6	3.6	6	1.69	4.2
Sintering Temperature	1	1.26	1.26	2.29	3	4.4	8.4	0.71	1.8
Nitrogen Pressure	1	2.71	2.71	4.93	3	4.4	8.4	2.16	5.3
Sintering Time	1	1.20	1.20	2.17	3	4.4	8.4	0.65	1.6
Surface Coating	1	0.21	0.21	0.39	3	4.4	8.4	-0.34	0.0
Setter Material	2	1.14	0.57	1.04	2.6	3.6	6	0.04	0.0
Error	18	9.89	0.55						41.3

Table 3.12. Summary of results on ANOVA of Taguchi array on $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition for examination of the weight loss.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	15.60	3.12	4.20	2.2	2.8	4.3	11.88	17.6
Crucible Type	2	24.70	12.35	16.62	2.6	3.6	6	23.21	34.3
Sintering Temperature	1	2.99	2.99	4.03	3	4.4	8.4	2.25	3.3
Nitrogen Pressure	1	3.06	3.06	4.12	3	4.4	8.4	2.32	3.4
Sintering Time	1	0.09	0.09	0.12	3	4.4	8.4	-0.65	0.0
Surface Coating	1	3.67	3.67	4.93	3	4.4	8.4	2.92	4.3
Setter Material	2	4.12	2.06	2.77	2.6	3.6	6	2.63	3.9
Error	18	13.37	0.74						33.1

Table 3.13. Summary of results on ANOVA of Taguchi array on $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition for examination of the density.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	62.87	12.57	9.80	2.2	2.8	4.3	56.46	17.8
Crucible Type	2	17.94	8.97	6.99	2.6	3.6	6	15.37	4.8
Sintering Temperature	1	71.97	71.97	56.10	3	4.4	8.4	70.68	22.2
Nitrogen Pressure	1	51.36	51.36	40.04	3	4.4	8.4	50.08	15.7
Sintering Time	1	24.83	24.83	19.36	3	4.4	8.4	23.55	7.4
Surface Coating	1	38.03	38.03	29.64	3	4.4	8.4	36.74	11.6
Setter Material	2	27.93	13.97	10.89	2.6	3.6	6	25.37	8.0
Error	18	23.09	1.28						12.5

Table 3.14. Summary of results on ANOVA of Taguchi array on $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ composition for examination of the reaction layer thickness.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	4.32	0.86	2.80	2.2	2.8	4.3	2.77	12.4
Crucible Type	2	2.96	1.48	4.79	2.6	3.6	6	2.34	10.5
Sintering Temperature	1	1.10	1.10	3.55	3	4.4	8.4	0.79	3.5
Nitrogen Pressure	1	0.93	0.93	3.00	3	4.4	8.4	0.62	2.8
Sintering Time	1	0.11	0.11	0.37	3	4.4	8.4	-0.20	0.0
Surface Coating	1	4.15	4.15	13.45	3	4.4	8.4	3.84	17.2
Setter Material	2	3.26	1.63	5.28	2.6	3.6	6	2.64	11.8
Error	18	5.56	0.31						41.9

Table 3.15. Summary of results on ANOVA of Taguchi array on Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ composition for examination of the weight loss.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	71.59	14.32	3.56	2.2	2.8	4.3	51.46	20.2
Crucible Type	2	56.52	28.26	7.02	2.6	3.6	6	48.46	19.1
Sintering Temperature	1	6.42	6.42	1.59	3	4.4	8.4	2.40	0.9
Nitrogen Pressure	1	0.17	0.17	0.04	3	4.4	8.4	-3.85	0.0
Sintering Time	1	10.68	10.68	2.65	3	4.4	8.4	6.66	2.6
Surface Coating	1	20.06	20.06	4.98	3	4.4	8.4	16.03	6.3
Setter Material	2	16.31	8.16	2.03	2.6	3.6	6	8.26	3.2
Error	18	72.48	4.03						47.6

Table 3.16. Summary of results on ANOVA of Taguchi array on $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ composition for examination of the density.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	23.66	4.73	1.87	2.2	2.8	4.3	11.01	4.3
Crucible Type	2	18.69	9.35	3.69	2.6	3.6	6	13.63	5.3
Sintering Temperature	1	84.33	84.33	33.33	3	4.4	8.4	81.80	31.8
Nitrogen Pressure	1	0.84	0.84	0.33	3	4.4	8.4	-1.69	0.0
Sintering Time	1	3.93	3.93	1.55	3	4.4	8.4	1.40	0.5
Surface Coating	1	50.65	50.65	20.02	3	4.4	8.4	48.12	18.7
Setter Material	2	29.94	14.97	5.92	2.6	3.6	6	24.88	9.7
Error	18	45.54	2.53						29.8

Table. 3.17. Summary of results on mechanical properties as a function of distance from the as-sintered surfaces for the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition (TRSN-44).

			Fracture Toughness (MPa√m)	Fracture Toughness (MPa√m)	Toughness Difference Comparison	Toughness Difference Comparison
Specimen ID	Distance From Surface (mm)	Hardness (GPa)	Evans & Charles	Anstis et al	Near Surface/ Bulk	Near Surface/ Bulk
TRSN-						
44-01	0.78	12.7	6.4	5.7	6.4	5.7
44-01	1.81	11.5	6.0	5.1	6.3	5.4
44-01	3.80	14.5	6.5	5.6	0.1	0.3
44-01	11.10	12.8	6.4	5.7		
Average		12.9	6.3	5.5		
44-02	0.73	14.4	7.0	6.5	7.0	6.5
44-02	2.08	14.1	6.5	5.6	6.7	6.3
44-02	4.19	13.4	6.8	6.4	0.3	0.2
44-02	11.42	12.2	6.8	6.9		
Average		13.5	6.8	6.4		
44-03	0.85	7.3	5.3	5.1	5.3	5.1
44-03	1.71	7.6	5.4	5.1	5.4	5.6
44-03	3.41	6.1	5.5	6.3	-0.1	-0.5
44-03	8.40	6.7	5.4	5.5		
Average		6.9	5.4	5.5		
44-04	1.78	12.7	7.6	9.4		
44-04	5.03	12.2	7.8	10.8		
44-04	7.47	12.9	7.7	9.8		
Average		11.2	7.1	8.9		
44-05	0.76	15.3	7.3	7.2	7.3	7.2
44-05	1.60	13.8	6.6	5.7	6.8	6.1
44-05	2.85	14.4	6.8	6.0	0.6	1.1
44-05	10.85	14.5	6.9	6.4		
Average		14.5	6.9	6.4		
44-06	0.34	14.1	6.0	4.7	6.0	4.7
44-06	1.21	14.9	7.1	6.6	6.8	6.1
44-06	2.78	14.3	6.5	5.5	-0.8	-1.4
44-06	10.48	14.0	6.8	6.2		
Average		14.3	6.6	5.8		

Table. 3.17. (continued)

			Fracture Toughness (MPa√m)	Fracture Toughness (MPa√m)	Toughness Difference Comparison	Toughness Difference Comparison
Specimen ID	Distance From Surface (mm)	Hardness (GPa)	Evans & Charles	Anstis et al	Near Surface/ Bulk	Near Surface/ Bulk
TRSN-						
44-07	0.55	16.4	6.8	5.7	6.8	5.7
44-07	0.80	15.8	6.8	5.8	7.0	7.0
44-07	1.94	15.6	7.5	7.6	-0.2	-1.3
44-07	7.89	11.0	6.8	7.7		
Average		14.7	7.0	6.7		
44-08	0.88	13.7	6.8	6.4	6.8	6.4
44-08	1.91	13.7	7.2	7.5	7.0	7.5
44-08	6.91	10.8	6.7	7.5	-0.1	-1.1
Average		12.7	6.9	7.1		
44-09	0.88	17.1	7.4	6.8	7.4	6.8
44-09	1.33	14.4	6.9	6.4	7.0	6.5
44-09	1.78	14.8	7.1	6.8	0.4	0.3
44-09	9.57	15.5	7.1	6.4		
Average		15.5	7.1	6.6		
44-10	1.60	15.3	7.1	6.7	7.1	6.7
44-10	4.12	16.0	7.1	6.4	7.0	6.1
44-10	9.34	15.6	6.7	5.6	0.1	0.6
44-10	13.46	17.0	7.2	6.4		
Average		16.0	7.0	6.3		
44-11	0.30	12.5	7.5	9.2	7.5	9.2
44-11	0.80	16.2	7.5	7.3	7.5	7.4
44-11	1.40	17.0	7.2	6.4	0.0	1.8
44-11	8.23	15.5	7.7	8.5		
Average		15.3	7.5	7.8		
44-12	0.32	13.1	8.0	10.8	8.0	10.8
44-12	0.99	15.8	8.6	11.5	7.7	8.8
44-12	1.72	14.2	7.2	7.3	0.2	2.0
44-12	8.67	15.3	7.4	7.5		
Average		14.6	7.8	9.3		
44-13	0.64	14.2	6.8	6.2	6.8	6.2
44-13	1.94	14.3	6.9	6.5	6.9	6.4
44-13	2.65	14.3	6.9	6.4	-0.1	-0.2
44-13	8.03	14.4	6.9	6.5		
Average		14.3	6.9	6.4		

Table. 3.17. (continued)

Specimen ID	Distance From Surface (mm)	Hardness (GPa)	Fracture Toughness (MPa√m) Evans & Charles	Fracture Toughness (MPa√m) Anstis et al	Toughness Difference Comparison Near Surface/ Bulk	Toughness Difference Comparison Near Surface/ Bulk
TRSN-						
44-14	0.89	11.8	7.0	7.7	7.0	7.7
44-14	2.20	10.6	7.6	11.0	7.3	8.8
44-14	4.52	12.3	7.2	8.3	-0.3	-1.2
44-14	10.27	13.4	7.1	7.2		
Average		12.0	7.2	8.5		
44-18	0.68	15.9	7.7	8.1	7.7	8.1
44-18	1.36	15.3	8.0	9.4	7.7	8.2
44-18	2.43	15.6	7.5	7.5	0.0	-0.1
44-18	5.56	16.1	7.6	7.6		
Average		15.7	7.7	8.2		
44-19	0.97	16.2	7.1	6.3	7.1	6.3
44-19	2.16	15.5	7.3	7.0	7.3	8.2
44-19	4.42	12.6	7.4	8.9	-0.2	-1.9
44-19	7.62	12.5	7.6	9.5		
44-19	11.94	12.2	7.0	7.5		
Average		13.8	7.3	7.8		
44-22	0.78	16.2	7.5	7.5	7.5	7.5
44-22	1.47	16.5	7.5	7.3	7.6	8.5
44-22	2.71	15.1	7.9	9.1	-0.1	-1.0
44-22	7.01	13.3	7.6	9.0		
Average		15.3	7.6	8.2		
44-23	0.44	16.7	8.4	10.5	8.4	10.5
44-23	1.27	16.9	8.0	8.6	7.7	8.2
44-23	2.36	15.6	7.8	8.5	0.8	2.3
44-23	8.45	14.5	7.3	7.4		
Average		15.9	7.9	8.7		
44-24	0.74	15.0	7.0	6.4	7.0	6.4
44-24	1.56	15.0	6.4	5.3	6.6	5.9
44-24	2.99	13.9	7.1	7.0	0.4	0.5
44-24	4.30	11.1	6.3	6.0		
44-24	7.94	15.3	6.5	5.3		
Average		14.1	6.7	6.0		

Table. 3.17. (continued)

Specimen ID	Distance From Surface (mm)	Hardness (GPa)	Fracture Toughness (MPa√m) Evans & Charles	Fracture Toughness (MPa√m) Anstis et al	Toughness Difference Comparison Near Surface/ Bulk	Toughness Difference Comparison Near Surface/ Bulk
TRSN-						
44-25	1.25	15.6	5.5	3.9	6.1	4.7
44-25	1.01	16.0	6.1	4.7	5.9	4.6
44-25	2.28	15.5	5.8	4.3	0.2	0.0
44-25	5.56	13.7	6.5	5.7		
Average		15.2	6.0	4.6		
44-26	0.47	15.1	6.7	5.7	6.7	5.7
44-26	2.53	16.1	6.3	4.9	6.4	5.3
44-26	4.61	15.5	6.2	4.8	0.3	0.4
44-26	8.02	13.4	6.7	6.2		
Average		15.0	6.5	5.4		
44-27	0.68	15.5	6.0	4.6	6.0	4.6
44-27	2.02	13.5	6.7	6.2	6.5	5.7
44-27	4.48	12.0	6.3	5.7	-0.4	-1.1
44-27	8.28	14.6	6.3	5.1		
Average		13.9	6.3	5.4		
44-28	0.46	17.0	6.4	5.0	6.4	5.0
44-28	1.07	15.8	6.4	5.1	6.4	5.2
44-28	2.35	15.9	6.6	5.3	0.0	-0.2
44-28	6.86	14.0	6.2	5.1		
Average		15.7	6.4	5.1		
44-29	0.62	15.7	6.7	5.6	6.7	5.6
44-29	1.37	13.4	6.0	4.8	6.1	5.0
44-29	2.41	13.9	6.0	4.7	0.6	0.6
44-29	7.03	12.8	6.3	5.4		
Average		14.0	6.2	5.1		
44-30	0.85	15.7	6.5	5.2	6.5	5.2
44-30	1.47	15.6	6.8	5.8	6.6	5.5
44-30	2.52	16.0	6.8	5.8	-0.1	-0.3
44-30	7.19	15.4	6.3	4.9		
Average		15.7	6.6	5.4		

Table. 3.17. (continued)

			Fracture Toughness (MPa√m)	Fracture Toughness (MPa√m)	Toughness Difference Comparison	Toughness Difference Comparison
Specimen ID	Distance From Surface (mm)	Hardness (GPa)	Evans & Charles	Anstis et al	Near Surface/ Bulk	Near Surface/ Bulk
TRSN-						
44-31	0.57	16.7	6.6	5.3	6.6	5.3
44-31	1.58	14.4	6.5	5.5	6.4	5.6
44-31	3.19	12.3	6.3	5.6	0.2	-0.3
44-31	8.19	13.0	6.5	5.7		
Average		14.1	6.5	5.5		
44-32	0.49	16.3	6.4	5.0	6.4	5.0
44-32	1.36	14.3	6.7	5.8	6.5	5.5
44-32	2.23	14.5	6.2	5.0	-0.1	-0.5
44-32	7.35	14.3	6.5	5.5		
Average		14.9	6.4	5.3		
44-33	0.43	16.0	6.2	4.8	6.2	4.8
44-33	1.20	15.6	6.4	5.0	6.5	5.4
44-33	2.32	14.4	6.5	5.4	-0.2	-0.6
44-33	7.20	13.5	6.4	5.5		
44-33	8.36	14.3	6.6	5.7		
Average		14.8	6.4	5.3		

Table. 3.18. Summary of results on mechanical properties as a function of distance from the as-sintered surfaces for the $\text{Si}_3\text{N}_4\text{-SrO-Yb}_2\text{O}_3\text{-La}_2\text{O}_3$ composition (TRSN-45).

Specimen ID	Distance From Surface (mm)	Hardness (GPa)	Fracture Toughness (MPa $\sqrt{\text{m}}$) Evans & Charles	Fracture Toughness (MPa $\sqrt{\text{m}}$) Anstis et al	Toughness Difference Comparison Near Surface/ Bulk	Toughness Difference Comparison Near Surface/ Bulk
TRSN-						
45-04	0.84	11.1	6.8	7.6	6.8	7.6
45-04	1.43	11.2	7.0	8.1	7.0	8.0
45-04	5.48	10.7	7.0	8.4	-0.1	-0.4
45-04	10.88	12.1	7.0	7.5		
Average		11.3	6.9	7.9		
45-05	0.70	10.7	6.8	7.6	6.8	7.6
45-05	1.20	10.5	6.8	8.0	6.9	8.5
45-05	2.30	10.3	7.0	8.8	-0.1	-0.9
45-05	8.76	9.6	6.9	8.7		
Average		10.3	6.9	8.3		
45-07	0.93	10.6	6.7	7.4	6.7	7.4
45-07	2.18	10.1	5.8	5.2	6.2	6.8
45-07	4.31	8.9	6.3	7.3	0.5	0.7
45-07	8.77	9.3	6.6	7.9		
Average		9.7	6.4	6.9		
45-09	0.85	11.3	6.8	7.3	6.8	7.3
45-09	1.34	11.6	5.2	4.0	6.0	6.2
45-09	2.31	10.4	6.3	6.2	0.8	1.1
45-09	4.18	8.3	6.5	8.4		
Average		10.4	6.2	6.5		
45-10	1.06	16.5	7.0	6.1	7.0	6.1
45-10	1.77	13.8	7.3	7.7	7.1	7.8
45-10	2.81	13.6	7.0	6.8	-0.1	-1.7
45-10	5.01	12.3	7.0	7.6		
45-10	11.20	10.0	7.0	9.0		
Average		13.2	7.1	7.4		

Table. 3.18. (continued)

			Fracture Toughness (MPa√m)	Fracture Toughness (MPa√m)	Toughness Difference Comparison	Toughness Difference Comparison
Specimen ID	Distance From Surface (mm)	Hardness (GPa)	Evans & Charles	Anstis et al	Near Surface/ Bulk	Near Surface/ Bulk
TRSN-						
45-11	0.51	13.2	6.8	6.6	6.8	6.6
45-11	1.10	15.1	7.0	6.3	6.2	5.1
45-11	3.07	14.2	5.5	4.1	0.7	1.5
45-11	10.87	12.1	6.0	5.0		
Average		13.7	6.3	5.5		
45-12	0.55	14.3	7.4	7.7	7.4	7.7
45-12	1.13	14.7	6.5	5.4	6.3	5.3
45-12	1.81	14.9	6.6	5.5	1.0	2.5
45-12	8.06	11.7	5.9	4.9		
Average		13.9	6.6	5.9		
45-13	0.49	10.0	6.8	8.1	6.8	8.1
45-13	1.25	14.9	6.6	5.7	6.0	5.0
45-13	6.86	11.8	5.8	4.7	0.7	3.1
45-13	11.55	11.3	5.7	4.6		
Average		12.0	6.2	5.8		
45-14	0.88	12.1	6.6	6.4	6.6	6.4
45-14	1.25	12.8	5.7	4.5	6.5	6.9
45-14	2.08	11.7	6.8	7.2	0.1	-0.5
45-14	11.38	9.8	6.9	8.9		
Average		11.6	6.5	6.7		

Table. 3.19. Summary of results on mechanical properties as a function of distance from the as-sintered surfaces for the $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ composition (TRSN-46).

Specimen ID	Distance From Surface (mm)	Hardness (GPa)	Fracture Toughness ($\text{MPa}\sqrt{\text{m}}$) Evans & Charles	Fracture Toughness ($\text{MPa}\sqrt{\text{m}}$) Anstis et al	Toughness Difference Comparison Near Surface/ Bulk	Toughness Difference Comparison Near Surface/ Bulk
TRSN-						
46-05	0.57	7.3	5.2	4.9	5.2	4.9
46-05	0.88	8.6	5.7	5.4	5.4	5.0
46-05	1.92	8.8	6.2	6.7	-0.2	-0.1
46-05	3.60	8.6	4.8	3.8		
46-05	10.64	8.4	5.0	4.1		
Average		8.4	5.4	5.0		
46-06	0.67	14.7	4.7	3.3	4.7	3.3
46-06	1.30	15.9	7.8	8.3	7.4	7.4
46-06	2.91	16.3	7.1	6.3	-2.7	-4.1
46-06	10.17	14.1	7.2	7.5		
Average		15.2	6.7	6.3		
46-07	0.76	15.5	5.6	4.0	5.6	4.0
46-07	1.89	16.4	6.2	4.7	6.2	5.2
46-07	3.10	13.8	5.5	4.1	-0.6	-1.2
46-07	4.36	13.7	6.7	6.2		
46-07	10.65	11.3	6.3	6.0		
Average		14.1	6.1	5.0		
46-09	0.51	13.9	6.4	5.3	6.4	5.3
46-09	1.15	15.2	6.2	4.9	5.4	4.0
46-09	3.19	15.7	4.9	3.4	1.0	1.4
46-09	10.85	14.6	5.0	3.6		
Average		14.8	5.6	4.3		
46-10	0.74	14.8	6.3	5.1	6.3	5.1
46-10	1.98	14.9	7.0	6.4	5.7	5.1
46-10	3.94	14.1	3.6	2.5	0.6	0.0
46-10	5.04	13.2	5.8	4.6		
46-10	10.10	9.4	6.3	6.9		
Average		13.3	5.8	5.1		

Table. 3.19. (continued)

Specimen ID	Distance From Surface (mm)	Hardness (GPa)	Fracture Toughness (MPa√m) Evans & Charles	Fracture Toughness (MPa√m) Anstis et al	Toughness Difference Comparison Near Surface/ Bulk	Toughness Difference Comparison Near Surface/ Bulk
TRSN-						
46-11	0.53	13.2	7.3	8.1	7.3	8.1
46-11	1.42	14.7	7.3	7.3	6.7	6.7
46-11	2.65	15.2	6.9	6.2	0.6	1.5
46-11	4.87	12.3	5.2	3.9		
46-11	11.88	11.7	7.4	9.3		
Average		13.4	6.8	7.0		
46-12	0.73	14.7	7.3	7.3	7.3	7.3
46-12	1.78	16.5	6.8	5.6	7.0	6.9
46-12	2.51	14.2	6.9	6.5	0.2	0.5
46-12	10.22	13.0	7.4	8.5		
Average		14.6	7.1	7.0		
46-13	0.58	15.0	7.3	7.3	7.3	7.3
46-13	1.30	15.5	6.7	5.6	6.9	6.6
46-13	1.98	15.0	6.5	5.4	0.4	0.7
46-13	4.33	13.5	7.3	8.0		
46-13	9.75	13.1	7.1	7.5		
Average	1	14.4	7.0	6.8		
46-18	1.02	16.2	5.8	4.2	5.8	4.2
46-18	1.56	15.9	4.8	3.3	5.6	4.3
46-18	2.59	16.5	5.4	3.8	0.2	-0.1
46-18	4.55	12.6	6.3	5.5		
46-18	8.67	12.1	5.8	4.8		
Average	1	14.7	5.6	4.3		
46-23	0.68	14.2	6.2	5.0	6.2	5.0
46-23	1.47	14.6	4.4	3.0	5.5	4.4
46-23	2.51	12.9	5.9	4.7	0.6	0.5
46-23	8.47	12.7	6.4	5.6		
Average		13.6	5.7	4.6		

Table 3.20. Summary of ANOVA results for grand averages, variable mean level effects and the variable total effect of the arrays for the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition.

	Hardness (GPa)	Fracture Toughness (MPa $\sqrt{\text{m}}$)	Toughness Difference (Surface/Interior)
Grand Average	14.31	6.82	0.00
Packing Powder			
Mixture	13.43	6.43	-0.70
Low Oxygen	15.47	6.47	0.07
Oxidized	13.43	8.17	0.13
BN	14.10	6.87	-0.67
None	14.93	7.03	0.93
Mix*	14.47	5.93	0.23
Total Effect	2.03	2.23	1.63
Crucible			
Graphite	14.75	6.70	0.70
BN	13.50	7.63	0.15
RBSN	14.67	6.12	-0.85
Total Effect	1.25	1.52	1.55
Temperature			
1850/1900	14.18	6.80	-0.47
1900/1950	14.37	6.83	0.23
Total Effect	0.18	0.02	0.70
Pressure			
Low	14.05	7.02	0.45
High	14.43	6.72	-0.23
Total Effect	0.38	-0.30	0.68
Time			
2/1	13.85	6.10	0.15
2/2	14.53	7.18	-0.08
Total Effect	0.68	1.08	0.23
Coating			
Yes	13.73	7.52	-0.20
No	14.59	6.47	0.10
Total Effect	0.86	-1.05	0.30
Setter			
BN	14.27	6.52	0.20
None	13.72	6.73	-0.43
SiC	14.93	7.20	0.23
Total Effect	1.22	0.68	0.67

Table 3.21. Summary of results on ANOVA of Taguchi array on Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition for examination of the hardness.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	10.00	2.00	7.66	2.2	2.8	4.3	8.69	28.4
Crucible Type	2	5.86	2.93	11.22	2.6	3.6	6	5.34	17.5
Sintering Temperature	1	0.13	0.13	0.51	3	4.4	8.4	-0.13	0.0
Nitrogen Pressure	1	0.59	0.59	2.25	3	4.4	8.4	0.33	1.1
Sintering Time	1	1.87	1.87	7.15	3	4.4	8.4	1.61	5.3
Surface Coating	1	2.95	2.95	11.28	3	4.4	8.4	2.69	8.8
Setter Material	2	4.45	2.23	8.53	2.6	3.6	6	3.93	12.9
Error	18	4.70	0.26						26.1

Table 3.22. Summary of results on ANOVA of Taguchi array on Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition for examination of the average fracture toughness.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	8.77	1.75	8.63	2.2	2.8	4.3	7.75	25.6
Crucible Type	2	7.02	3.51	17.28	2.6	3.6	6	6.62	21.8
Sintering Temperature	1	0.00	0.00	0.01	3	4.4	8.4	-0.20	0.0
Nitrogen Pressure	1	0.36	0.36	1.77	3	4.4	8.4	0.16	0.5
Sintering Time	1	4.62	4.62	22.74	3	4.4	8.4	4.42	14.6
Surface Coating	1	4.41	4.41	21.70	3	4.4	8.4	4.21	13.9
Setter Material	2	1.46	0.73	3.60	2.6	3.6	6	1.06	3.5
Error	18	3.66	0.20						20.1

Table 3.23. Summary of results on ANOVA of Taguchi array on Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition for examination of the fracture toughness difference from the surface to the interior.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Packing Powder	5	5.65	1.13	33.60	2.2	2.8	4.3	5.48	27.8
Crucible Type	2	7.41	3.71	110.23	2.6	3.6	6	7.34	37.3
Sintering Temperature	1	1.96	1.96	58.31	3	4.4	8.4	1.93	9.8
Nitrogen Pressure	1	1.82	1.82	54.22	3	4.4	8.4	1.79	9.1
Sintering Time	1	0.20	0.20	6.02	3	4.4	8.4	0.17	0.9
Surface Coating	1	0.36	0.36	10.71	3	4.4	8.4	0.33	1.7
Setter Material	2	1.69	0.85	25.19	2.6	3.6	6	1.63	8.3
Error	18	0.60	0.03						5.3

to the observed variations. These would include (1) heating rates, (2) application of nitrogen pressure, (3) furnace and crucible loadings and (4) conditioning of the crucibles. Both the heating rates and application of nitrogen pressure were controlled manually for the heat treatments. Thus, while they were intended to be consistent, they are susceptible to variation based on operator differences. The furnace and crucible loadings were not held constant from one heat treatment to the next. For example, in one test the crucible would contain several samples and in the next test it would only contain one. In retrospect, the specimen decompositions would be affected by the other samples within the crucible environment. The conditioning of the crucibles would also tend to slightly alter the immediate environment surrounding the specimens. While the packing powders were 'fresh' material for each test, the crucibles were not. Multiple firings in a crucible would result in reaction products on the inner surfaces. This was most pronounced with the graphite crucible where a green surface coating was developed on the inner surface indicating the formation of SiC.

A set of optimum conditions for firing of the various compositions were determined based on maximizing the sintered density, minimizing the visible reaction layer or minimizing the weight loss. The results for each composition are shown in Tables 3.24 through 3.26. As indicated, the conditions for optimum density, reaction layer or weight loss values are not necessarily the same for each of the attributes. A set of parameters for firing to obtain the best overall combination of minimum reaction layer thickness, minimum weight loss (or gain) and maximum density is given in Table 3.27. To further determine the effects of the chemical and physical gradient on the mechanical properties, samples of the three compositions were prepared using the optimum conditions listed for $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (TRSN-45).

Table 3.24. Optimized firing parameters for TRSN-44 gas-pressure sintered samples containing Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

Firing Parameter	Optimum Condition for Maximum Density	Condition Effect	Optimum Condition for Minimum Reaction Zone	Condition Effect	Optimum Condition for Minimum Weight Loss	Condition Effect
Packing Powder	Low Ox. or Mix*	Moderate	Mix*	Moderate	Mixture or Low Ox.	Moderate
Crucible Type	Graphite or RBSN	Moderate	BN	Very Weak	RBSN or BN	Weak
Temperature (°C)	1900/1950	Weak	1900/1950	Very Weak	1850/1900	Weak
Pressure (MPa)	0.6/3.4	Weak	0.6/3.4	Very Weak	0.3/3.4	Weak
Time (h)	2/2	Weak	2/1	Weak	2/2	Weak
Coating Presence	No	Weak	No	Weak	No	Weak
Setter Material	SiC	Weak	SiC	Weak	SiC or BN	Weak

Table 3.25. Optimized firing parameters for TRSN-45 gas-pressure sintered samples containing $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$.

Firing Parameter	Optimum Condition for Maximum Density	Condition Effect	Optimum Condition for Minimum Reaction Zone	Condition Effect	Optimum Condition for Minimum Weight Loss	Condition Effect
Packing Powder	BN or Oxidized	Moderate	None or Oxidized	Strong	Oxidized or Low Ox.	Moderate
Crucible Type	Graphite or BN	Moderate	BN or RBSN	Moderate	RBSN or BN	Moderate
Temperature (°C)	1900/1950	Moderate	1900/1950	Weak	1850/1900	Weak
Pressure (MPa)	0.6/1.0	Moderate	0.6/1.0	Weak	0.3/3.4	Weak
Time (h)	2/2	Moderate	2/2	Weak	2/2	Weak
Coating Presence	Yes	Moderate	Yes	Weak	No	Moderate
Setter Material	BN or SiC	Weak	SiC or BN	Weak	BN or SiC	Weak

Table 3.26. Optimized firing parameters for TRSN-46 gas-pressure sintered samples containing $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$.

Firing Parameter	Optimum Condition for Maximum Density	Condition Effect	Optimum Condition for Minimum Reaction Zone	Condition Effect	Optimum Condition for Minimum Weight Loss	Condition Effect
Packing Powder	BN or Low Ox.	Moderate	None or Oxidized	Moderate	Oxidized or Low Ox.	Strong
Crucible Type	Graphite	Moderate	RBSN or BN	Weak	RBSN or BN	Strong
Temperature (°C)	1900/1950	Strong	1850/1900	Weak	1850/1900	Moderate
Pressure (MPa)	0.6/1.0	Very Weak	0.3/0.6	Weak	0.3/3.4	Very Weak
Time (h)	2/2	Weak	2/1	Weak	2/2	Weak
Coating Presence	Yes	Moderate	No	Weak	No	Moderate
Setter Material	SiC or BN	Moderate	BN or None	Weak	SiC or BN	Weak

Table 3.27. Combined optimum firing conditions to maximize densification and minimize both reaction layer thickness and weight loss.

Firing Parameter	TRSN-44	TRSN-45	TRSN-46
Packing Powder	Mix*	Oxidized	Oxidized
Crucible Type	RBSN	BN	BN
Temperature (°C)	1900/1950	1900/1950	1900/1950
Pressure (MPa)	0.6/3.4	0.6/1.0	0.6/1.0
Time (h)	2/2	2/2	2/2
Coating Presence	No	No	No
Setter Material	SiC	BN	BN

Examination of the ANOVA results on the grand averages for the different variables given in Tables 3.5, 3.6 and 3.7 for the three compositions shows the reaction layer thickness is more pronounced for the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ and $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ compositions than with the $\text{Si}_3\text{N}_4\text{-6\% Y}_2\text{O}_3\text{-2\% Al}_2\text{O}_3$ composition. This is believed due to the lower liquidus temperature and better densification behavior of the $\text{Si}_3\text{N}_4\text{-6\% Y}_2\text{O}_3\text{-2\% Al}_2\text{O}_3$ materials. The better densification at lower temperatures would tend to seal the surface more effectively and limit the diffusion of volatile species from the specimens during the early stage sintering.

Another observation that will be pertinent in later discussions is that the visible reaction zones consisted of multiple distinct regions as illustrated in Fig. 3.1. This was true for essentially all samples from the three different sintering additive compositions. Such distinct regions are reminiscent of the phase transitions observed in classic diffusion couple experiments.

The level results in Tables 3.5-3.7 also indicate that the packing powder has the greatest total effect on the visible formation of the reaction layer for all of the compositions tested in this study. This is also reflected in the F-test values and percent contribution for the packing powder shown in Tables 3.8, 3.11 and 3.14. The $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ composition also showed that the crucible type, surface coating and setter material had an appreciable effect on the thickness of the reaction layer. These other contributions for that composition are also probably caused by the poorer densification exhibited by this composition.

For all of the compositions tested, the crucible type was a significant factor in affecting the observed weight loss. High weight losses, as shown in Fig. 3.2, were associated with the use of graphite crucibles and indicate a reaction of CO or C with the samples according to

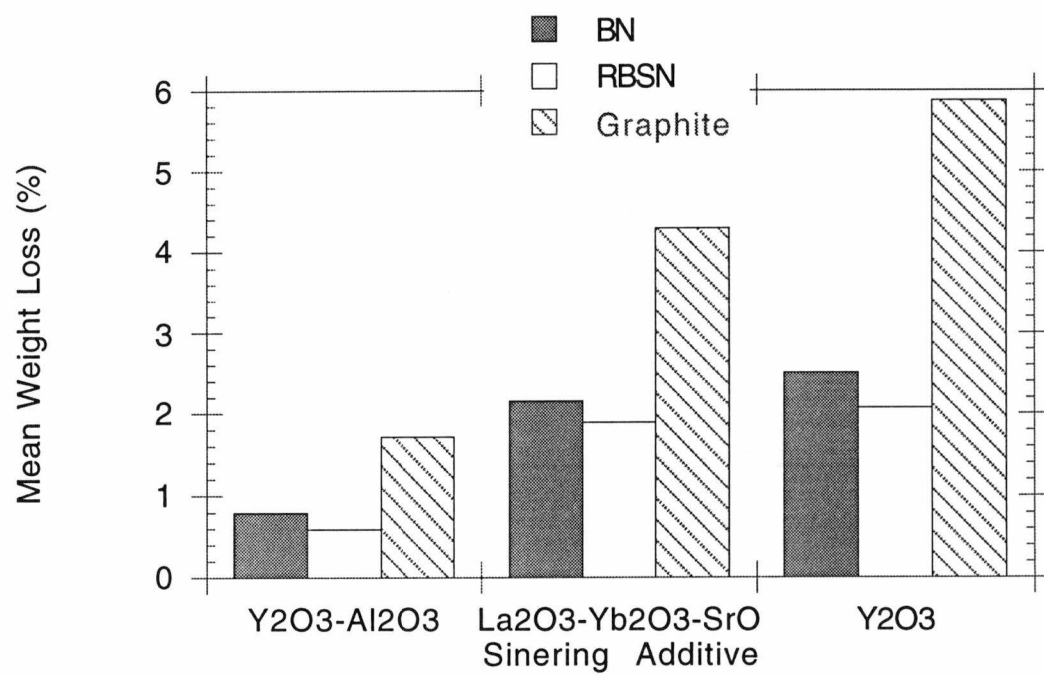


Fig. 3.2. Observed mean weight losses during GPS of silicon nitride for the different crucible types and compositions.

reactions 3.4, 3.5 and 3.6. These reactions form volatile species which would result in an observed weight loss. The CO_2 formed, in turn, reacts with the available carbon forming additional CO that can return to further decompose the sample.

The low losses associated with packing powders containing Si_3N_4 indicates that the Si, O and N volatility is tied to the establishment of an equilibrium atmosphere surrounding the specimens. Likewise, the packing powders containing no Si_3N_4 (i.e. BN and 'None') had high weight losses indicating that the specimens themselves had to decompose to establish the equilibrium atmosphere. This spontaneous weight loss probably occurs during the initial stages of the high temperature heating cycle.

In some cases, weight gains were actually observed to result during the high temperature sintering. These conditions occurred with the oxidized silicon nitride packing powder and application of high nitrogen pressure. The observed weight gains are attributable to (1) nitrogen gas absorption into the intergranular liquid phase, (2) the possible formation of $\text{Si}_2\text{N}_2\text{O}$ by reaction Eq. 3.7 and (3) minimal weight loss due to SiO volatilization from the samples caused by the decomposition of the packing powder.

The application of high nitrogen gas pressure was influential in reducing weight losses (by reactions Eqs. 3.1, 3.2 and 3.4). Since the pressure was applied only in the second stage, its effect would impact only weight changes in that step. These observations suggest that the weight losses that occur during the first stage are concerned with the establishment of a protective atmosphere high in SiO (since the nitrogen pressure was low in every test). The weight losses that occur during the second stage are associated with the decomposition of the Si_3N_4 (by reactions Eqs. 3.1, 3.2 and 3.4) or the incorporation of nitrogen into the liquid phase (by reactions Eqs. 3.6 and 3.7).

As mentioned before, the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition achieved high densities for all of the firing conditions used in the tests, however, the other two compositions with more refractory grain boundary phases showed quite variable densification. The Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition and Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ composition exhibited lower densities. Because of the refractory nature of the sintering additives for these compositions, temperature was the most important factor affecting densification. In addition, at the lower initial sintering temperature of 1850°C, these compositions did not achieve closed porosity prior to the second high temperature grain growth step. Consequently, for the tests where high gas pressure was used during the second step, further densification was inhibited by trapped gas. For the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 samples where closed porosity was achieved even at the lower initial temperature, high gas pressure applied during the second sintering step was effective to improve densification.

The results showed that sintering in the graphite crucibles appeared to improve densification, however, this result can be misleading. The reactions in the graphite crucibles have been shown to result in weight losses attributable to SiO vaporization. The densities of the oxygen deficient phases formed are higher than the oxygen rich phases. Consequently, the % theoretical density which is based on the initial composition is calculated to be too high.

The effect of packing powder on the densification for the various compositions is shown in Fig. 3.3. As indicated, only a small effect on densification of the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 samples was observed. However, the other two compositions showed much more strong of an effect. For the Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ samples, the highest densities were achieved with either BN or oxidized Si_3N_4 as packing powder. The Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ samples exhibited the best densification with BN or low oxygen Si_3N_4 packing powder.

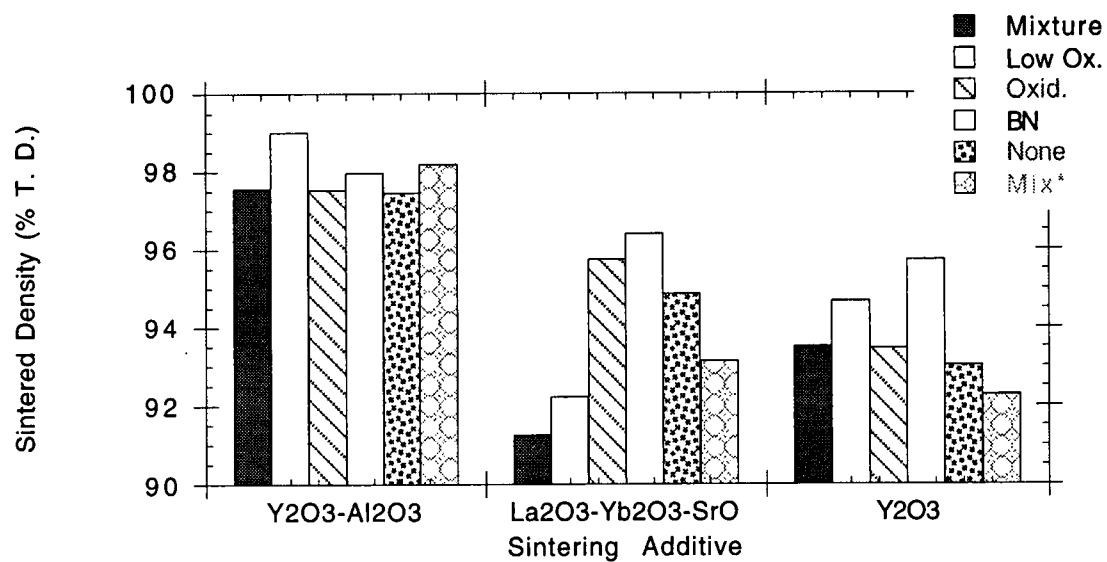


Fig.3.3. Effect of packing powder on densification during GPS of silicon nitride for the different compositions.

Combining the visual reaction layer observations with the simultaneous occurrence of weight loss, it is obvious that they are related. Previous work had identified SiO loss as a major contributor to the weight loss.¹⁹⁷ If one considers the loss to be diffusion controlled, the diffusivity can be estimated using the following relationship:

$$X = \sqrt{Dt} \quad [\text{Eq. 3.10}]$$

where X = diffusion distance (cm)

D = diffusivity (cm^2/s)

t = diffusion time (s)

,using the grand averages for the diffusion distances and times of 3-4 hours, the apparent diffusivities can be calculated to be: $1.9\text{-}2.5 \times 10^{-6} \text{ cm}^2/\text{s}$ for $\text{Si}_3\text{N}_4\text{-}6\% \text{ Y}_2\text{O}_3\text{-}2\% \text{ Al}_2\text{O}_3$, $6.0\text{-}7.9 \times 10^{-6} \text{ cm}^2/\text{s}$ for $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ samples, and $5.0\text{-}6.7 \times 10^{-6} \text{ cm}^2/\text{s}$ for $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ samples. The oxygen diffusivities in various silicate glass melts is in the range of 10^{-4} to $10^{-7} \text{ cm}^2/\text{s}$ at temperatures of $1900\text{-}1950^\circ\text{C}$.^{198,199} So the calculated diffusivity for SiO loss and reaction layer formation are consistent with a diffusion type process.

The high apparent diffusivity associated with the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ and $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ materials are believed to be somewhat misleading, however. Because of the refractory nature of these intergranular phases, these materials should have higher melt viscosities than the $\text{Si}_3\text{N}_4\text{-}6\% \text{ Y}_2\text{O}_3\text{-}2\% \text{ Al}_2\text{O}_3$ materials. Based on the Stokes-Einstein expression relating viscosity to diffusivity, the high melt viscosities should result in lower diffusivities. However, remember that SiO volatilization and loss occurs from exposed surfaces. These samples did not densify as readily as the $\text{Si}_3\text{N}_4\text{-}6\% \text{ Y}_2\text{O}_3\text{-}2\% \text{ Al}_2\text{O}_3$

materials. Hence, they had open porosity that extended below the bulk surface well into the high temperature sintering cycle. From previous work and experience, it is estimated that at 1850°C, the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 will reach > 93% T. D. after ~30 minutes. (Closed porosity, i.e. no porosity open to the exposed surfaces, is typically obtained at densities > 93% T. D.) Consequently, this composition did experience most of the high temperature exposure with closed porosity and thus, the diffusivity calculations are probably accurate. On the other hand, the Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ and Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ compositions would not achieve > 93% T. D. (closed porosity) after 2 hours at 1850°C and only after ~2 hours at 1900°C. Therefore, these compositions spent much of the high temperature cycle with open porosity. SiO and Si loss could therefore take place from these exposed pores and result in larger physical and compositional gradients and increased weight losses.

These hypotheses are consistent with the observations. They indicate that the phenomenon associated with the formation of the physical and composition gradients is more critical with materials that do not densify readily than with compositions where closed porosities are achieved more quickly.

Phase Analysis and Characterization

While weight losses indicated Si, O and N volatilization and subsequent reactions occurred between the samples and graphite crucibles, oxygen depletion at exposed surfaces was also found in samples fired in non-graphite crucibles. Examination with an electron microprobe of a Si_3N_4 - Y_2O_3 - Al_2O_3 sample sintered in a BN crucible (with low oxygen Si_3N_4 packing powder) showed an oxygen gradient across the surface reaction zone with the surfaces

being deficient (Fig. 3.4). The region of low oxygen concentration extended from the as-sintered surface to about 0.5 mm below. This particular sample had a visible reaction layer of ~1.5 mm. Like before, the diffusivity can be estimated (using a diffusion distance of 0.5 mm and a time of 4 hours) as $1.7 \times 10^{-7} \text{ cm}^2/\text{s}$. Although lower than previously calculated, this value is still in the range for oxygen diffusion in silicate melts at temperatures of 1900-1950°C.

Also shown in Fig. 3.4 is a $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ sample fired in a graphite crucible (with BN packing powder) which showed a high oxygen concentration adjacent to the exposed surface and a sharp decrease at ~0.15 mm into the bulk material. This particular sample had a visible reaction layer of ~1.4 mm. The high oxygen concentration at the surface is attributable to B_2O_3 that is associated with the BN powder surfaces and its volatilization and deposition on the surface during firing. Thus, the high concentration of oxygen at the surface.

Overall, the oxygen content of the sample fired in the graphite crucible is lower than the material fired in the BN crucible under more oxidizing conditions. The weight loss differences between the two samples reflects this difference in SiO , Si and N volatilization (2.5% versus 0.6%). All of the other conditions of temperature, time and nitrogen pressure were the same. This behavior indicates that the losses of SiO , Si and N were occurring during sintering for essentially all samples at high temperature.

X-ray analysis was performed of the samples sintered under the optimum conditions as described in Table 3.27. The analysis was done on as-sintered surfaces as well as surfaces where various amounts of material were removed by machining from the exposed surfaces. The penetration depth of the x-rays into silicon nitride was calculated to be on the order of

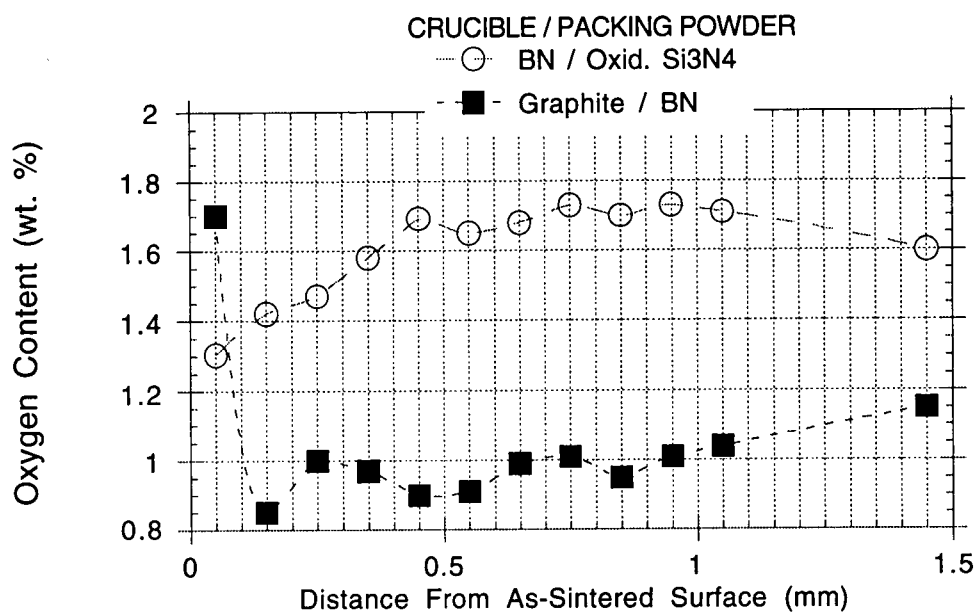


Fig. 3.4. Oxygen concentration as a function of distance from the as-sintered surfaces of GPS Si₃N₄-Y₂O₃-Al₂O₃ specimens fired in graphite or BN crucibles.

70 μm (or 0.07 mm).²⁰⁰ So the x-ray analyses done in these tests are an average over a small region adjacent to the examined surface.

The x-ray analysis on as-sintered surfaces of $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ samples (labeled TRSN-44) sintered in BN crucibles showed melilite ($\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$) present on the surface (Fig. 3.5). As one gets away from the as-sintered surface, the x-ray patterns indicate other crystalline phases appear as shown in Figs. 3.6 through 3.8. Only $\beta\text{-Si}_3\text{N}_4$ was observed in x-ray patterns from the interior regions (≥ 1 mm from surface) indicating the intergranular phase was amorphous in this region in this case. These results are further indication that SiO loss occurs at the exposed sample surfaces during high temperature firing resulting in the crystallization of oxygen deficient phases compared to those on the interior.

The x-rays of the $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ containing materials (labeled TRSN-45) are shown in Figs. 3.9 through 3.12. Crystalline materials were apparent on the as-sintered surface. The numerous components in this system made positive identification of the phases difficult. However, the patterns for the as-sintered and 0.1 mm surfaces were similar to those for $\text{La}_5(\text{SiO}_4)_3\text{N}$. At 0.5 mm from the as-sintered surface crystalline material was present, but it was not identified.

The x-ray analysis of the $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ sample surfaces (labeled TRSN-46) showed a similar trend to that observed for the $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ material (Figs. 3.13 through 3.16). Here, $\text{Y}_4\text{Si}_2\text{N}_2\text{O}_7$ (J-phase as shown in Fig. 3.17) was observed on the as-sintered surface indicating oxygen loss from the initial composition. At 0.1 mm from the as-sintered surface, melilite was present suggesting appreciable oxygen depletion even at this distance. It should be pointed out that these samples were fired in BN crucibles with oxidized packing powder. The data indicate that the as-sintered surface may actually be higher in

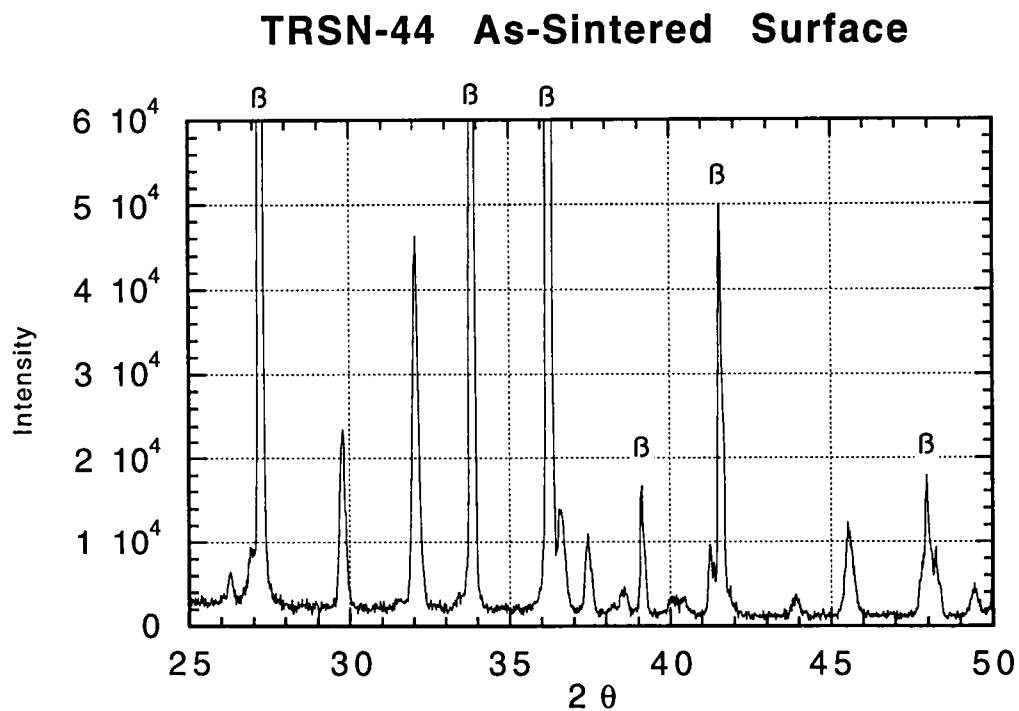
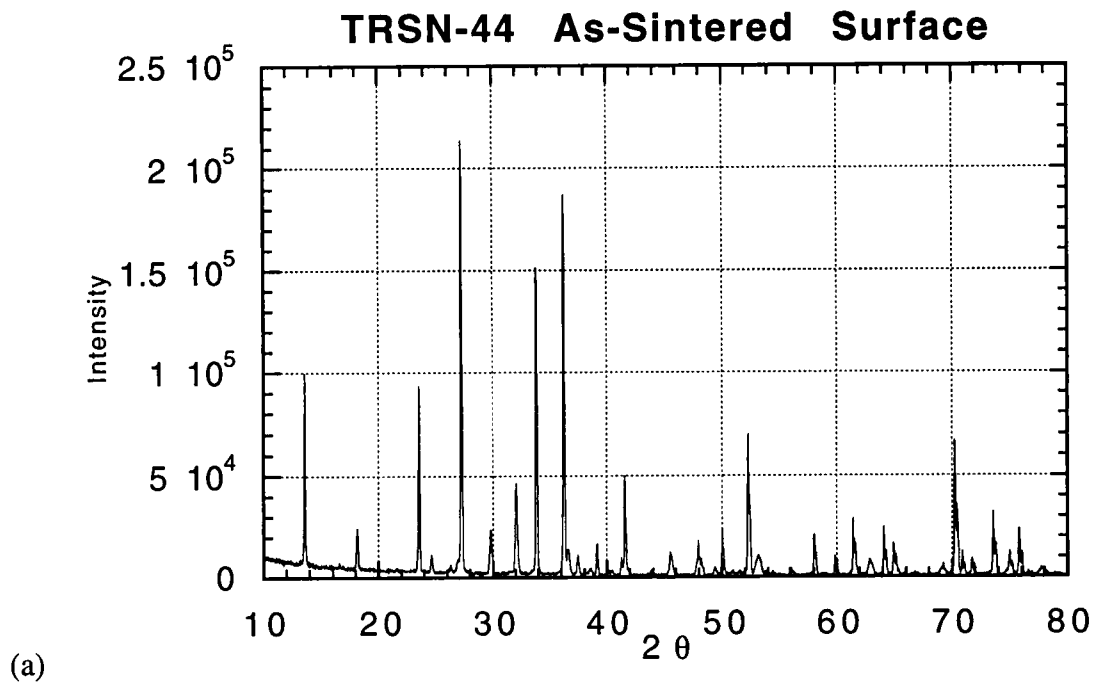
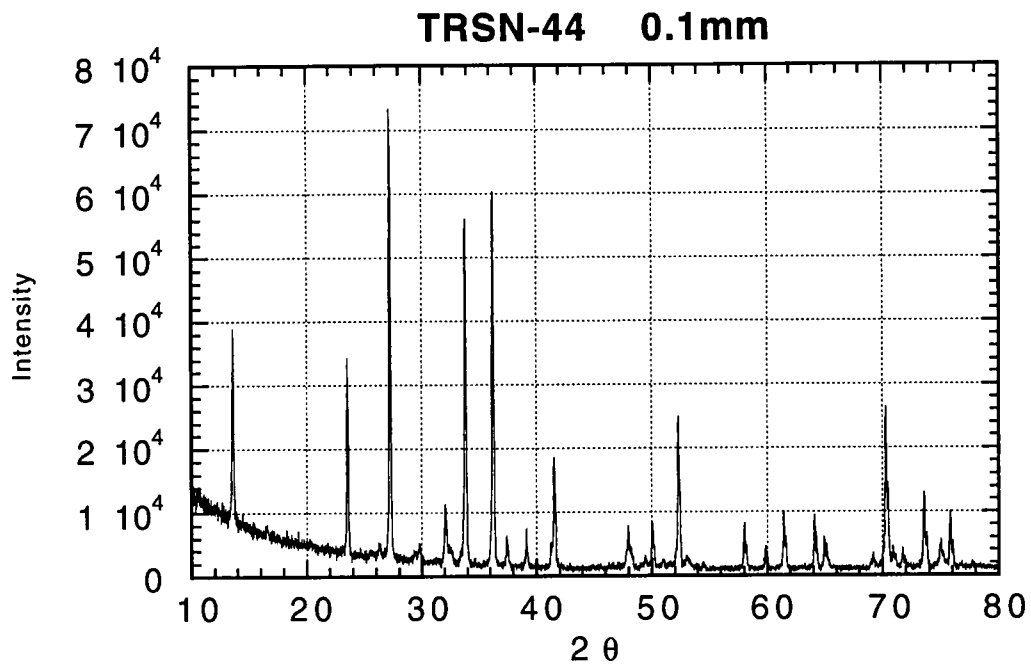
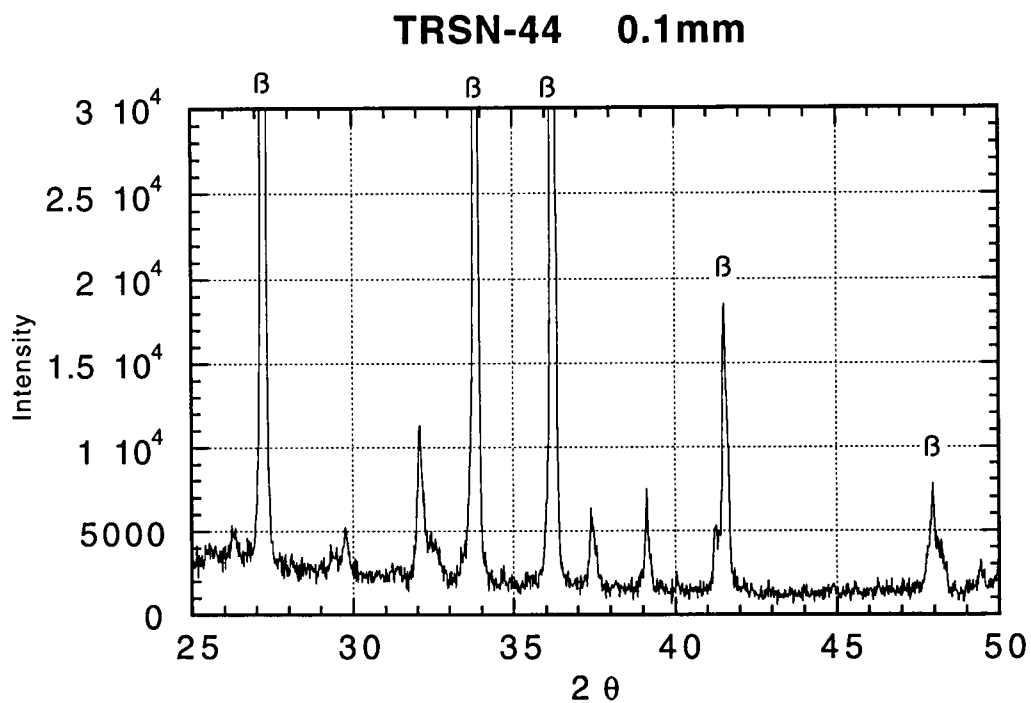


Fig. 3.5. X-ray diffraction results on as-sintered surface of GPS Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 materials. (a) Scan from 10 - 80° 2θ , (b) scan from 25 - 50° 2θ .

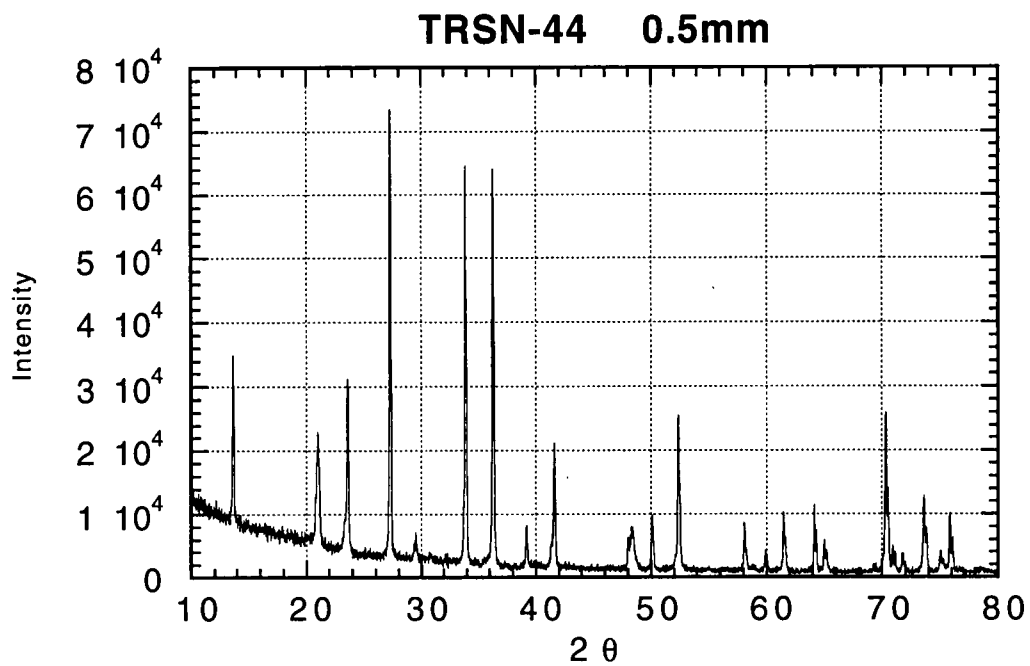


(a)

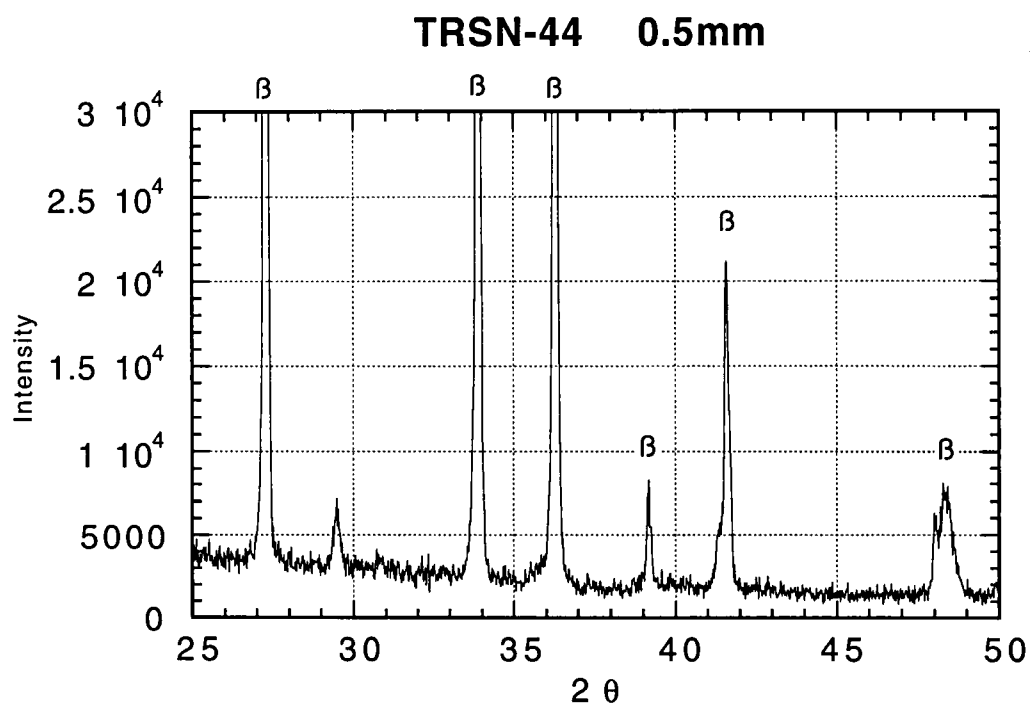


(b)

Fig. 3.6. X-ray diffraction results on surface 0.1 mm from as-sintered surface of GPS Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 materials. (a) Scan from 10-80° 2θ , (b) scan from 25-50° 2θ .



(a)



(b)

Fig. 3.7. X-ray diffraction results on surface 0.5 mm from as-sintered surface of GPS Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 materials. (a) Scan from 10-80° 2θ , (b) scan from 25-50° 2θ .

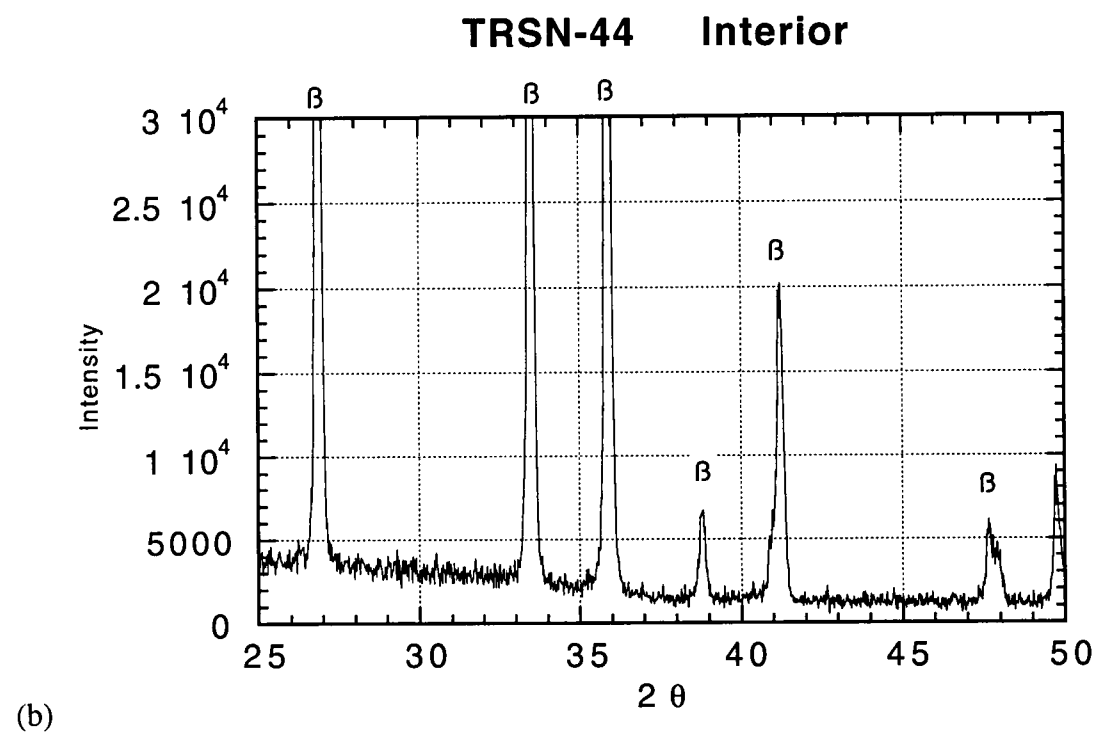
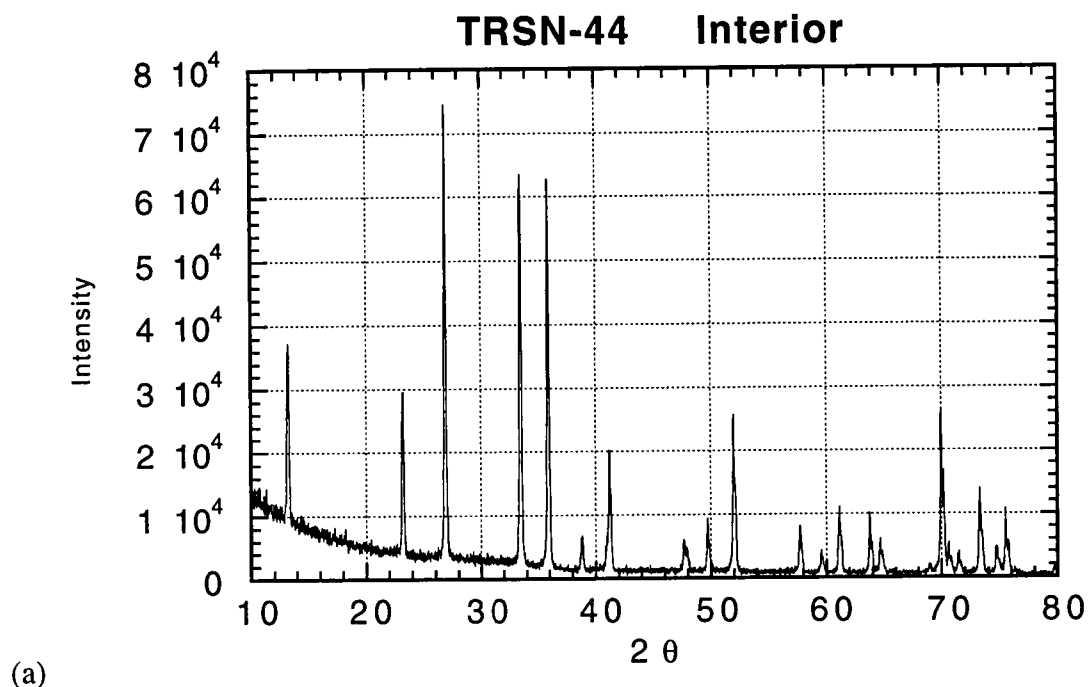


Fig. 3.8. X-ray diffraction results on surface >1 mm from as-sintered surface of GPS Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 materials. (a) Scan from 10-80° 2θ , (b) scan from 25-50° 2θ .

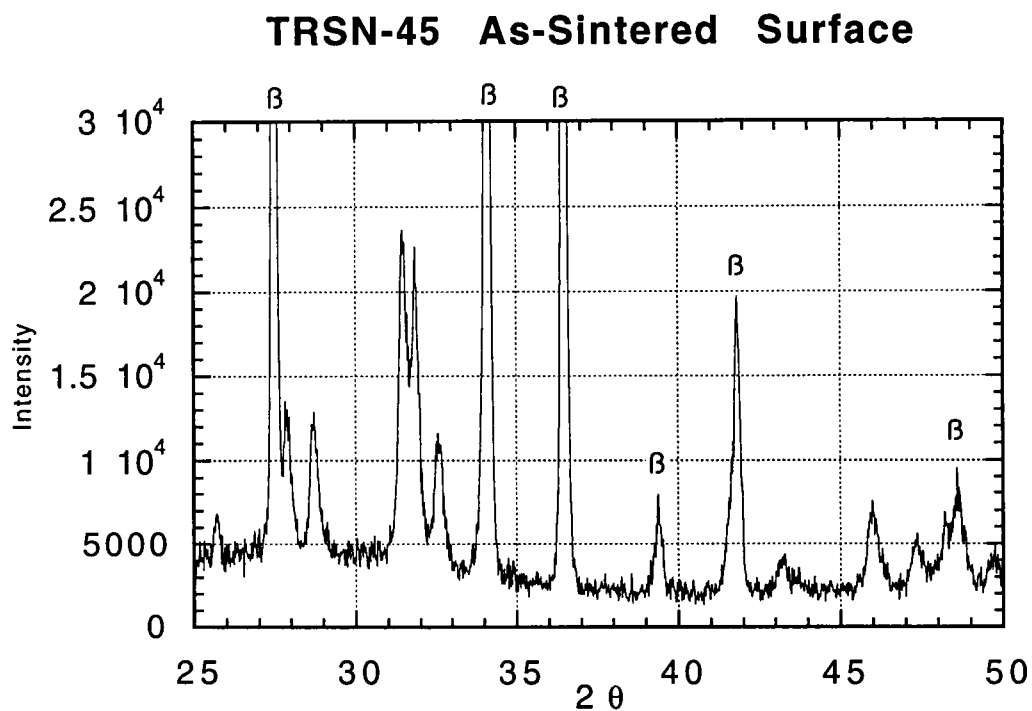
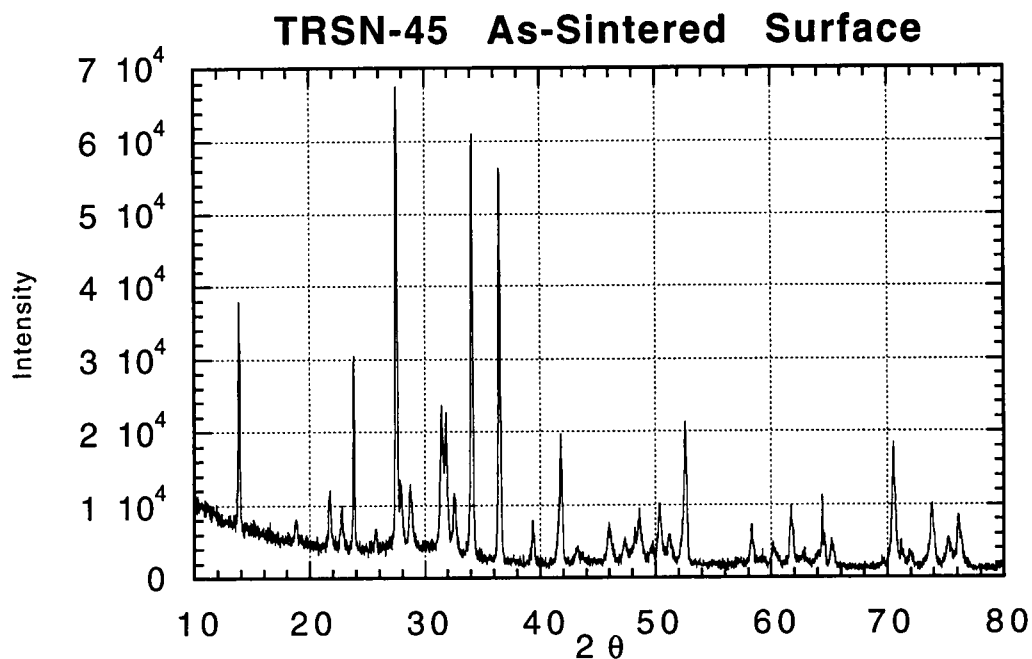


Fig. 3.9. X-ray diffraction results on as-sintered surface of GPS Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ materials. (a) Scan from 10 - 80° 2θ , (b) scan from 25 - 50° 2θ .

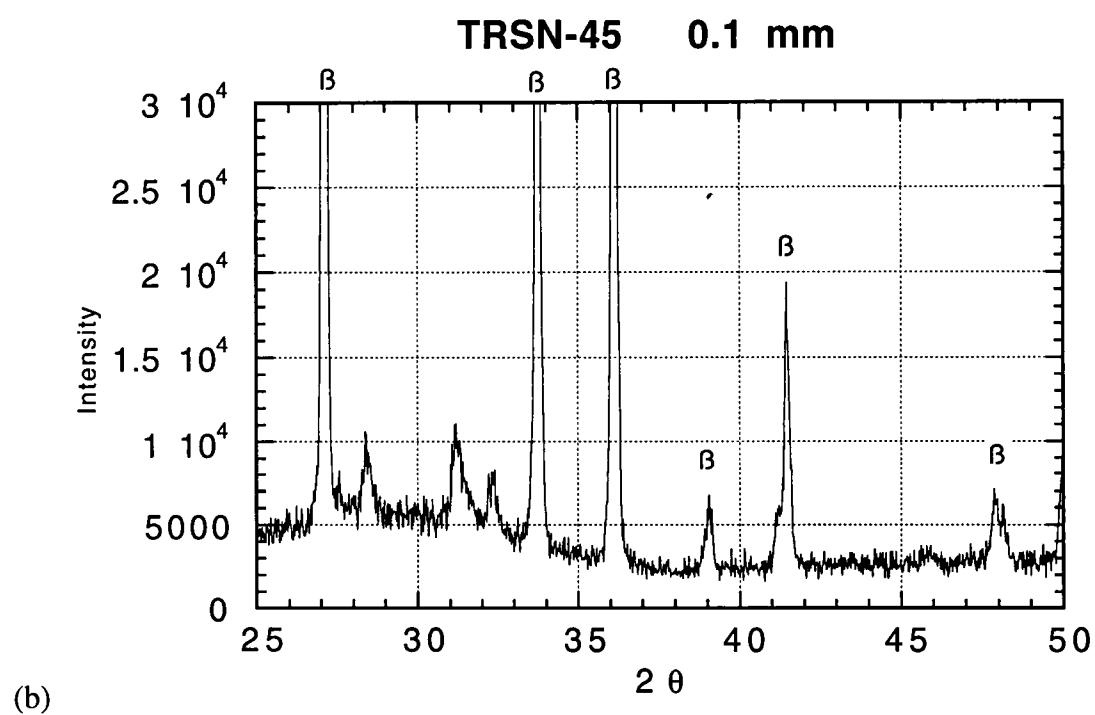
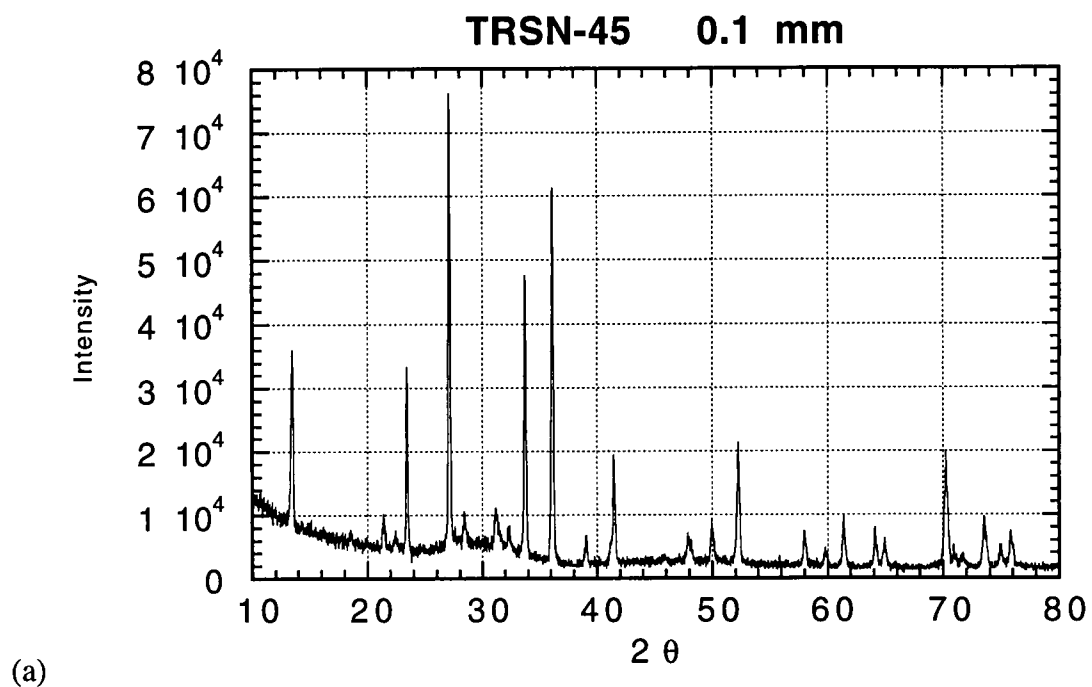


Fig. 3.10. X-ray diffraction results on surface 0.1 mm from as-sintered surface of GPS $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ materials. (a) Scan from $10\text{-}80^\circ 2\theta$, (b) scan from $25\text{-}50^\circ 2\theta$.

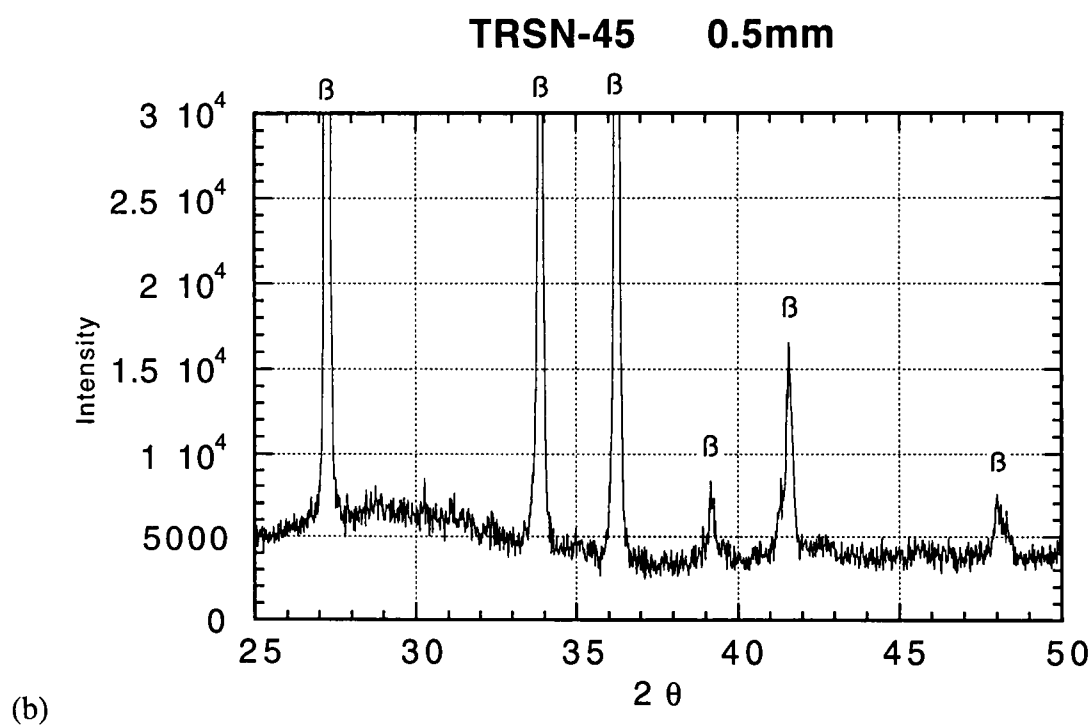
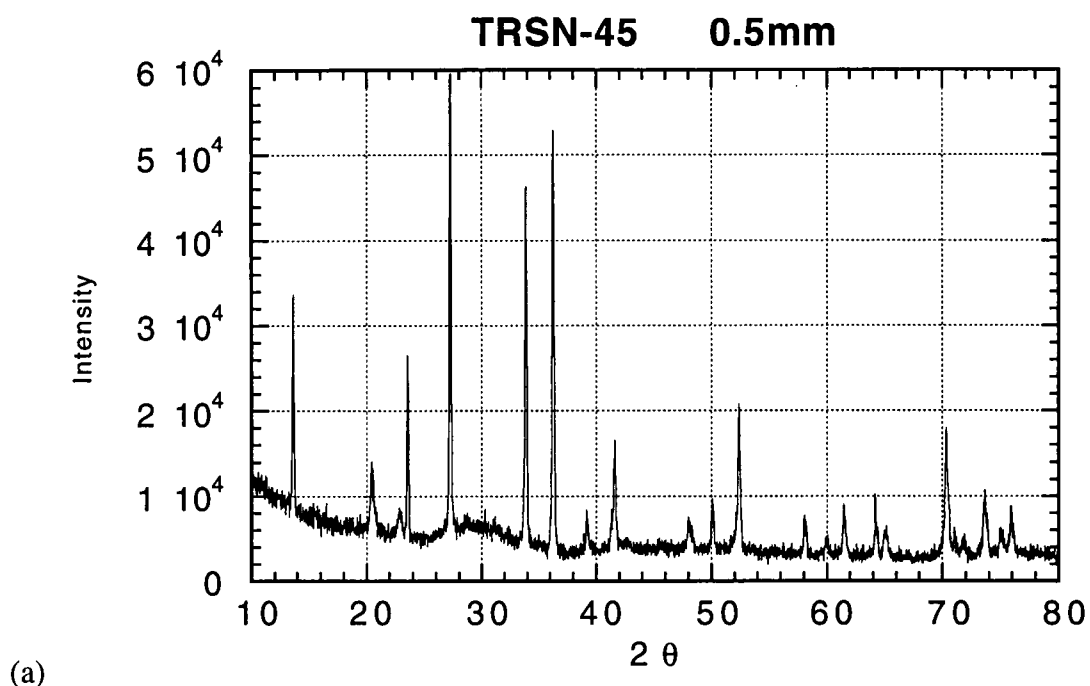


Fig. 3.11. X-ray diffraction results on surface 0.5 mm from as-sintered surface of GPS $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ materials. (a) Scan from $10\text{-}80^\circ 2\theta$, (b) scan from $25\text{-}50^\circ 2\theta$.

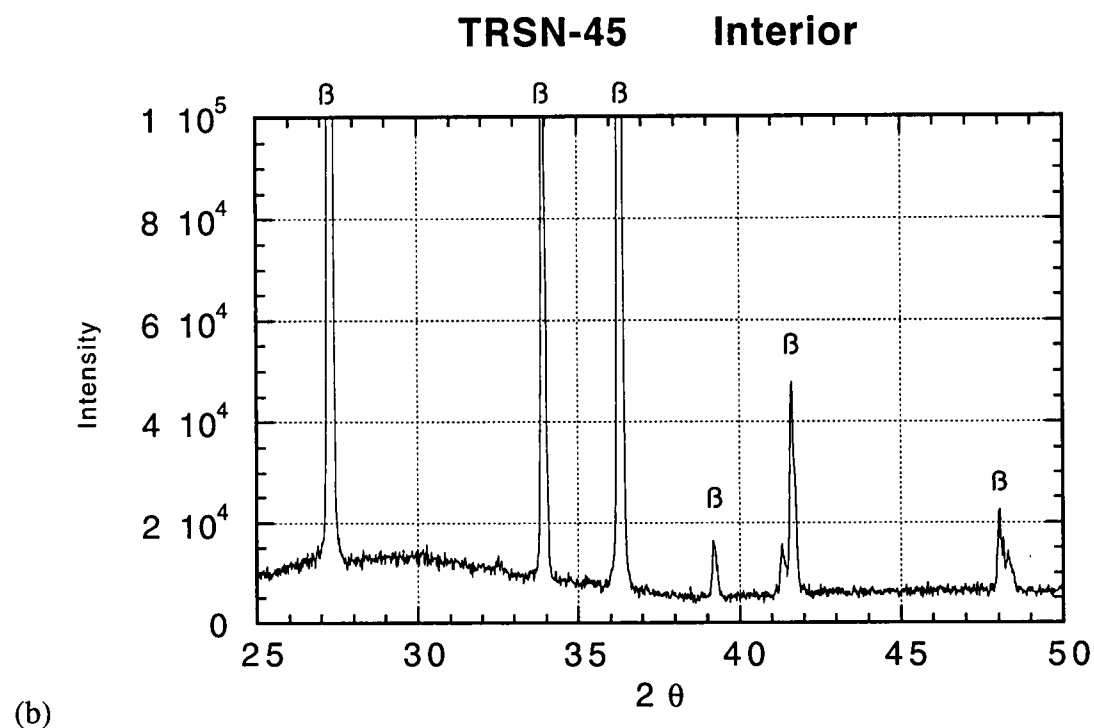
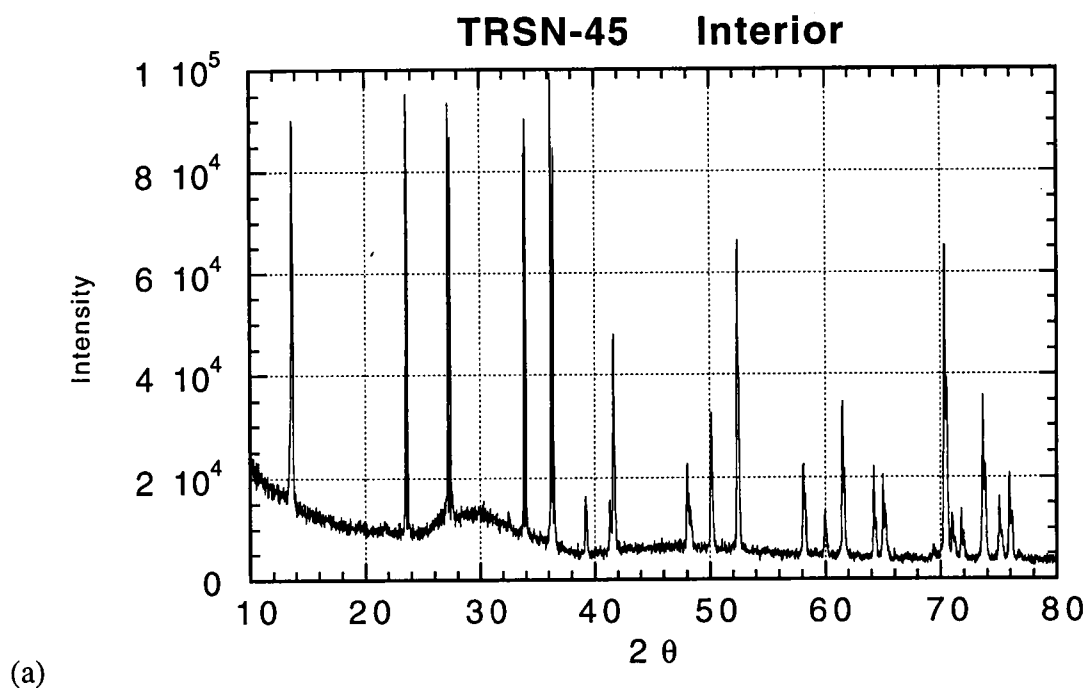


Fig. 3.12. X-ray diffraction results on surface >1 mm from as-sintered surface of GPS $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ materials. (a) Scan from $10\text{-}80^\circ 2\theta$, (b) scan from $25\text{-}50^\circ 2\theta$.

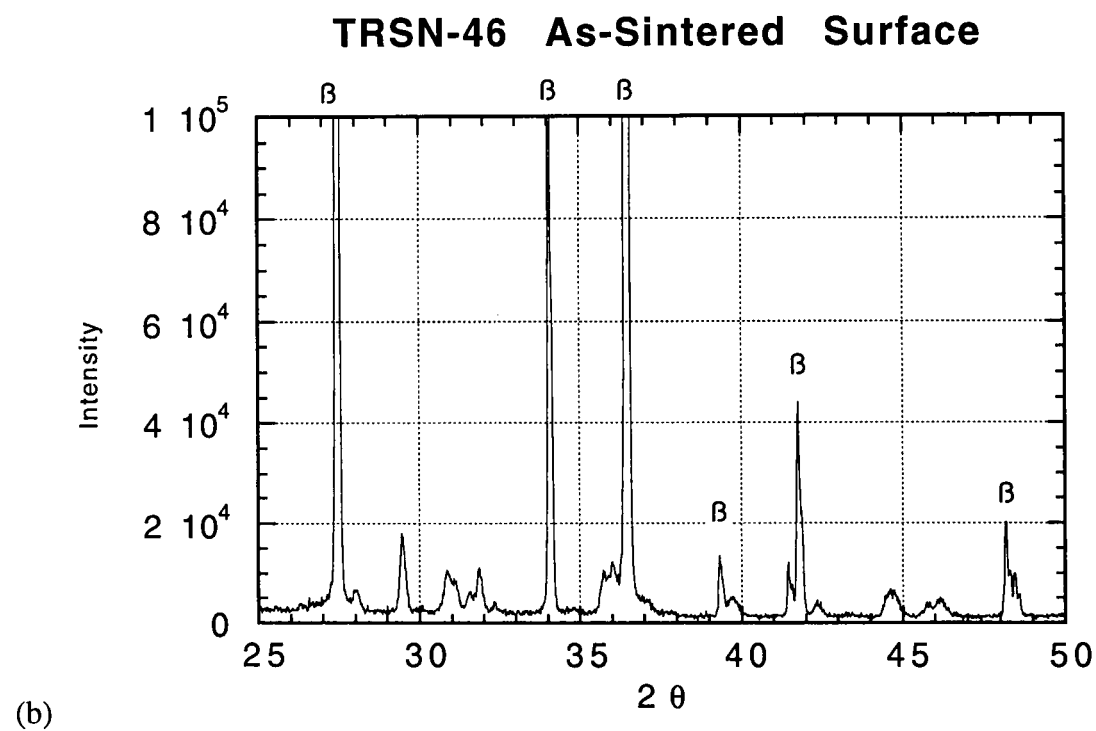
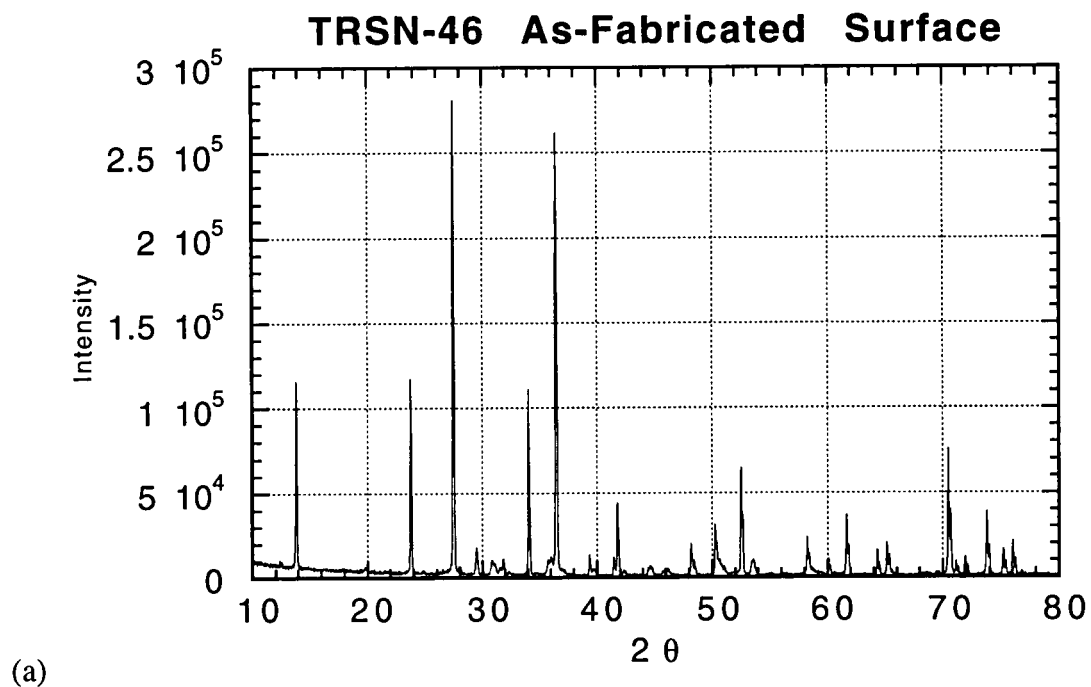


Fig. 3.13. X-ray diffraction results on as-sintered surface of GPS Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ materials.

(a) Scan from 10 - 80° 2θ , (b) scan from 25 - 50° 2θ .

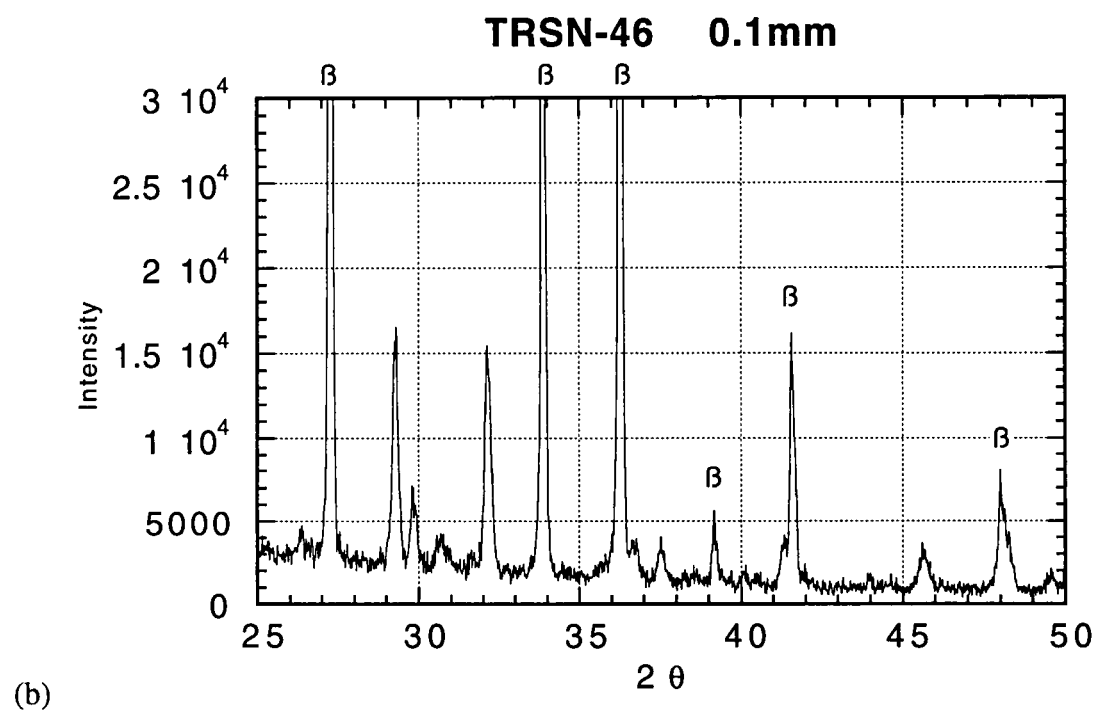
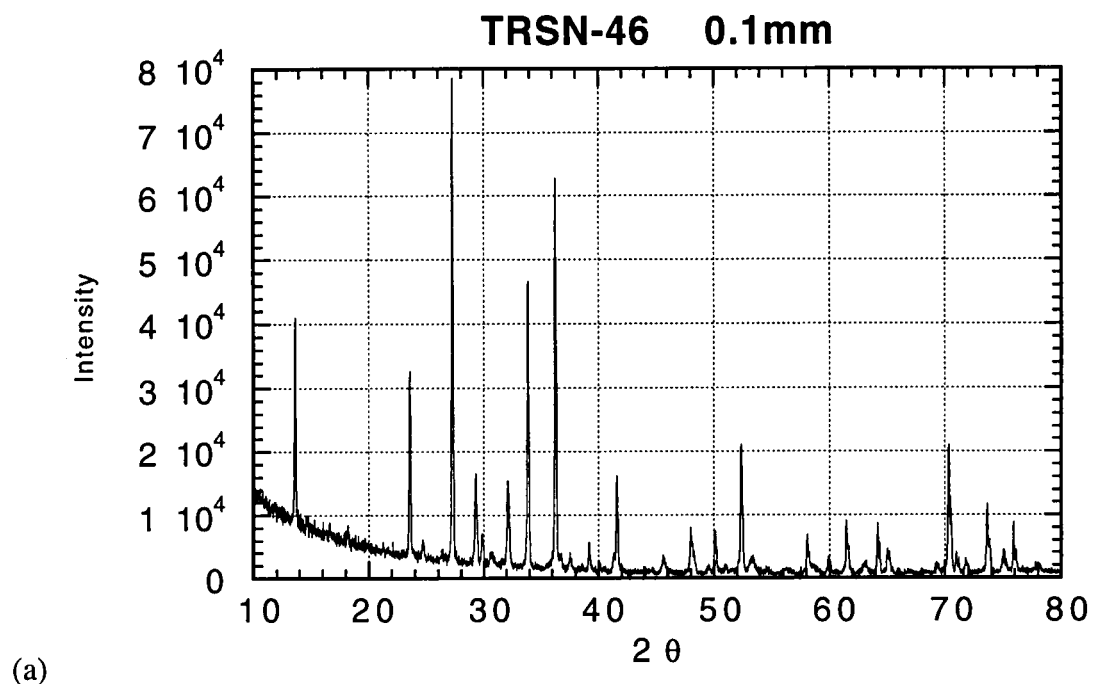


Fig. 3.14. X-ray diffraction results on surface 0.1 mm from as-sintered surface of GPS $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ materials. (a) Scan from $10\text{-}80^\circ 2\theta$, (b) scan from $25\text{-}50^\circ 2\theta$.

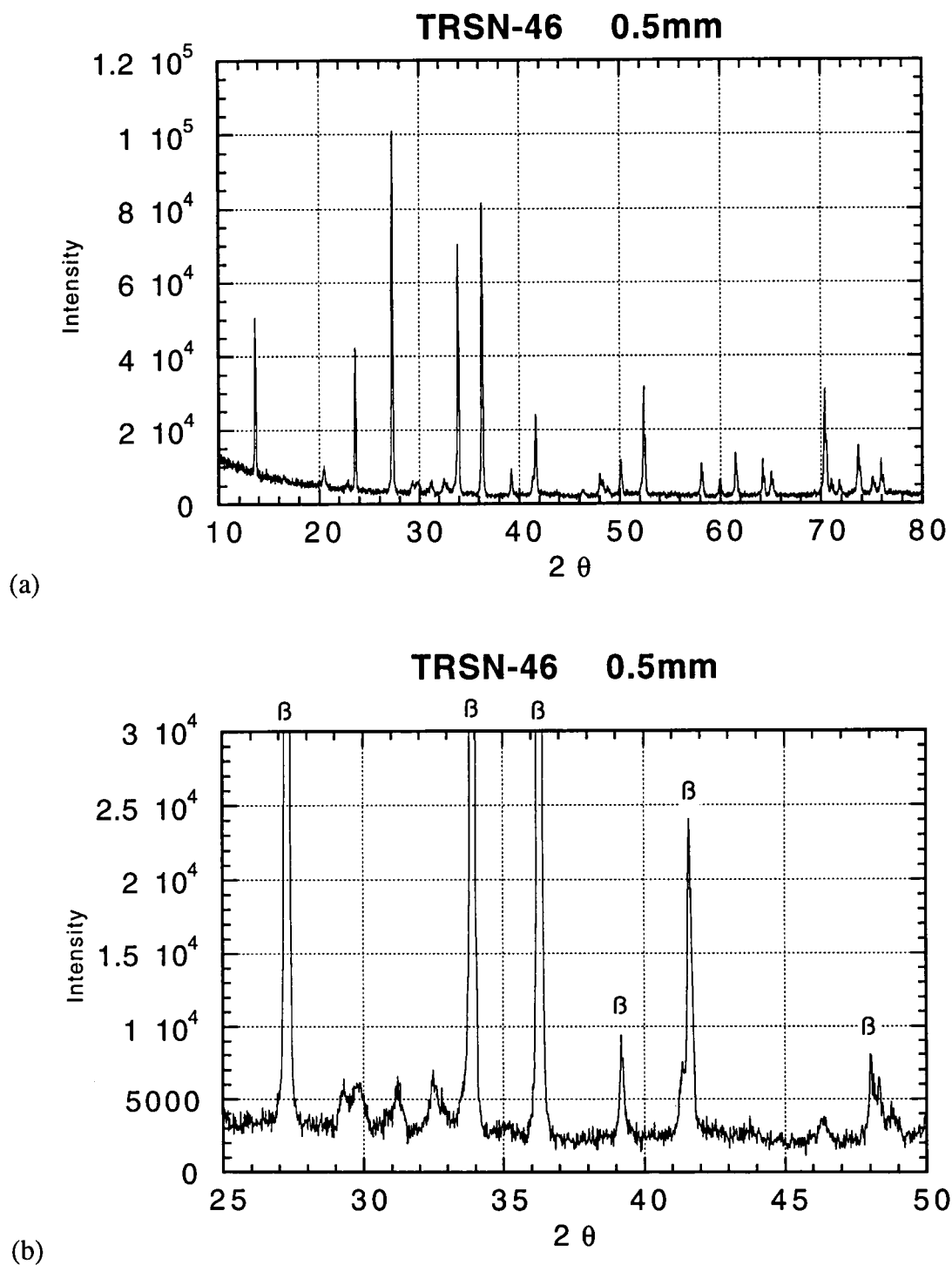


Fig. 3.15. X-ray diffraction results on surface 0.5 mm from as-sintered surface of GPS $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ materials. (a) Scan from $10\text{-}80^\circ 2\theta$, (b) scan from $25\text{-}50^\circ 2\theta$.

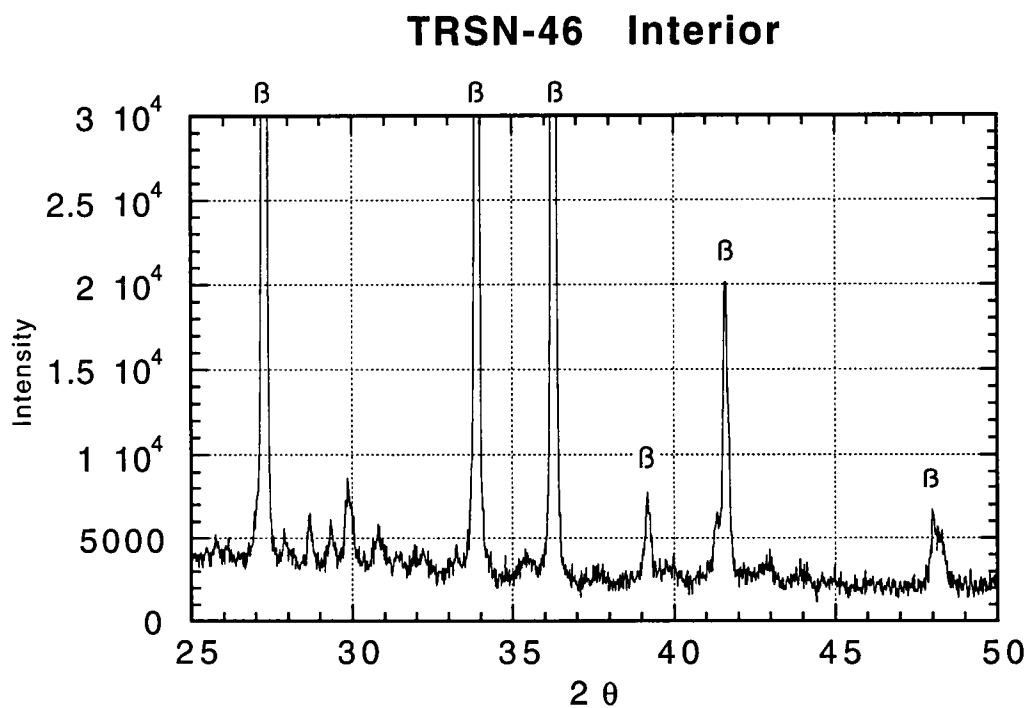
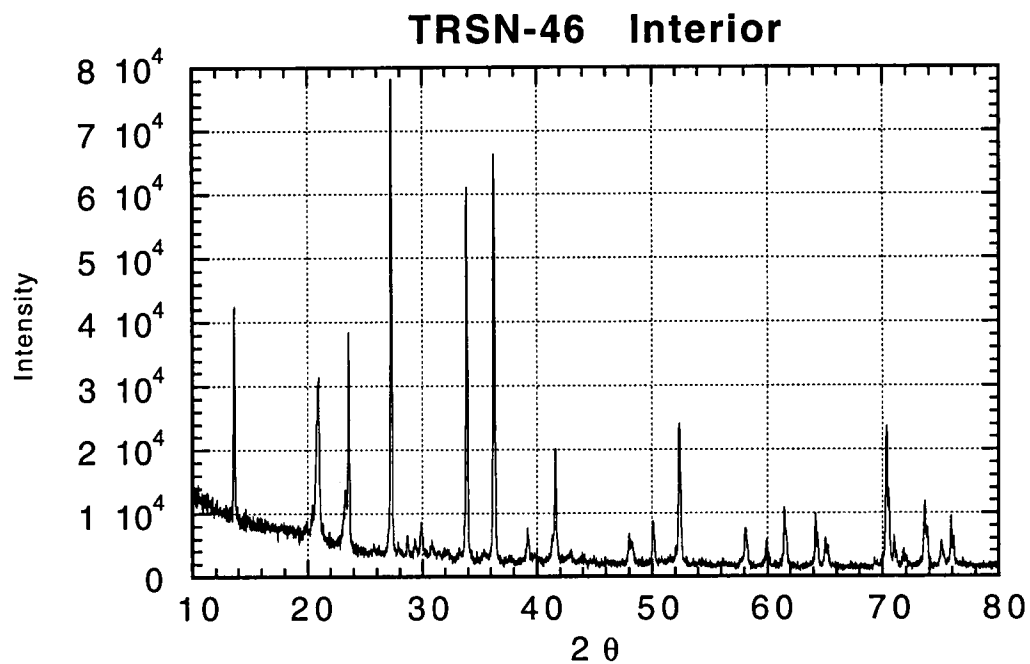


Fig. 3.16. X-ray diffraction results on surface >1 mm from as-sintered surface of GPS $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ materials. (a) Scan from 10-80° 2θ , (b) scan from 25-50° 2θ .

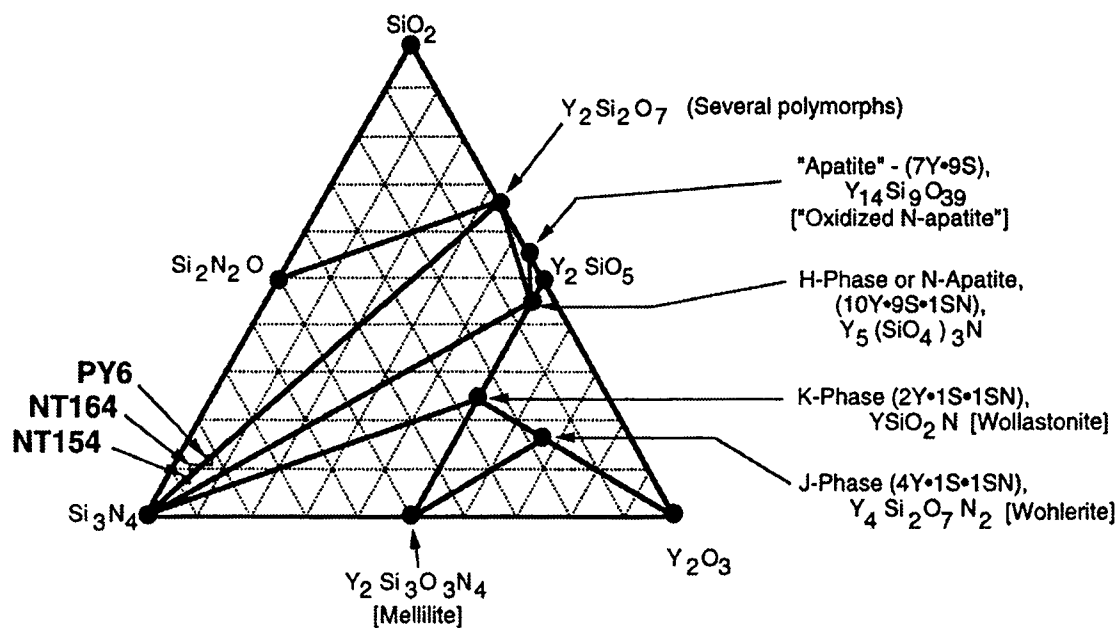


Fig. 3.17. Phase diagram of Si_3N_4 - SiO_2 - Y_2O_3 system showing intermediate phases.

oxygen content than the material 0.1 mm below the surface. This suggests that the high SiO in the protective atmosphere is sufficient to change the composition. The x-ray diffraction pattern at 0.5 mm for the as-sintered surface showed some crystalline material other than β -Si₃N₄, but it did not correspond to any Si-Y-O-N phase in the literature.

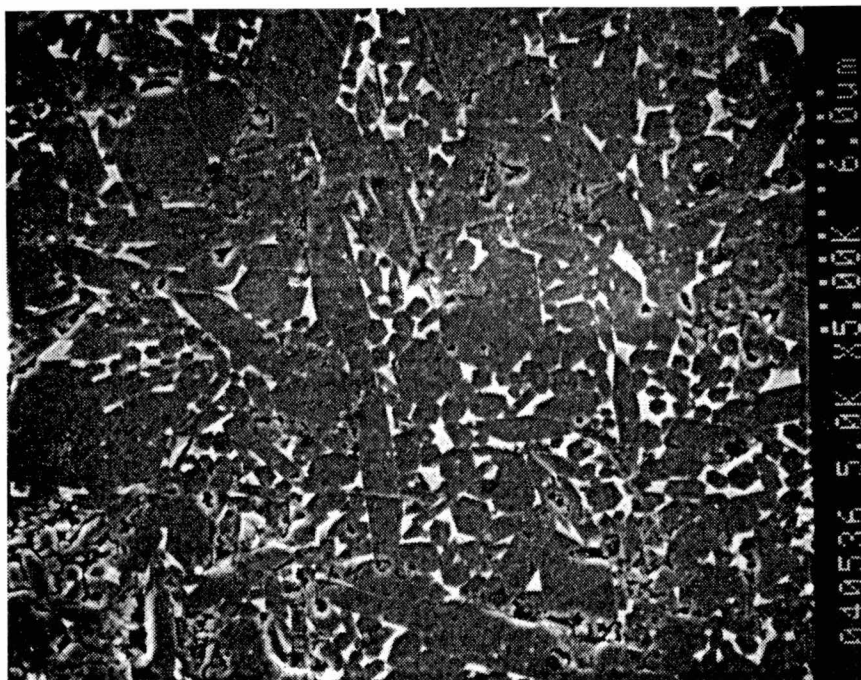
Microstructure Characterization

The microstructures were examined from the exposed as-sintered surfaces to the interior or bulk of the samples. Microstructural differences can be observed between material near the as-sintered surfaces compared to the bulk material. The polished and plasma etched surfaces of selected specimens from the physical/composition gradient study are shown in Figs. 3.18 through 3.21.

The specimen with Si₃N₄-Y₂O₃-Al₂O₃ composition shown in Fig. 3.18 exhibited larger grain sizes in the interior bulk as compared to the near surface region. As will be shown later, this difference is also reflected in the fracture toughness differential between the two areas. This particular specimen was sintered in a RBSN crucible with the Mix* packing powder combination at 1900°C/1950°C for 2h/2h at low nitrogen pressure. The observed weight loss was 1.7 wt. % and the visible reaction layer thickness was 0.98 mm. These conditions do not apparently result in sufficient nitrogen concentration to promote grain growth near the surface.

On the other hand, the sample with Si₃N₄-Y₂O₃-Al₂O₃ composition shown in Fig. 3.19 has larger grains in the near surface region. This particular specimen was sintered in a graphite crucible with the low oxygen packing powder combination at 1850°C/1900°C for 2h/2h at high nitrogen pressure. The observed weight loss was 1.1 wt. % and the visible reaction

(a)



(b)

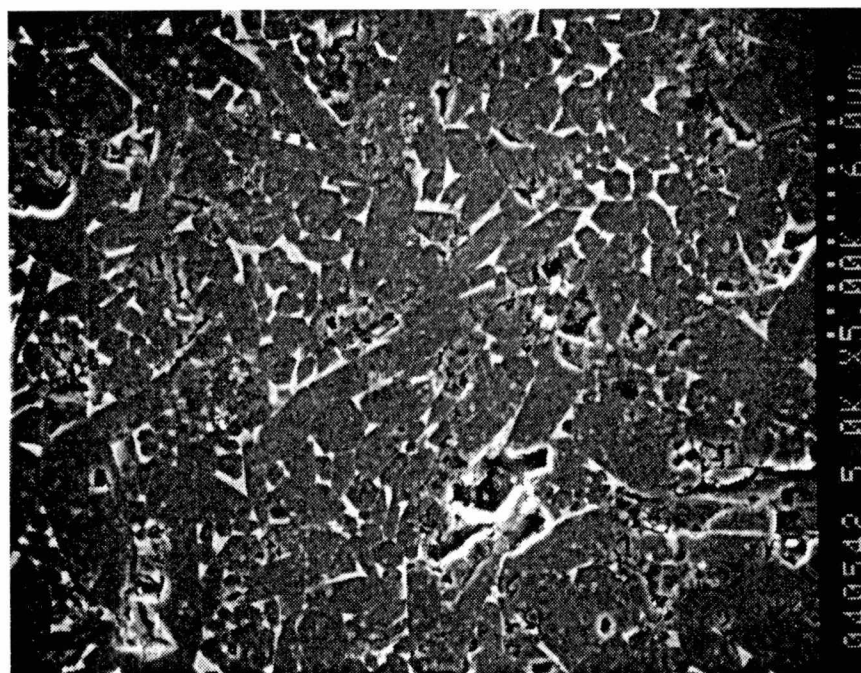
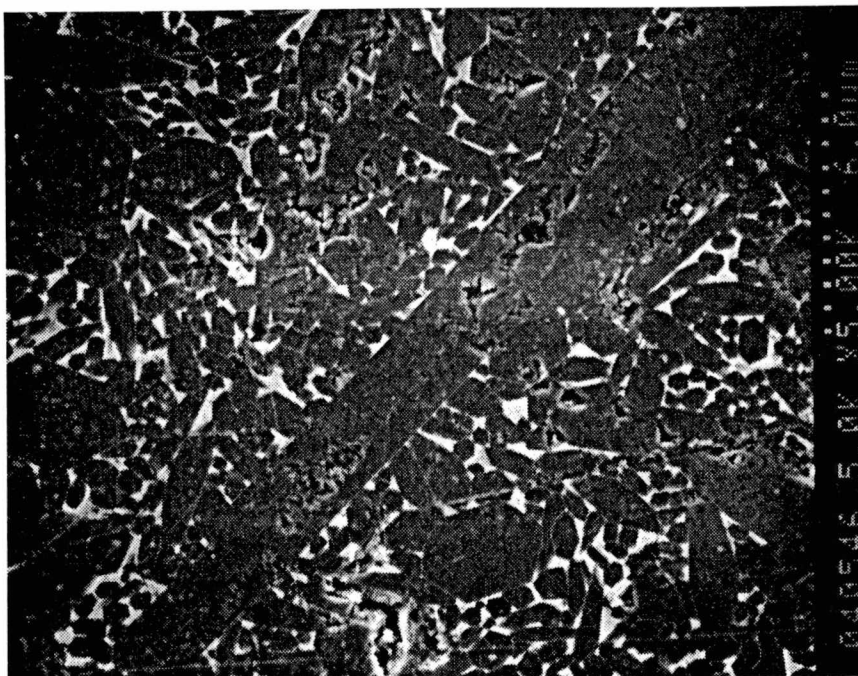


Fig. 3.18. Etched surface of sample TRSN-44-13 showing microstructure variation from the as-sintered surface into the specimen interior. (a) Near as-sintered surface, (b) ~1 mm from as-sintered surface, (c) ~2 mm from as-sintered surface and (d) $\gg 2$ mm from as-sintered surface in the bulk of the material.

(c)



(d)

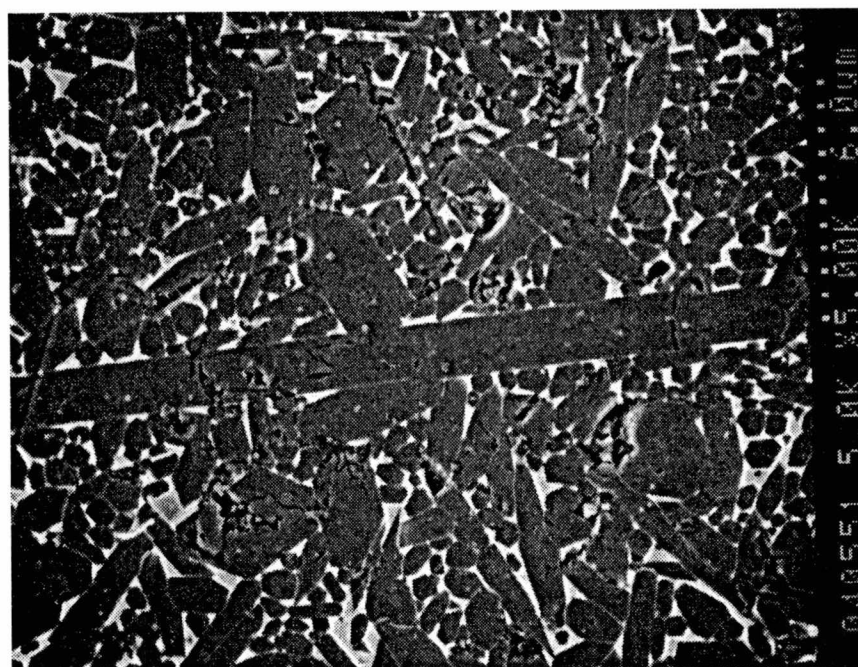
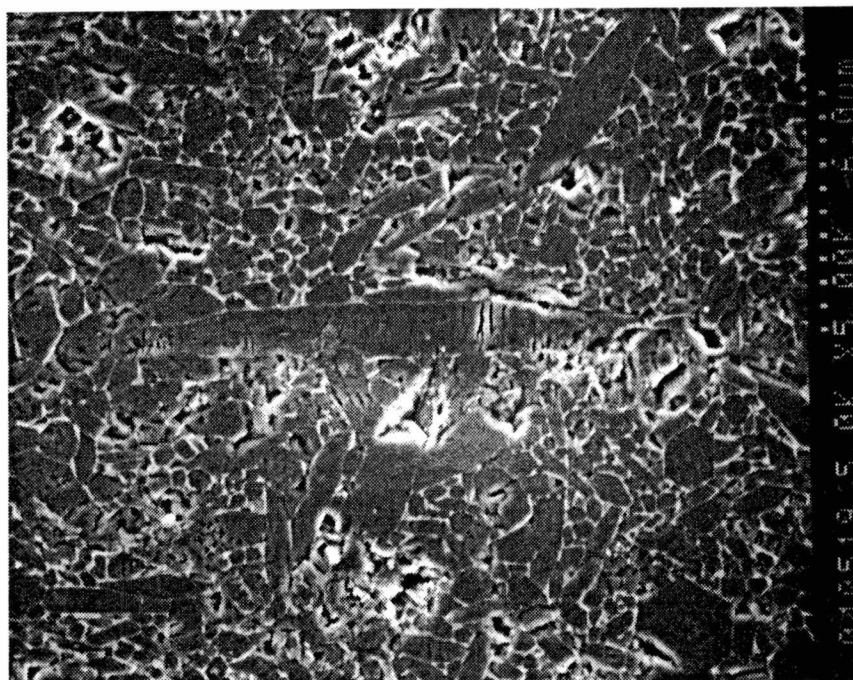


Fig. 3.18. (continued) Etched surface of sample TRSN-44-13 showing microstructure variation from the as-sintered surface into the specimen interior. (a) Near as-sintered surface, (b) ~1 mm from as-sintered surface, (c) ~2 mm from as-sintered surface and (d) >>2 mm from as-sintered surface in the bulk of the material.

(a)



(b)

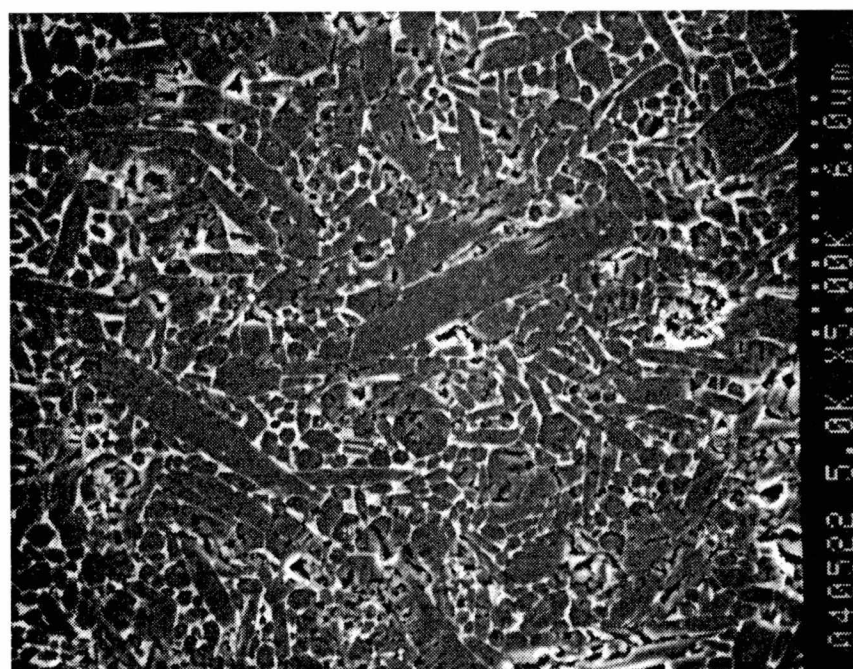
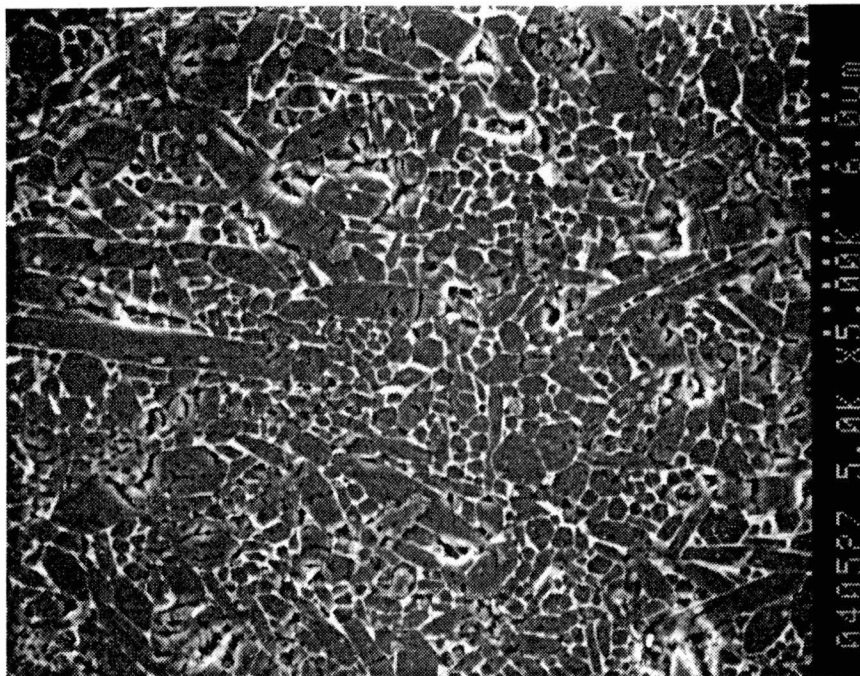


Fig. 3.19. Etched surface of sample TRSN-44-18 showing microstructure variation from the as-sintered surface into the specimen interior. (a) Near as-sintered surface, (b) ~1 mm from as-sintered surface, (c) ~2 mm from as-sintered surface and (d) >>2 mm from as-sintered surface in the bulk of the material.

(c)



(d)

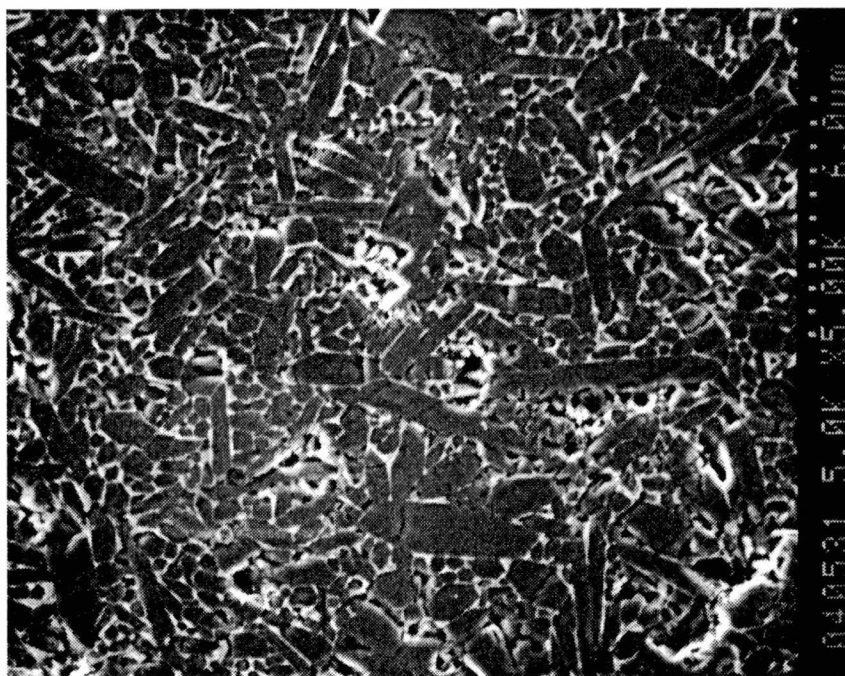


Fig. 3.19. (continued). Etched surface of sample TRSN-44-18 showing microstructure variation from the as-sintered surface into the specimen interior. (a) Near as-sintered surface, (b) ~1 mm from as-sintered surface, (c) ~2 mm from as-sintered surface and (d) >>2 mm from as-sintered surface in the bulk of the material.

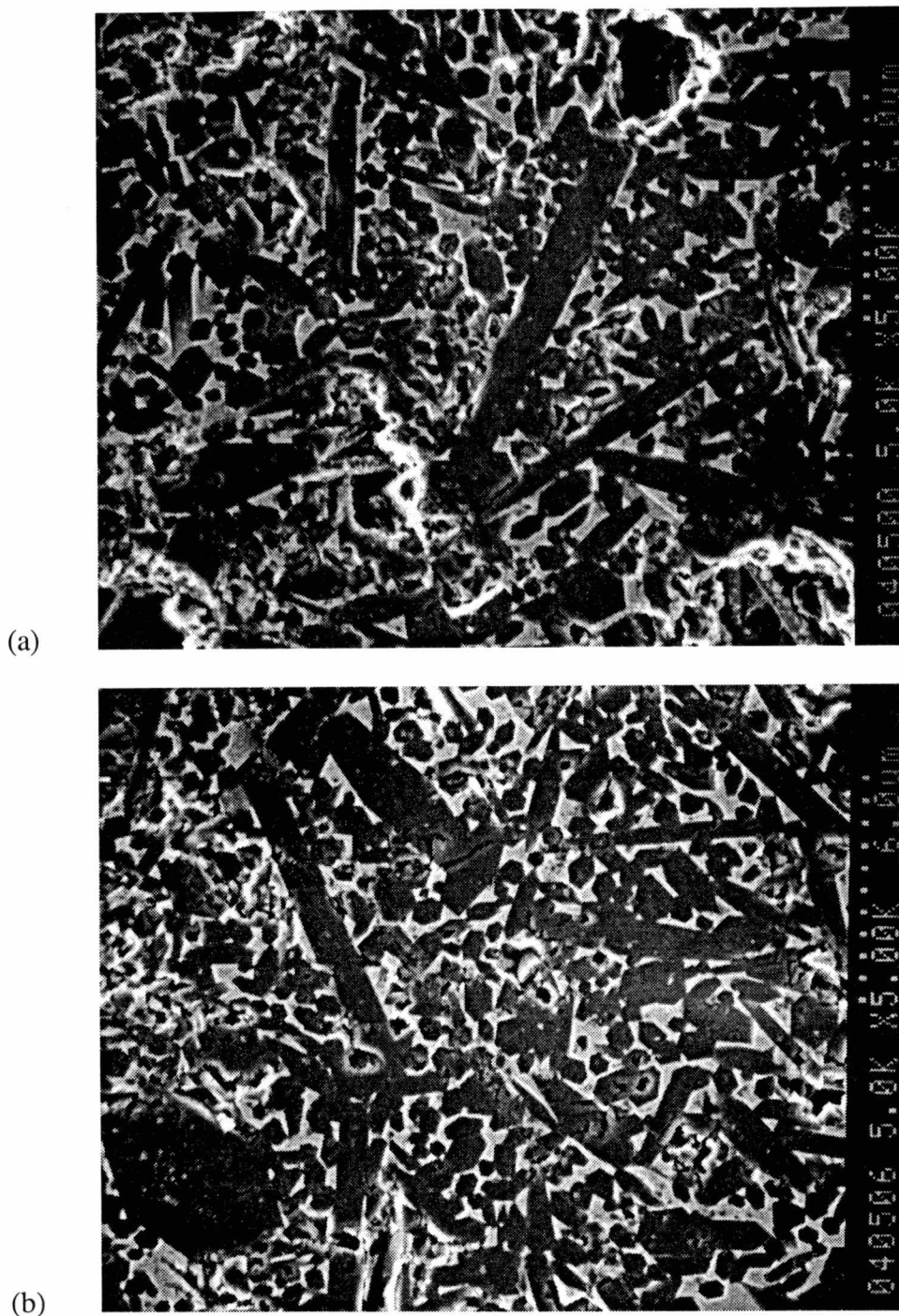
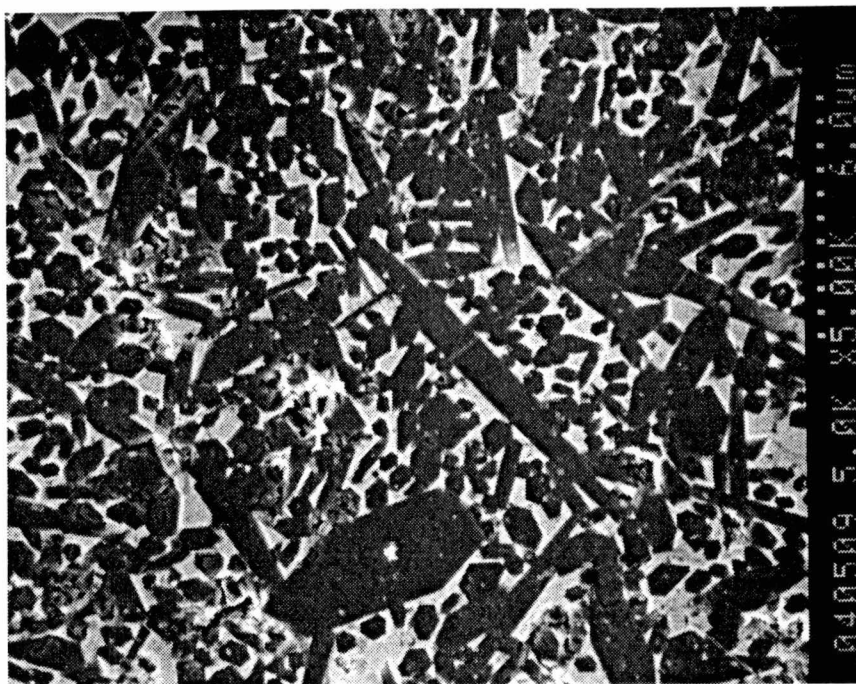
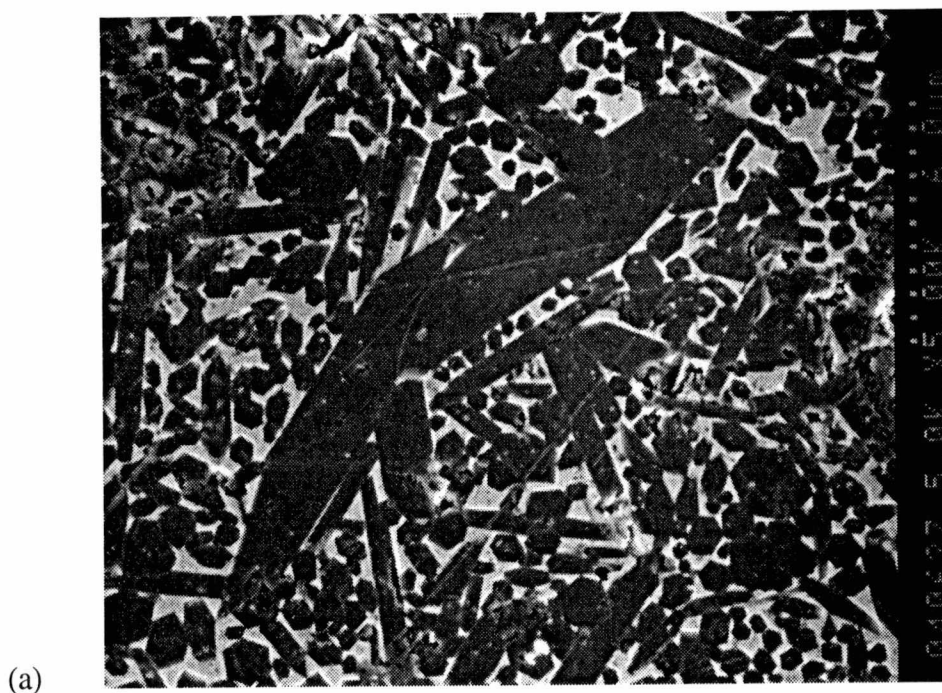


Fig. 3.20. Etched surface of sample TRSN-45-12 showing microstructure variation from the as-sintered surface into the specimen interior. (a) Near as-sintered surface, (b) ~1 mm from as-sintered surface, (c) $\gg 2$ mm from as-sintered surface in the bulk of the material.



(c)

Fig. 3.20 (continued). Etched surface of sample TRSN-45-12 showing microstructure variation from the as-sintered surface into the specimen interior. (a) Near as-sintered surface, (b) ~1 mm from as-sintered surface, (c) $\gg 2$ mm from as-sintered surface in the bulk of the material.



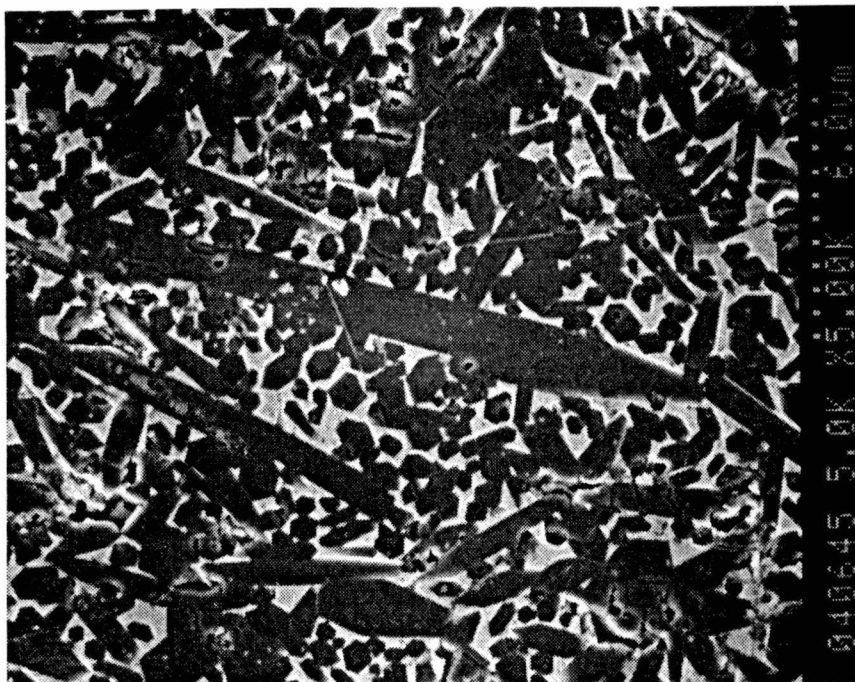
(a)



(b)

Fig. 3.21. Etched surface of sample TRSN-45-13 showing microstructure variation from the as-sintered surface into the specimen interior. (a) Near as-sintered surface, (b) ~ 1 mm from as-sintered surface, (c) ~ 2 mm from as-sintered surface and (d) $\gg 2$ mm from as-sintered surface in the bulk of the material.

(c)



(d)

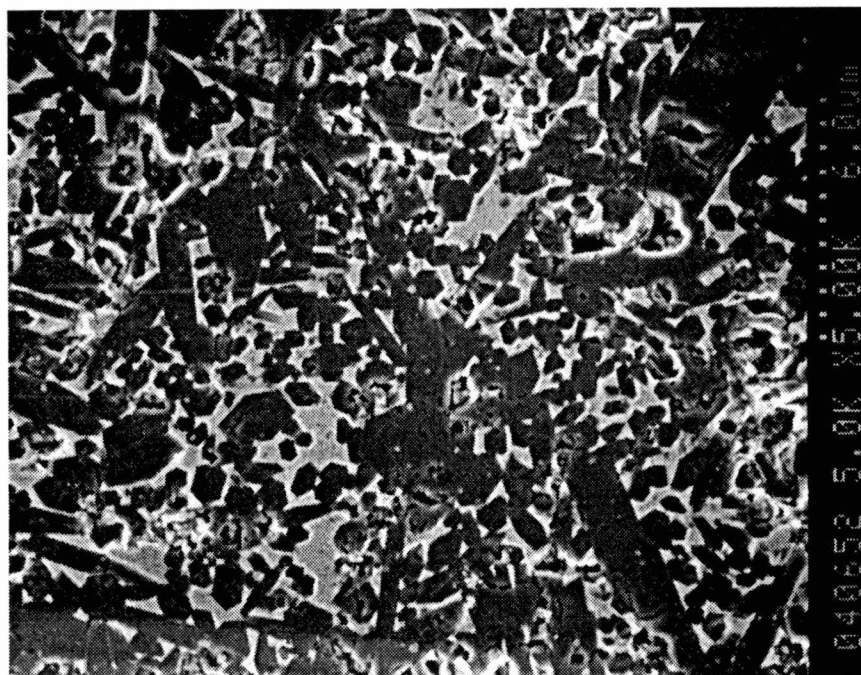


Fig. 3.21 (continued). Etched surface of sample TRSN-45-13 showing microstructure variation from the as-sintered surface into the specimen interior. (a) Near as-sintered surface, (b) ~1 mm from as-sintered surface, (c) ~2 mm from as-sintered surface and (d) >>2 mm from as-sintered surface in the bulk of the material.

layer thickness was 1.7 mm. In contrast, these conditions do apparently result in sufficient nitrogen concentration to promote grain growth near the surface.

The microstructure of a $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ containing material is shown in Fig. 3.20. As shown, larger grains were evident in the near surface region. This particular specimen was sintered in a BN crucible with no packing powder at 1900°C/1950°C for 2h/2h at low nitrogen pressure. The observed weight loss was 4.4 wt. % and the visible reaction layer thickness was 2.3 mm. These conditions result in appreciable increase in nitrogen concentration in the liquid phase in the near surface region and significant grain growth.

The microstructure variation observed in the $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ containing materials is also illustrated in Fig. 3.21. This particular specimen was sintered under the same conditions as the $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ composition material shown in Fig. 3.18. In other words, in a RBSN crucible with the Mix* packing powder combination at 1900°C/1950°C for 2h/2h at low nitrogen pressure. The observed weight loss was 4.8 wt. % and the visible reaction layer thickness was 2.8 mm. In contrast to the $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ composition material, these conditions do apparently result in sufficient nitrogen concentration to promote grain growth near the surface. This sample showed a significant differential in fracture toughness between the interior (lower) and the near surface regions (higher).

Generally, near the as-sintered surface in some samples, large $\beta\text{-Si}_3\text{N}_4$ grains can be observed, whereas at distances ≥ 0.5 mm from the surface grain sizes typical of the bulk material (>2 mm) are observed. At intermediate distances from the surface, median grain sizes can be seen. As will be discussed, the large grains near the as-sintered surfaces are a possible reason for the lower observed strengths and increase in fracture toughness. Also

the damage tolerance is related to the larger grain sizes and higher fracture toughness near the as-sintered surface.

An explanation for the appearance of large grains near the exposed surfaces is based on the changes in composition that take place in this region. The loss of SiO and Si from the as-sintered surfaces would tend to drive the composition in the near-surface region higher in nitrogen. Because of its generally lower concentration in the molten glass, nitrogen availability and diffusion in the liquid is considered to be the limiting species in the grain growth mechanism. Consequently, the oxygen loss and higher nitrogen concentration in the near-surface regions encourage grain growth of the β -Si₃N₄.

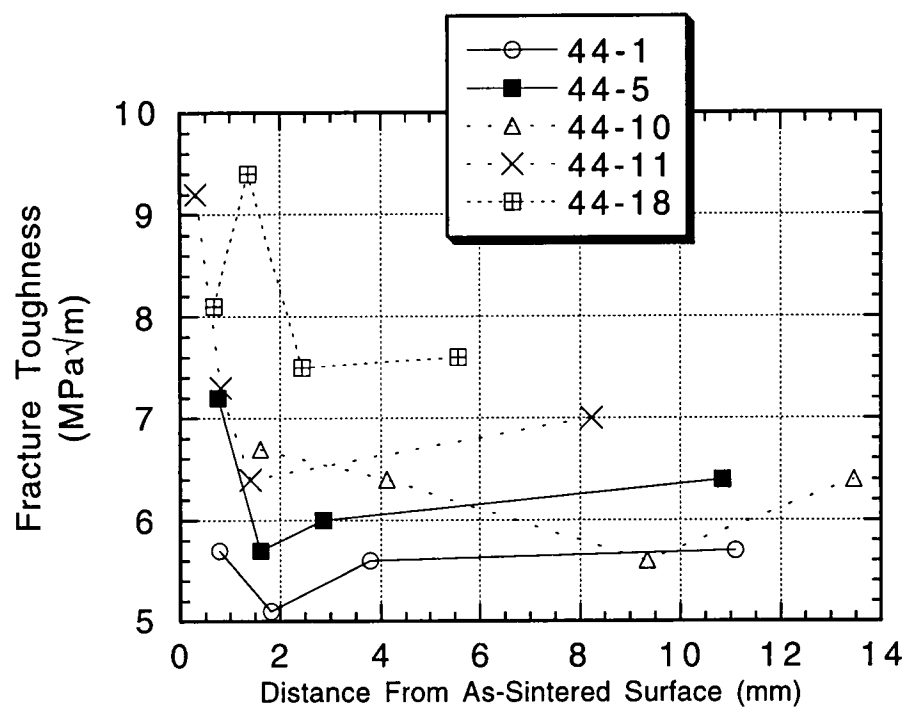
Mechanical Property Measurements Across Gradients

Specimens that attained $\geq 95\%$ T. D. were sectioned and polished. These include all of the Si₃N₄-6% Y₂O₃-2% Al₂O₃ samples and selected ones from the other two compositions. Variations in the indent fracture toughness (by two methods) and hardness were observed across the compositional and physical gradients as shown in Tables 3.17, 3.18 and 3.19.

The ANOVA results on the hardness shown in Table 3.21, indicates the packing powder, crucible type and setter material were all significant contributors (at the 99% confidence level) to the average hardness. Since the hardness is most affected by the density, these factors are important because of how they influenced the densification process. The fracture toughness ANOVA results indicated oxidized packing powder, BN crucible type and longer sintering times all contributed to higher fracture toughness.

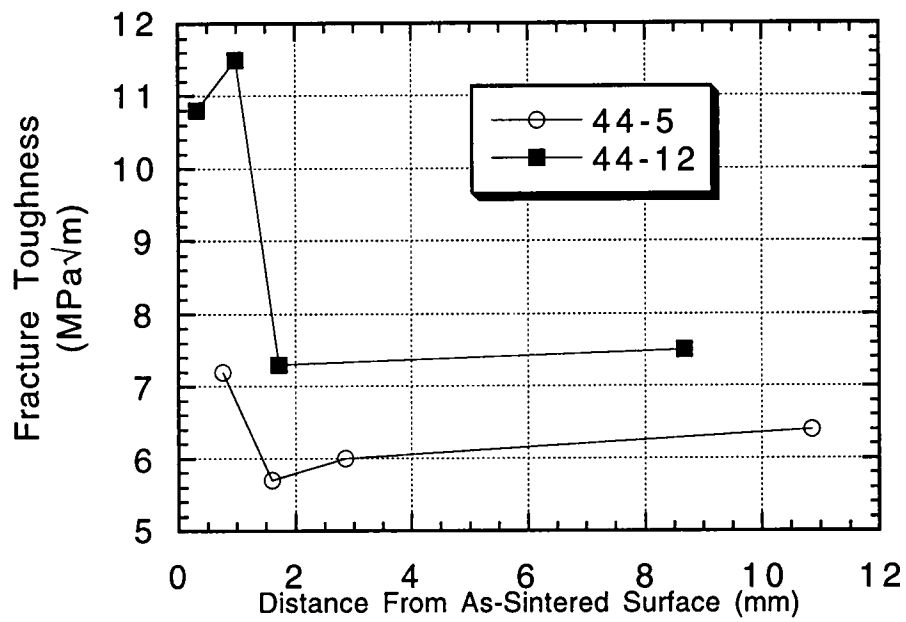
However, much more interesting from the standpoint of the physical and compositional gradient analysis is the difference in the toughness between the near-surface regions (< 1 mm) and the bulk fracture toughness (average of toughnesses >1 mm). These are the regions with distinct differences in microstructure and phase composition. Note that in the listing of the data in Tables 3.17, 3.18 and 3.19 positive numbers indicate higher fracture toughness at the surface compared to the bulk and negative numbers indicate higher toughnesses in the interior bulk of the specimens. The ANOVA results in Table 3.23 indicate the packing powder, crucible type, temperature and nitrogen pressure have major contributions to the toughness differential. From the data shown in Table 3.21, it is apparent that the same conditions for each of the variables promoting weight loss (i.e. SiO, Si and N) also exhibit the higher fracture toughness in the near-surface regions. These conditions would include 'None' as the packing powder, graphite crucibles, high temperatures and low nitrogen pressures. Such conditions would result in oxygen depletion in the near surface region and correspondingly this would increase the nitrogen concentration in the liquid phase. As just discussed, nitrogen is considered the limiting species in grain growth which was also observed in the near surface region. The larger grain size would increase the fracture toughness. A plot of the toughness as a function of distance from the as-sintered surface for the samples fired in graphite crucibles is shown in Fig. 3.22. The high toughness in the near surface region is clearly evident.

The mechanical properties of the specimens fired using the optimized sintering conditions were determined. These evaluations included testing of as-sintered surfaces as well as ones where the tensile surface of the MOR bars was at a set distance from the as-sintered surface. The change in flexural strength as a function of surface material removed is shown in Figs. 3.23 and 3.24. As indicated, the strength of as-sintered surfaces of



(a)

Fig. 3.22. Fracture toughness variations across physical/chemical gradients.



(b)

Fig. 3.22. (Continued) Fracture toughness variations across physical/chemical gradients.

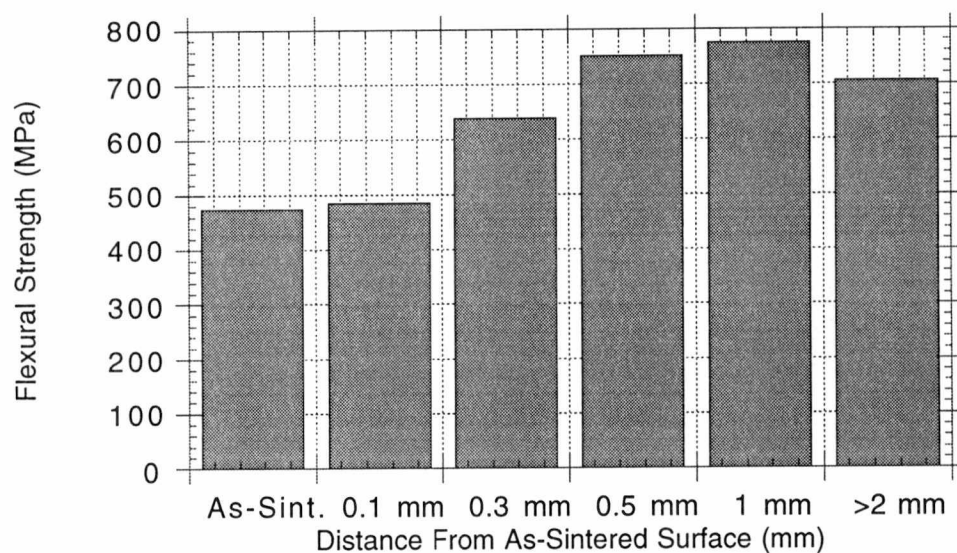


Fig. 3.23. Flexural strength of GPS Si₃N₄-6% Y₂O₃-2% Al₂O₃ as a function of material removed from the as-sintered surface. Bulk sintered density was 98.8 % T. D.

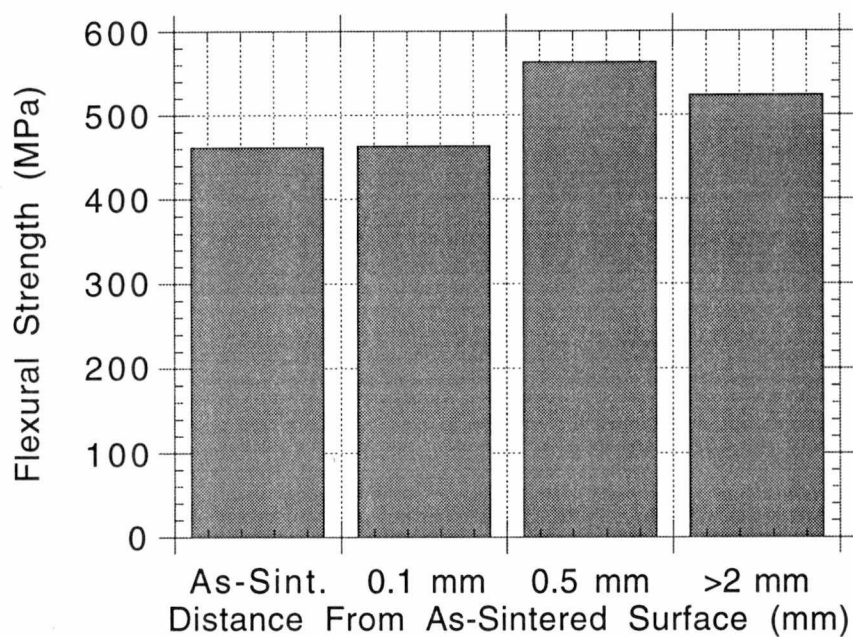


Fig. 3.24. Flexural strength of GPS $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ as a function of material removed from the as-sintered surface. Bulk sintered density was 100 % T. D.

specimens with composition $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ were reduced by more than 30% compared to the bulk material. The reduction in strength in the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ samples was not as dramatic at ~15%. In both cases, the bulk strengths were observed after removal of ≥ 0.5 mm of material from the as-sintered surfaces. This distance corresponds well to the region of low oxygen (and low oxygen phases) as observed in the electron microprobe examination and the x-ray phase analysis.

Also shown, are the strength changes that occur when a 10 kg diamond indent is made on the surface tensile surface of the test bar (Figs. 3.25 and 3.26). Interestingly, all of the strengths of the $\text{Si}_3\text{N}_4\text{-6\% Y}_2\text{O}_3\text{-2\% Al}_2\text{O}_3$ materials are reduced to about the same level even though the as-sintered and as-machined surface strengths are considerably different. In the case of the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ samples, the indented strength of the as-sintered surface was higher than the indented strength for the machined surfaces. Thus one can conclude that the damage tolerance of as-sintered surfaces from GPS silicon nitride is as good or better than machined surfaces. The good flaw tolerance of the as-sintered surfaces is attributable to the high fracture toughness in this region.

Gradient Formation Mechanisms

The data from these experiments indicate that oxygen diffuses out of the samples. Volatilization and loss of SiO from the specimen exposed surfaces is the major cause of weight loss from the samples. The loss of oxygen probably occurs by interstitial diffusion of molecular oxygen, which has been found to be the major transport mechanism in silicate glass melts.^{198,199} The data also show that the loss of SiO is concentrated at the surface and is diffusion controlled.

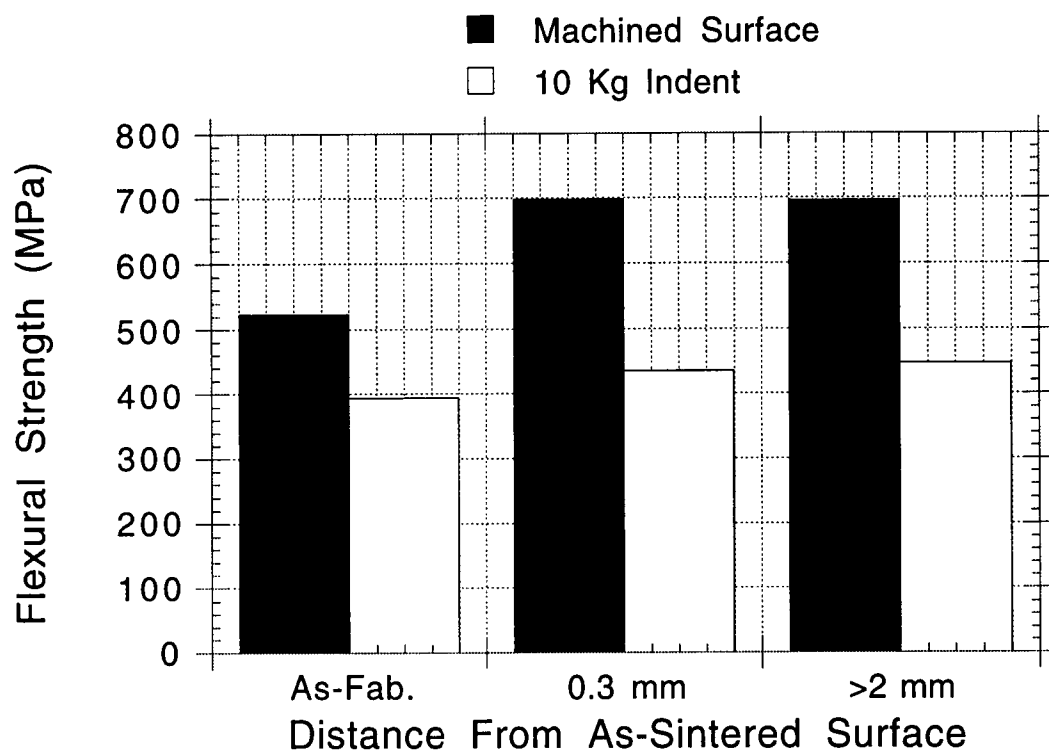


Fig. 3.25. Flexural strength of GPS Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 as a function of material removed from the as-sintered surface.

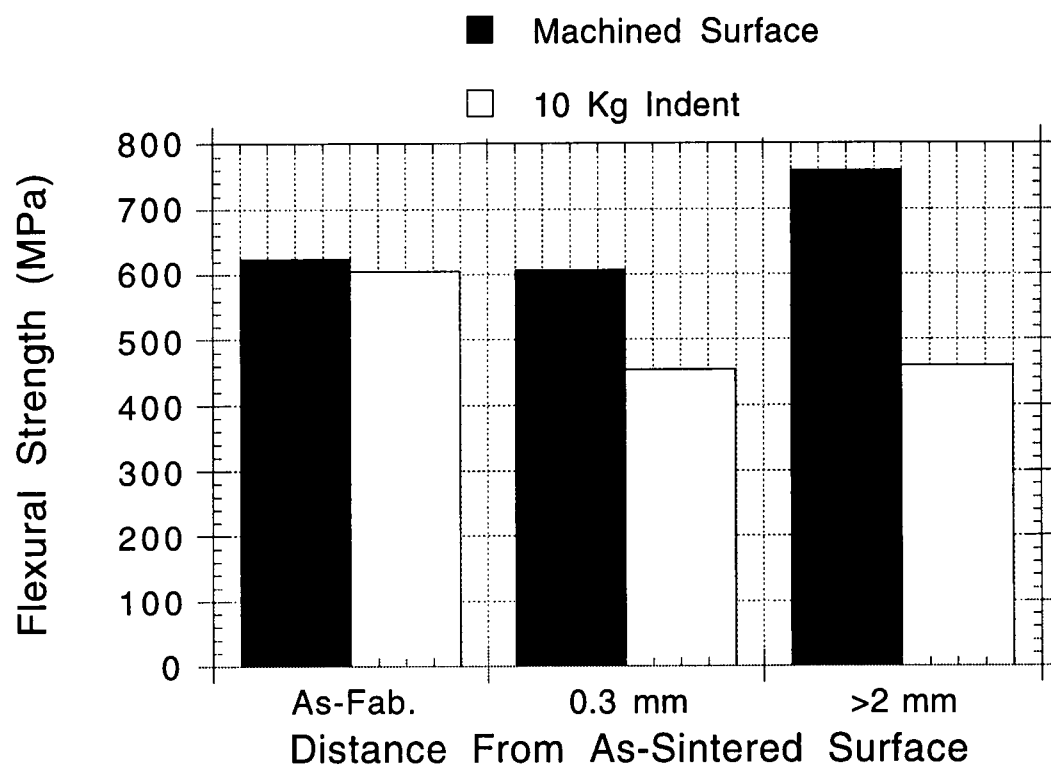


Fig. 3.26. Flexural strength of GPS $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ as a function of material removed from the as-sintered surface.

Simultaneous to the oxygen diffusion out, the high gas pressure can cause nitrogen to diffuse into the specimens. Nitrogen diffusivity in oxynitride glass melts is unknown, however, it has been estimated to be several orders of magnitude greater than oxygen diffusivity at temperatures of 1900°C. Other related data with silicate glasses (containing Na, K, Ca, and Mg) showed nitrogen diffusivity at 1100°C was $6.5 \times 10^{-2} \text{ cm}^2/\text{s}$ whereas oxygen diffusion was $1.5 \times 10^{-7} \text{ cm}^2/\text{s}$.¹⁹⁹ Thus, in the present results it is believed that nitrogen diffusion can permeate the entire volume of the specimens.

Nitrogen can dissolve into the liquid either physically or chemically. The physical solubility in the oxynitride intergranular liquid phases in silicon nitrides was estimated to be quite low on the order of $< 1 \times 10^{-4} \text{ g/cm}^3$ at temperatures of 1900°C and gas pressures of 5 MPa.²⁰¹ The chemical solubility was calculated to be more substantial, however, at the relatively low nitrogen overpressures used in these studies the chemical solubility is still considered low.²⁰¹ In any case, these conditions could only tend to increase the nitrogen contents in the liquid phase.

These phenomena suggest that the observed physical gradients are due, at least in part, to compositional changes across phase fields. The change in composition with SiO loss is illustrated in the $\text{Si}_3\text{N}_4\text{-YN-SiO}_2\text{-Y}_2\text{O}_3$ phase diagram (Fig. 3.27). It shows that the loss of SiO drives the composition across three tie lines between phase fields. the visual observation of distinct regions within the chemical/physical reaction layers also suggests phase composition variations similar to those observed in a diffusion couple. At the Si_3N_4 -melilite tie line, decomposition of Si_3N_4 would drive the composition up to the right. These conclusions correlate with the observed phases by x-ray diffraction, the oxygen deficient areas in the near surface region, the enhanced grain growth and increase in toughness observed to occur across the gradients.

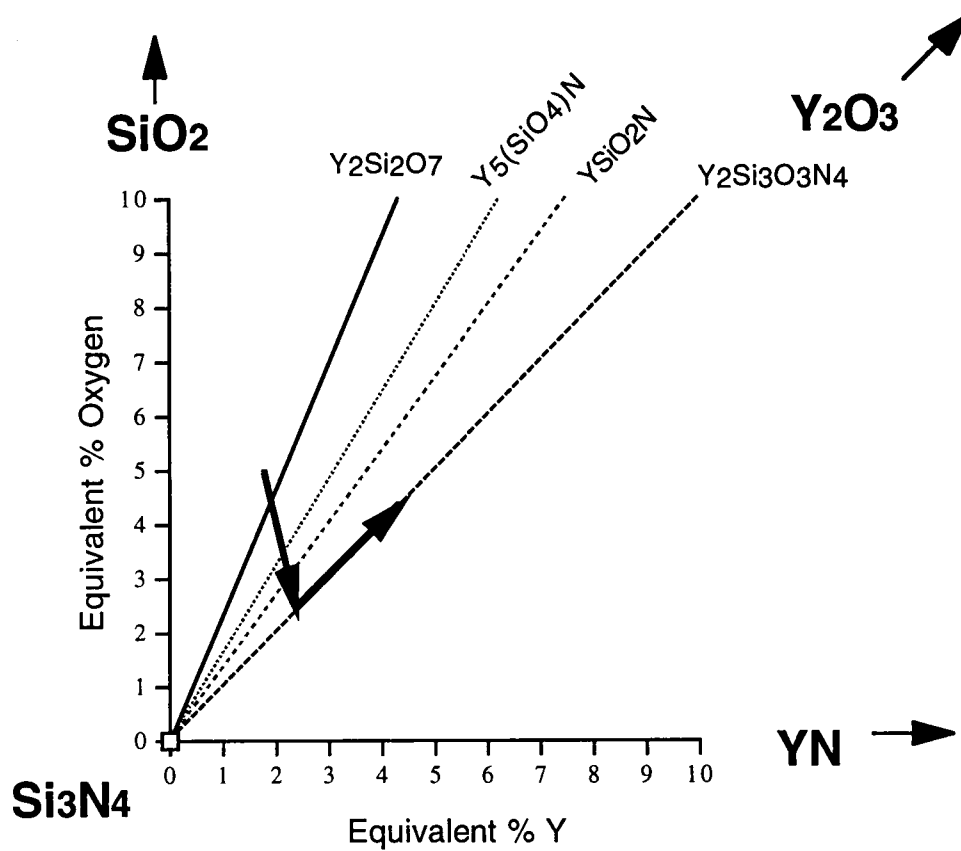


Fig. 3.27. Silicon nitride corner of the Si_3N_4 -YN- SiO_2 - Y_2O_3 phase diagram showing how the loss of SiO from GPS samples can result in compositional changes across several phase fields.

Conclusions

The results show that gas-pressure sintering (GPS) can be used to densify silicon nitride containing a wide variety of sintering additives. Parameters affecting the sintering behavior include the packing powder composition, crucible type, sintering temperature, nitrogen pressure, sintering time, use of barrier/protective coatings, and setter type. Optimum conditions for densification, minimization of weight loss and minimization of gradient layer thickness depend mainly on the sample composition.

During high temperature GPS processing, chemical and physical gradients develop from the exposed surfaces to the interior regions. The gradients are due to the furnace conditions and the environment adjacent to the samples. Loss of SiO from the exposed surfaces results in the formation of nitrogen-rich phases, such as melilite on the as-sintered surfaces. Along with the compositional gradients, mechanical property differences also exist between the as-sintered surfaces and the bulk materials.

The visible gradient thickness is related to the densification behavior of the different compositions. For example, the $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ composition exhibited fast densification and attained closed porosity quickly. Consequently, the visible gradient thickness was small. In comparison, the other two compositions retained open porosity conditions longer in the sintering schedule and developed much thicker gradient layers. The packing powder was the most significant parameter affecting the gradient layer thickness and the particular powder combination depended upon the sample composition. In general, the Mix* combination gave the thinnest gradient layer dimensions. This may be due to the fact that it decomposed to create the protective atmosphere, but was not in direct contact with the specimen surfaces. The visual examination of the samples revealed that the gradient layers

consisted of distinct zones reminiscent of a diffusion couple. The visible gradient dimensions were found to correspond well to the diffusivity of oxygen in silicate melts.

Observations on the weight losses during GPS, indicated that with graphite crucibles there are reactions that continuously deplete the protective atmosphere surrounding the specimens. The result was high weight losses. The type of packing powder was also found to impact the weight losses. Ones containing Si_3N_4 powder had lower weight losses than those without any (i.e. 'None' and BN). This indicates that in the case of no Si_3N_4 in the packing powder, the specimens themselves had to decompose to create the protective atmosphere. The results also showed the sintering temperature to have a significant contribution to the observed weight losses. As expected, lower temperatures produced lower weight losses. This suggests higher temperatures increase the equilibrium concentration of Si, O and N species in the atmosphere so the specimens or packing powder must decompose more. It is also indicative of a diffusion controlled process.

High nitrogen pressures during the second stage of sintering resulted in lower weight losses. This is consistent with the reaction that is believed to contribute to the weight losses. Namely, Si_3N_4 decomposition into Si and N. High nitrogen pressure would inhibit the decomposition and may even be incorporated into the liquid phase. Since the high nitrogen pressure was applied only during the second stage, this implies that oxygen loss occurs during the initial high temperature exposure and nitrogen is the major contributor to weight losses during the second stage.

While weight losses were associated with the presence of coatings, it is believed that it is due to the nature of the coatings applied in the present study and not to coatings in general. BN was the surface coating in the present case which may have inhibited densification and

maintained open porosity for an extended period. This would cause the observed high weight losses. Thus, it is concluded that coatings can be beneficial, but that these particular coatings are not.

The $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ materials densified well in all cases. For the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ and $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ compositions, temperature was the greatest contributor to achieving high densities. This is not surprising since these are both refractory compositions and the sintering conditions were minimal to obtaining good densification. In the study, BN packing powders, graphite crucibles and the presence of a surface coating were deemed to be the best for producing high densities. However, these parameters also contribute to high weight losses. It is believed that the loss of oxygen results in the formation of nitrogen-rich phases having high specific densities. Thus, a calculation of the theoretical density, using the phases for the initial composition with lower specific gravities, produces a misleading calculation of higher apparent density.

The loss of oxygen species from the exposed specimen surfaces causes an increase in the nitrogen concentration in the liquid phase in the near-surface region. Since nitrogen availability in the liquid is the limiting species for grain growth, the higher nitrogen concentration leads to the appearance of large grains near the surfaces compared to those developed in the bulk of the materials.

The changes in the microstructures across the gradients result in mechanical property differences. In some cases, high fracture toughness was observed in the near-surface regions. This was more evident when sintering parameters that promoted high weight losses (i.e. no packing powder, graphite crucibles, high temperatures and low nitrogen

pressures) were used. The fracture toughness was found to correlate well with the microstructure observations which indicated large grains in the near-surface region.

The strength of the as-sintered surfaces were low compared to the bulk of the materials. Bulk strength values were attained after ~0.5 mm of material was removed by machining from the as-sintered surfaces.

Electron microprobe profiles showed oxygen depletion in the near-surface regions. This suggests a oxygen diffusion mechanism and the diffusion distances are consistent with reported diffusivities in silicate melts. X-ray diffraction results confirmed the existence of nitrogen-rich phases in the near-surface regions.

The experimental results indicate that oxygen diffusion and volatilization occurs from the exposed specimen surfaces. This phenomenon results in high nitrogen contents in the near-surface region and suggests that the gradient layers are formed by compositional changes across phase fields.

CHAPTER IV

EFFECT OF SINTERING PARAMETERS ON MICROSTRUCTURE DEVELOPMENT DURING HIGH-TEMPERATURE GAS-PRESSURE- SINTERING

Obviously, the sintering conditions of temperature, time and heating rates will affect the microstructure development and properties. The kinetics and growth mechanisms of β - Si_3N_4 grains in oxynitride liquids have been studied extensively. Almost exclusively, however, the grain growth studies have used Y_2O_3 - Al_2O_3 as the sintering additives, densification temperatures $\leq 1800^\circ\text{C}$ and ambient nitrogen pressures (~ 1 ATM). Previous GPS studies have not examined the relationships between the various parameters. It is recognized that the understanding of the microstructure development during high temperature abnormal grain growth is limited.¹⁴⁶

The objective of this work was to examine the effects of GPS processing parameters on the densification, microstructure development and resultant mechanical properties of silicon nitride materials. A typical generic heating schedule for firing of ceramics is shown in Fig. 4.1. In any firing schedule such as the one shown, the important parameters affecting the microstructural development include the densification temperature, densification time, grain growth temperature, grain growth time and heating rates.

Other sintering parameters, such as packing powders, crucible types and nitrogen gas pressures were dealt with in the preceding chapter (Chapter 3). The goal was to identify the important sintering parameters related to the development of the interlocked elongated grain microstructure that are important for obtaining superior mechanical properties.

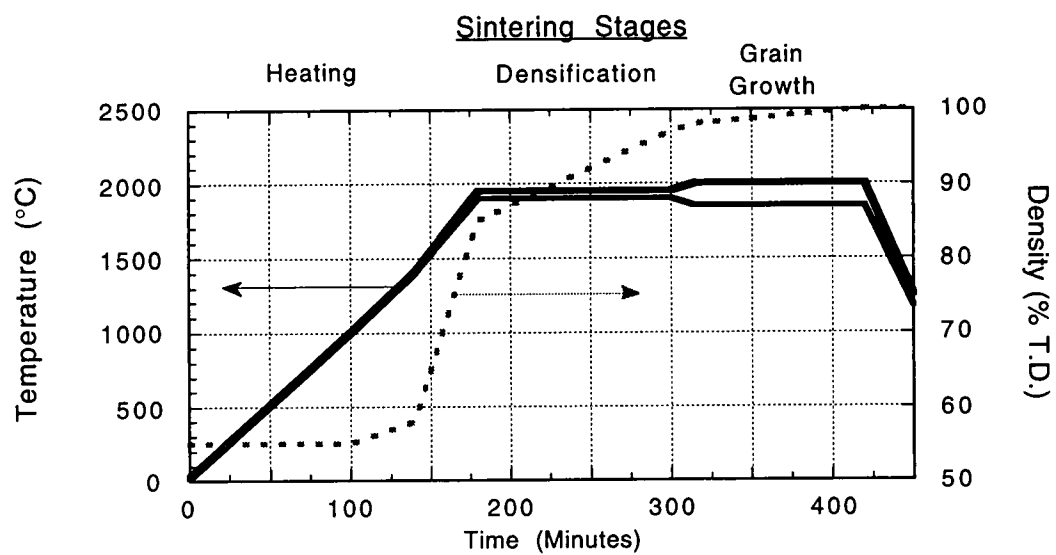


Fig. 4.1 Typical sintering schedule used to densify silicon nitride.

Experimental Design and Conditions

Fractional Factorial Experiments (Taguchi Orthogonal Arrays)

As discussed above, a number variables were studied. Thus, a Taguchi experimental orthogonal array was formulated to assess the impact of each of the variables on a two-step gas-pressure sintering process as shown in Table 4.1. The design was a L_8 ($4^1 \times 2^4$). As shown, the grain growth temperature examined four different temperatures, whereas the other parameters were examined at only two levels for each variable. prior to starting the experiments, the grain growth was believed to have the most effect on the mechanical properties. Consequently, it was afforded the greatest number of levels.

For each of the conditions, two compositions of silicon nitride with different intergranular phases were initially tested. These compositions are Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 , and Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen). These are two of the same compositions examined in Chapter 3.

Experimental Conditions

The starting materials consisted of appropriate amounts of Si_3N_4 , Al_2O_3 , La_2O_3 , Y_2O_3 , Yb_2O_3 , or SrO to form the desired intergranular phase.^a The oxygen content of the silicon nitride powders was taken into account in the calculation of the silica addition and milling was done in isopropanol to minimize any oxygen pickup during processing. The powders were turbomilled for ~2 h (1.3 wt.% PVP^b and 1 wt.% Darvan^c were added as dispersants)

^a Si_3N_4 - Ube, Japan, E10; Al_2O_3 - Reynolds, Malakoff, TX, RC-HP DBM; La_2O_3 , Y_2O_3 , Yb_2O_3 - Molycorp, White Plains, NY; >99.9%; SrO as SrCO_3 ; Mallinckrodt, St. Louis, MO; Reagent Grade

^b GAF Chemicals, Wayne, NJ: Polyvinylpyrrolidone K-15 ^c R. T. Vanderbilt, Norwalk, CT, 821A,

Table 4.1. Taguchi experimental design array for optimization of densification parameters to obtain silicon nitride ceramics with improved mechanical properties. The design is a L₈ (4¹ x 2⁴).

Test No.	Second Sintering Temperature (°C)	First Sintering Temperature (°C)	First Sintering Time (h) ^a	Second Sintering Time (h)	Heating Rate to First Sintering Temperature (°C/min)
1	2000	1900	2 (Min)	2	25
2	2000	1950	2.5 (Min+1)	1	10
3	1950	1900	2 (Min)	1	10
4	1950	1950	2.5 (Min+1)	2	25
5	1900	1900	3 (Min+1)	2	10
6	1900	1950	1.5 (Min)	1	25
7	1850	1900	3 (Min+1)	1	25
8	1850	1950	1.5 (Min)	2	10

^a Minimum time to obtain closed porosity (1900°C - 2h, 1950°C - 1.5h) with either no further hold time or a 1h additional hold time. Times defined as minimum (min) or minimum plus 1h (min + 1).

to fully deagglomerate and mix the various constituents. The mixtures were dried, screened to -200 mesh and isopressed at 207 MPa into discs approximately 7 cm in diameter and 2 cm thick. Binder burnout consisted of a heat-treatment to 600°C in air prior to sintering.

Sintering was performed in a graphite element furnace with gas overpressure capability. Based on the results from the previous chapter, the specimens were contained in BN crucibles with excess packing powder that was not in direct contact with the sample surfaces.

Densities were determined by the Archimedes' method. Selected samples of high density were machined into bend bar specimens with nominal dimensions of 3 mm x 4 mm x 50 mm. Flexural strength testing was done in four point bending with inner and outer spans of 20 mm and 40 mm, respectively. Fracture toughness was determined by an indentation and fracture method.

Results

Summaries of the densification, flexural strength and fracture toughness results are given in Tables 4.2 and 4.3 for the two different compositions. Initially, the high heating rate was to be 50°C/min in the Taguchi experimental array. However, during the first two sintering runs at this high heating rate, severe cracking of the samples with the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition occurred. Consequently, the high heating rate for the Taguchi experimental array was decreased to 25°C so intact samples could be obtained and the mechanical properties measured. As shown, high densities were achieved for all of the samples in the experimental array. Consequently, no significant effects on the final

densification were due to the processing conditions chosen. The conditions had been selected to obtain high densities so the effects on the flexural strength and fracture toughness could be better determined. The densities of the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ materials did show a slightly lower density with shorter densification times and lower grain growth temperatures as indicated in Figs. 4.2 and 4.3.

Summaries of the results for grand averages, variable mean level effects and the variable total effect of the orthogonal arrays are given in Tables 4.4 and 4.5. The summaries of the ANOVA results for the statistical parameters on the orthogonal arrays for the flexural strength and fracture toughness for the two different compositions are given in Tables 4.6 through 4.9. The combined optimum conditions for each of the variable levels for maximizing the strength and fracture toughness are given in Tables 4.10 and 4.11.

Discussion of Results

As indicated in Table 4.4 for the strength of the $\text{Si}_3\text{N}_4\text{-6\% Y}_2\text{O}_3\text{-2\% Al}_2\text{O}_3$ samples, the greatest total effect was attributed to the densification temperature, although the densification time and grain growth temperature both showed high total effects for the variable levels shown. The level effects for the different variables on the flexural strength of $\text{Si}_3\text{N}_4\text{-6\% Y}_2\text{O}_3\text{-2\% Al}_2\text{O}_3$ are graphically shown in Figs. 4.4 through 4.8.

The ANOVA results (Table 4.6), however, indicate the major contributors to the flexural strength at the $\geq 95\%$ confidence level were the densification temperature and densification time only. The large contribution for error associated with the strength, shown in Table 4.6, indicates one or more of several possibilities. It could be that some important factors were omitted, the experimental conditions were not controlled well, or measurement error

Table 4.2. Results from Taguchi experimental design array for optimization of densification parameters to obtain silicon nitride ceramics with improved mechanical properties. Composition is Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 . The design is a L_8 ($4^1 \times 2^4$). Only the first eight tests were used in the Taguchi evaluation.

Test No.	Final Sinter. Temp. (°C)	Initial Sinter. Temp. (°C)	Initial Sinter. Time (h) ^a	Final Sinter. Time (h)	Heating Rate to Initial Sinter. Temp. (°C/min)	Sintered Density (g/cm ³ , % T.D.)	Flexural Strength (MPa)	Fracture Toughness (MPa√m)
1	2000	1900	2 (Min)	2	25	3.24 99.4	679±41	8.4±0.3
2	2000	1950	2.5 (Min+1)	1	10	3.24 99.4	749±49	8.0±0.1
3	1950	1900	2 (Min)	1	10	3.24 99.3	542±37	8.3±0.1
4	1950	1950	2.5 (Min+1)	2	25	3.21 98.6	817±62	8.0±0.2
5	1900	1900	3 (Min+1)	2	10	3.25 99.6	627±52	8.2±0.2
6	1900	1950	1.5 (Min)	1	25	3.24 99.5	651±87	7.5±0.3
7	1850	1900	3 (Min+1)	1	25	3.23 99.1	662±37	8.2±0.1
8	1850	1950	1.5 (Min)	2	10	3.22 98.9	653±65	8.0±0.6
9	2000	1900	2 (Min)	0.1	25	3.22 98.7	653±65	7.9±0.4
10	1900	1950	1.5 (Min)	1	50	3.22 98.7	464±55	8.1±0.1

^a Minimum time to obtain closed porosity (1900°C - 2h, 1950°C - 1.5h) with either no further hold time or a 1h additional hold time. Times defined as minimum (min) or minimum plus 1h (min + 1).

Table 4.3. Results from Taguchi experimental design array for optimization of densification parameters to obtain silicon nitride ceramics with improved mechanical properties. Composition is $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen). The design is a L_8 ($4^1 \times 2^4$). Only the first eight tests were used in the Taguchi evaluation.

Test No.	Final Sinter. Temp. (°C)	Initial Sinter. Temp. (°C)	Initial Sinter. Time (h) ^a	Final Sinter. Time (h)	Heating Rate to Initial Sinter. Temp. (°C/min)	Sintered Density (g/cm ³ , % T.D.)	Flexural Strength (MPa)	Fracture Toughness (MPa√m)
1	2000	1900	2 (Min)	2	25	3.51 100	607±160	7.0±0.3
2	2000	1950	2.5 (Min+1)	1	10	3.50 100.0	574±47	5.7±0.5
3	1950	1900	2 (Min)	1	10	3.30 94.2	400	6.1
4	1950	1950	2.5 (Min+1)	2	25	3.48 99.2	503±43	5.0±0.5
5	1900	1900	3 (Min+1)	2	10	3.50 100.0	550±42	7.5±0.7
6	1900	1950	1.5 (Min)	1	25	3.46 98.8	428	4.7
7	1850	1900	3 (Min+1)	1	25	3.47 99.1	396±52	4.3±0.2
8	1850	1950	1.5 (Min)	2	10	3.42 97.7	362±38	4.6±0.1
9	2000	1900	2 (Min)	0.1	25	3.52 100	580±57	7.4±0.1
10	1900	1950	1.5 (Min)	1	50	3.31 95.1	428±47	4.9±0.2

^a Minimum time to obtain closed porosity (1900°C - 2h, 1950°C - 1.5h) with either no further hold time or a 1h additional hold time. Times defined as minimum (min) or minimum plus 1h (min + 1).

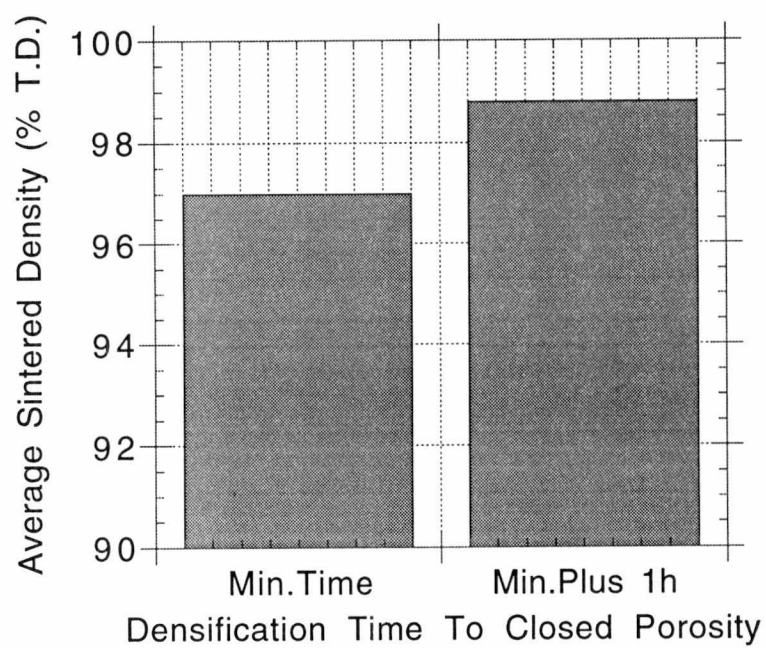


Fig. 4.2. Effect of densification time on the final densities of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ materials.

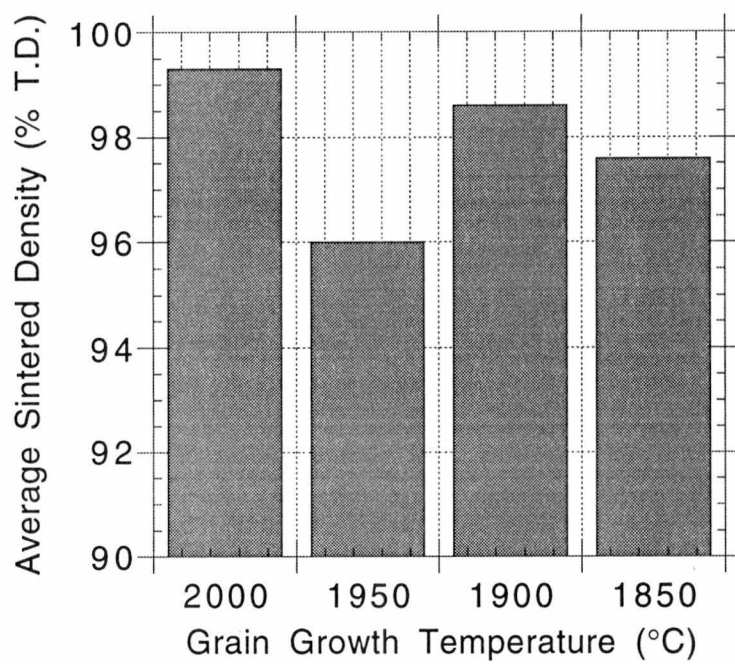


Fig. 4.3. Effect of grain growth temperature on the final densities of Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ materials.

Table 4.4. Summary of ANOVA results for the grand average and variable level effects for the Taguchi array to investigate GPS conditions on strength and toughness for the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition.

	Flexural Strength (MPa)	Fracture Toughness ($\text{MPa}\sqrt{\text{m}}$)
Grand Average	672.5	8.075
Grain Growth Temperature ($^{\circ}\text{C}$)		
2000	714	8.2
1950	679.5	8.15
1900	639	7.85
1850	657.5	8.1
Total Effect	75	0.35
Densification Temperature ($^{\circ}\text{C}$)		
1900	627.5	8.275
1950	717.5	7.875
Total Effect	90	0.4
Densification Time (Time to closed porosity)		
Min	631.25	8.05
Min+1	713.75	8.1
Total Effect	82.5	0.05
Grain Growth Time (Hours)		
2	694	8.15
1	651	8
Total Effect	43	0.15
Heating Rate ($^{\circ}\text{C}/\text{min}$)		
25	702.25	8.025
10	642.75	8.125
Total Effect	59.5	0.1

Table 4.5. Summary of ANOVA results for the grand average and variable level effects for the Taguchi array to investigate GPS conditions on strength and toughness for the Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition.

	Flexural Strength (MPa)	Fracture Toughness ($\text{MPa}\sqrt{\text{m}}$)
Grand Average	490	5.6125
Grain Growth Temperature ($^{\circ}\text{C}$)		
2000	590.5	6.35
1950	501.5	5.55
1900	489	6.1
1850	379	4.45
Total Effect	101.5	1.90
Densification Temperature ($^{\circ}\text{C}$)		
1900	513.25	6.225
1950	466.75	5
Total Effect	46.5	1.225
Densification Time (Time to closed porosity)		
Min	474.25	5.6
Min+1	505.75	5.625
Total Effect	31.5	0.025
Grain Growth Time (Hours)		
2	505.5	6.025
1	474.5	5.2
Total Effect	31	0.825
Heating Rate ($^{\circ}\text{C}/\text{min}$)		
25	483.5	5.25
10	496.5	5.975
Total Effect	13	0.725

Table 4.6. Summary of results on ANOVA of Taguchi array on The Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition for examination of the strength.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Grain Growth Temperature	3	6237	2079	1.03	2.92	4.07	7.59	162.00	0.3
Densification Temperature	1	16200	16200	8.00	3.46	5.32	11.3	14175.0	22.5
Densification Time	1	13612	13613	6.72	3.46	5.32	11.3	11587.5	18.4
Grain Growth Time	1	3698	3698	1.83	3.46	5.32	11.3	1673.00	2.7
Heating Rate	1	7080	7080	3.50	3.46	5.32	11.3	5055.5	8.0
Error	8	16200	2025						48.2

Table 4.7. Summary of results on ANOVA of Taguchi array on The Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition for examination of the fracture toughness.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Grain Growth Temperature	3	0.145	0.0483	1.21	2.92	4.07	7.59	0.03	2.9
Densification Temperature	1	0.32	0.32	8.00	3.46	5.32	11.3	0.28	32.7
Densification Time	1	0.005	0.005	0.12	3.46	5.32	11.3	-0.04	0.0
Grain Growth Time	1	0.045	0.045	1.12	3.46	5.32	11.3	0.00	0.6
Heating Rate	1	0.02	0.02	0.50	3.46	5.32	11.3	-0.02	0.0
Error	8	0.32	0.04						63.7

Table 4.8. Summary of results on ANOVA of Taguchi array on $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition for examination of the strength.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Grain Growth Temperature	3	45109	15036.3	27.82	2.92	4.07	7.59	43487.3	75.0
Densification Temperature	1	4324.5	4324.5	8.00	3.46	5.32	11.3	3783.9	6.5
Densification Time	1	1984.5	1984.5	3.67	3.46	5.32	11.3	1443.9	2.5
Grain Growth Time	1	1922	1922	3.56	3.46	5.32	11.3	1381.4	2.4
Heating Rate	1	338	338	0.63	3.46	5.32	11.3	-202.5	0.0
Error	8	4324.5	540.563						13.6

Table 4.9. Summary of results on ANOVA of Taguchi array on $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition for examination of the fracture toughness.

Variable	Degree of Freedom	Sum of the Squares	Mean Squares	F	90% Confidence Level	95% Confidence Level	99% Confidence Level	Pure Sum	% Contribution
Grain Growth Temperature	3	4.2737	1.4246	3.80	2.92	4.07	7.59	3.15	24.8
Densification Temperature	1	3.0012	3.0013	8.00	3.46	5.32	11.3	2.63	20.7
Densification Time	1	0.0012	0.0013	0.00	3.46	5.32	11.3	-0.37	0.0
Grain Growth Time	1	1.3612	1.3613	3.63	3.46	5.32	11.3	0.99	7.8
Heating Rate	1	1.0512	1.0513	2.80	3.46	5.32	11.3	0.68	5.3
Error	8	3.00	0.3752						41.4

Table 4.10. Optimum sintering conditions to maximize flexural strength and fracture toughness of Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 during gas pressure sintering.

Sintering Condition Variable	Optimum Condition to Maximize Strength	Variable to Significance	Optimum Condition to Maximize Toughness	Variable to Significance	Combined Optimum Conditions
Grain Growth Temp. ($^{\circ}\text{C}$)	2000 $^{\circ}\text{C}$	Moderate	2000 $^{\circ}\text{C}$	Very Low	2000 $^{\circ}\text{C}$
Densification Temp. ($^{\circ}\text{C}$)	1950 $^{\circ}\text{C}$	Moderate	1900 $^{\circ}\text{C}$	Moderate	1900 $^{\circ}\text{C}$
Densification Time (h) ^a	3 (Min+1)	Moderate	Either	None	2 (Min)
Grain Growth Time (h)	2	Low	2	Very Low	2
Heating Rate to Densification Temperature ($^{\circ}\text{C}/\text{min}$)	25 $^{\circ}\text{C}/\text{min}$	Moderate	10 $^{\circ}\text{C}/\text{min}$	Very Low	25 $^{\circ}\text{C}/\text{min}$

^a Minimum time to obtain closed porosity (1900 $^{\circ}\text{C}$ - 2h, 1950 $^{\circ}\text{C}$ - 1.5h) with either no further hold time or a 1h additional hold time. Times defined as minimum (min) or minimum plus 1h (min + 1).

Table 4.11. Optimum sintering conditions to maximize flexural strength and fracture toughness of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen). during gas pressure sintering.

Sintering Condition Variable	Optimum Condition to Maximize Strength	Variable to Significance	Optimum Condition to Maximize Toughness	Variable to Significance	Combined Optimum Conditions
Grain Growth Temp. (°C)	2000°C	High	2000°C	Moderate	2000°C
Densification Temp. (°C)	1900°C	Moderate	1900°C	High	1900°C
Densification Time (h) ^a	3 (Min+1)	Low	2 (Min)	Moderate	2 (Min)
Grain Growth Time (h)	2	Low	2	Moderate	2
Heating Rate to Densification Temperature (°C/min)	25 °C/min	Very Low	10°C/min	High	10°C/min

^a Minimum time to obtain closed porosity (1900°C - 2h, 1950°C - 1.5h) with either no further hold time or a 1h additional hold time. Times defined as minimum (min) or minimum plus 1h (min + 1).

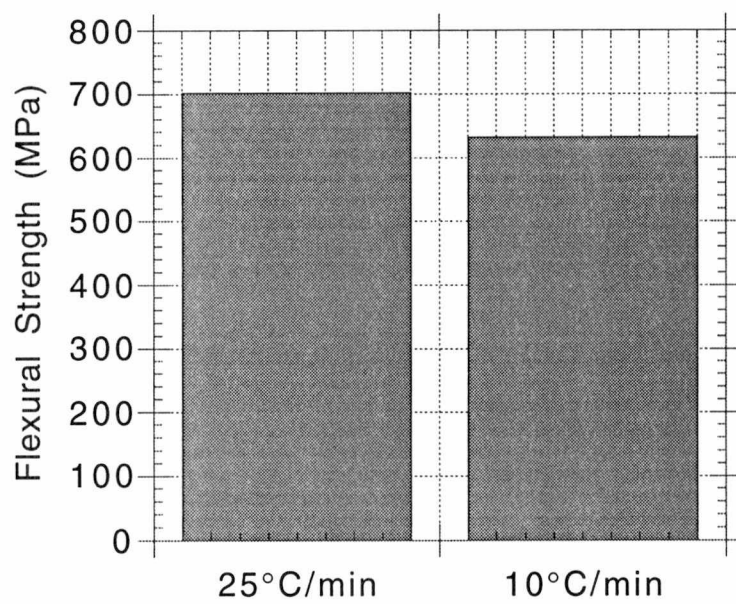


Fig. 4.4. Effect of heating rate on flexural strength of Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

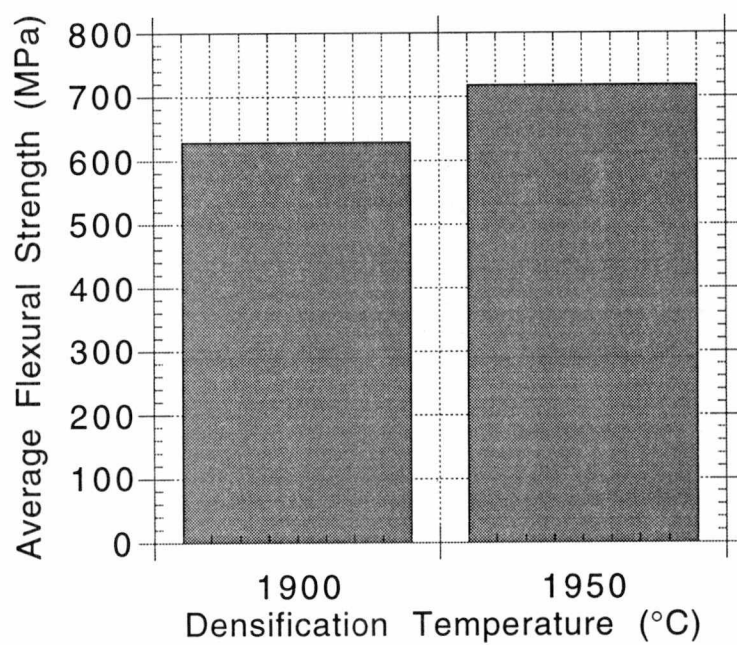


Fig. 4.5. Effect of densification temperature on flexural strength of Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

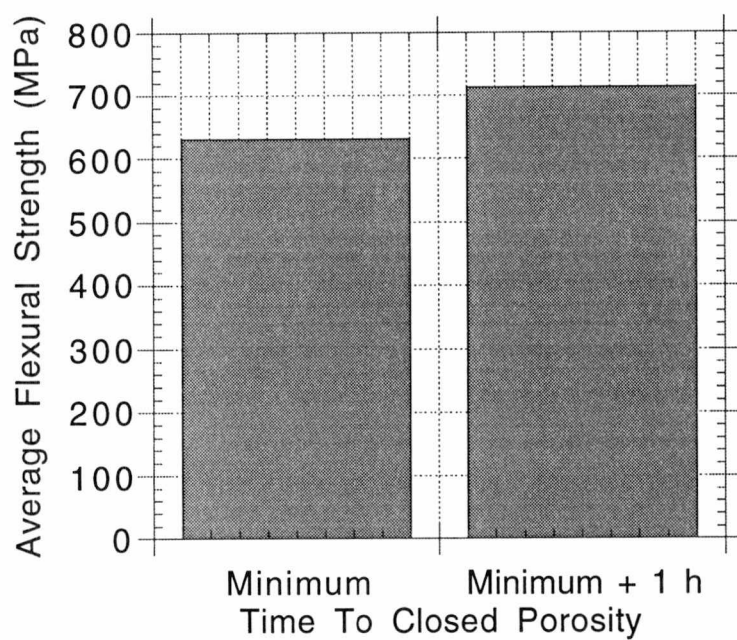


Fig. 4.6. Effect of densification time on the average flexural strength of gas pressure sintered Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

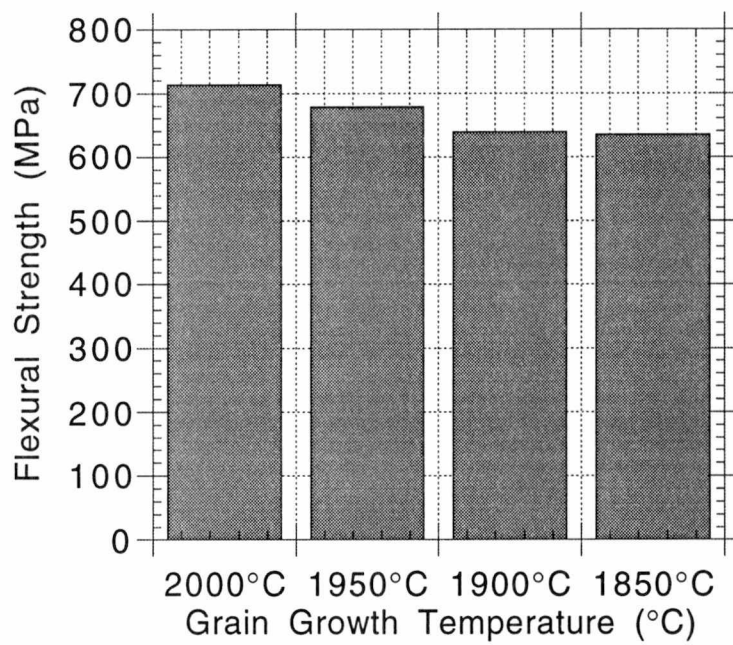


Fig. 4.7. Effect of grain growth temperature on the average flexural strength of gas pressure sintered Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

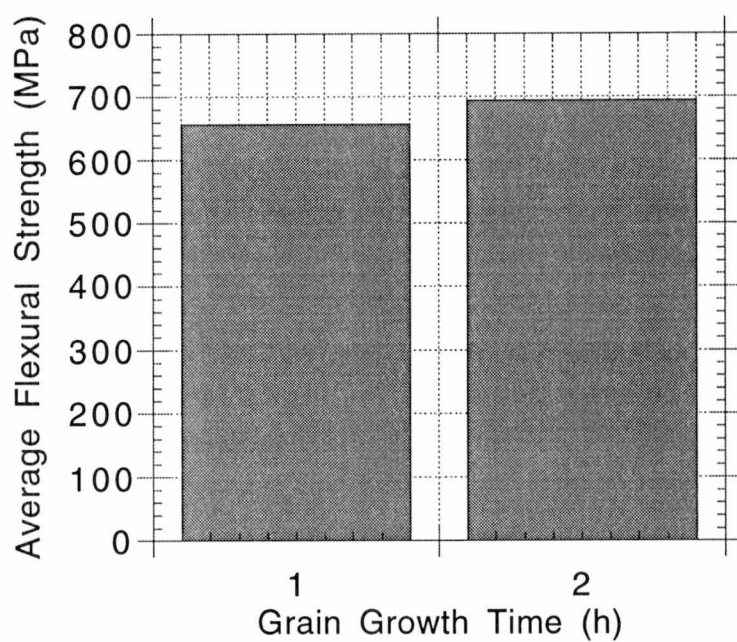


Fig. 4.8. Effect of grain growth time on the average flexural strength of gas pressure sintered Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

was excessive. Possible contributing factors to the error that are associated with the experimental conditions would include the actual sample heating rate, which is dependent on the furnace loading, and the β transformation rate.

The fracture toughness for the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 samples had the greatest effects associated with the densification temperature and grain growth temperature as shown in Table 4.4. However, in this case, the ANOVA results indicate that only the densification temperature was a significant factor (at $\geq 95\%$ confidence level). This is because the 1850°C grain growth temperature was significantly lower than the other experimental conditions and was the reason for the large total effect. On the other hand, the effect of the other three grain temperatures on strength were similar to one another and consequently diminished the total contribution attributed to this variable. The level effects for the different variables on the fracture toughness of Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 are graphically shown in Figs. 4.9 through 4.13. For the fracture toughness, the very large error contribution definitely indicates at least one major factor was not considered or that the error associated with the experimental methods is too large. Surprisingly, the other variables showed no significant contribution to the fracture toughness. This suggests that other factors, such as powder characteristics and β -phase nucleation conditions are significant control factors in determining the fracture toughness.

As will be shown in the next chapter, the α -to- β transformation is highly sensitive to temperature and even minor variations can greatly influence the behavior. During firing, small variations in the temperature of a specimen, especially during the heating cycle, could result from differences in the total furnace load between runs, small differences in crucible packing arrangements and any other variable that would effect the thermal transfer within the specimens.

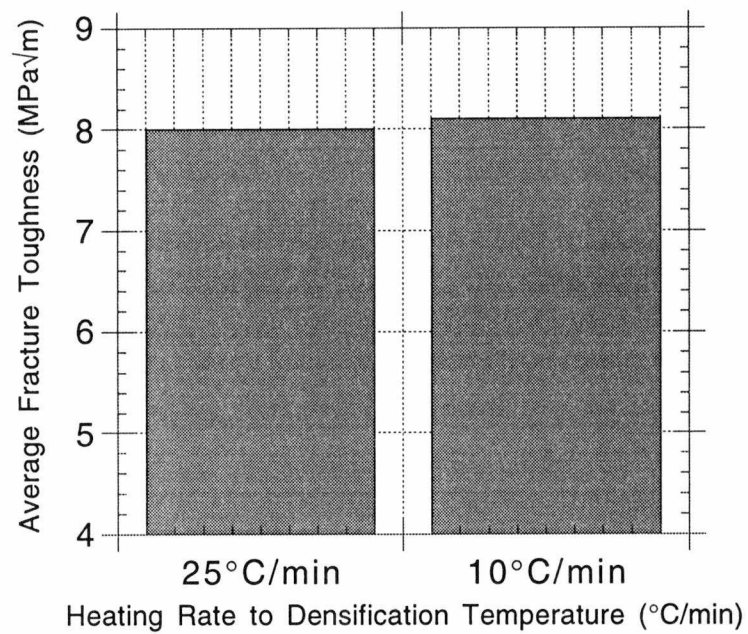


Fig. 4.9. Effect of heating rate on the average fracture toughness of gas pressure sintered Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

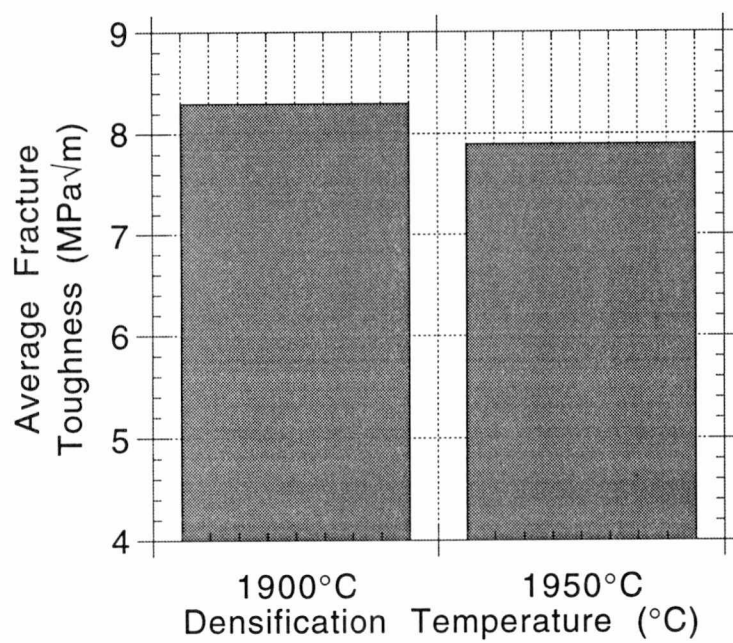


Fig. 4.10. Effect of densification temperature on the average fracture toughness of gas pressure sintered Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

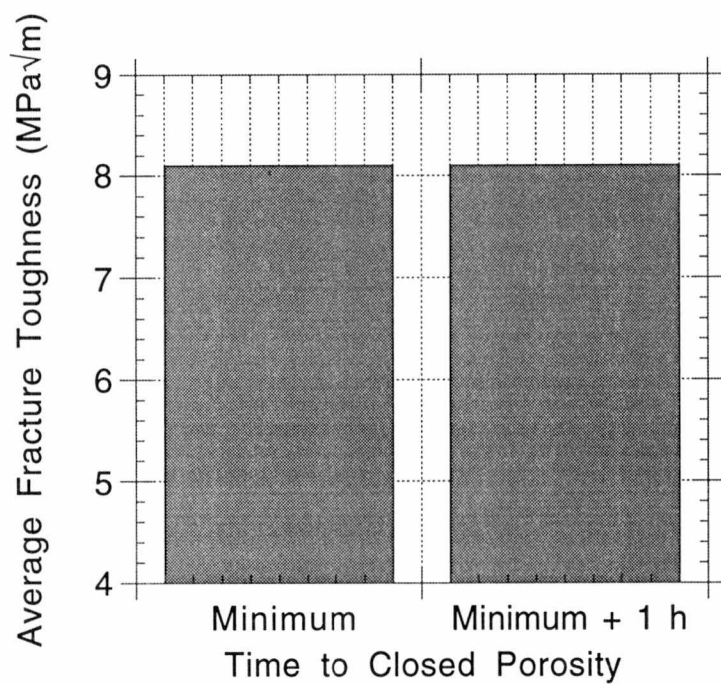


Fig. 4.11. Effect of densification time on the average fracture toughness of gas pressure sintered Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

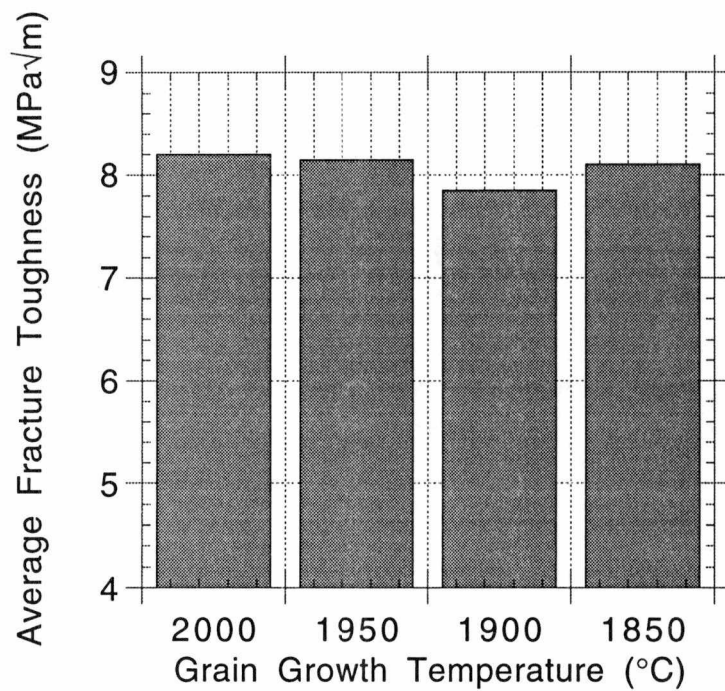


Fig. 4.12. Effect of grain growth temperature on the average fracture toughness of gas pressure sintered Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

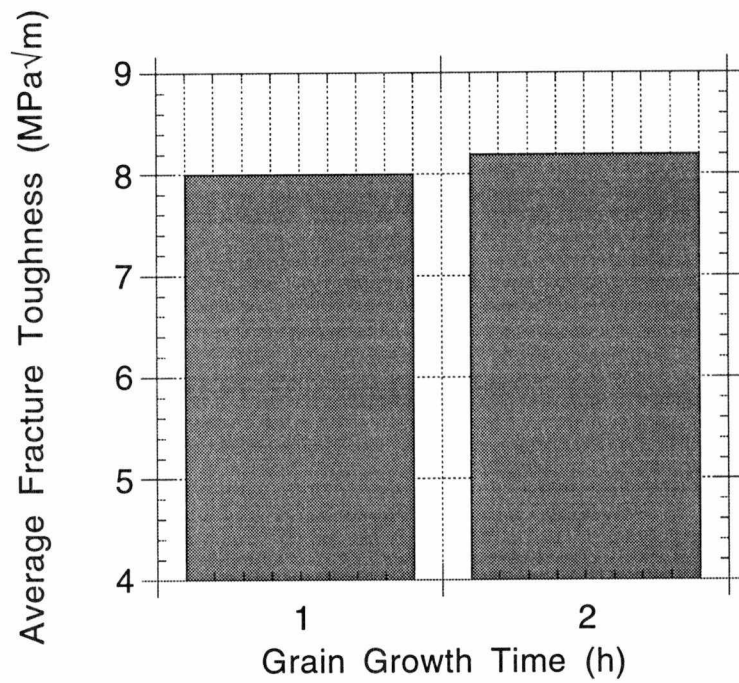


Fig. 4.13. Effect of grain growth time on the average fracture toughness of gas pressure sintered Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 .

The $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ samples showed significantly more deviation in the flexural strength and fracture toughness results depending on the processing conditions than the $\text{Si}_3\text{N}_4\text{-6\% Y}_2\text{O}_3\text{-2\% Al}_2\text{O}_3$ samples. The level effects for the different variables on the flexural strength of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ are graphically shown in Figs. 4.14 through 4.18. The most significant factor affecting the flexural strength (at the 95% confidence level) was the grain growth temperature as shown in Table 4.5. This was also shown in the ANOVA results given in Table 4.8. The other factor that was a significant contributor to the flexural strength (at the 95% confidence level) was the densification temperature. The low contribution due to error, in this case, implies that all of the major factors were considered in the experiments. Examination of the data indicated that temperatures $\geq 1900^\circ\text{C}$ were required to achieve high strength values. This is believed due to the refractory nature of this sintering additive system and higher temperatures were necessary for good densification.

The fracture toughness for the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ samples was most dependent on the densification temperature as shown in Tables 4.5 and 4.9. Other factors that made contributions included the grain growth temperature, grain growth time and the heating rate to the initial sintering temperature. The level effects for the different variables on the fracture toughness of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ are graphically shown in Figs. 4.19 through 4.23. Additional analysis in the following section was done to determine exactly why the lower densification temperature improves the fracture toughness, but it probably related to the nucleation and growth of the $\beta\text{-Si}_3\text{N}_4$ grains during the initial densification stages. The grain growth temperature results indicate that the higher temperatures result in larger grain sizes and increased fracture toughness. As with the densification temperature, the improved fracture toughness with the slower heating rate is probably related to the early $\beta\text{-Si}_3\text{N}_4$ growth during sintering.

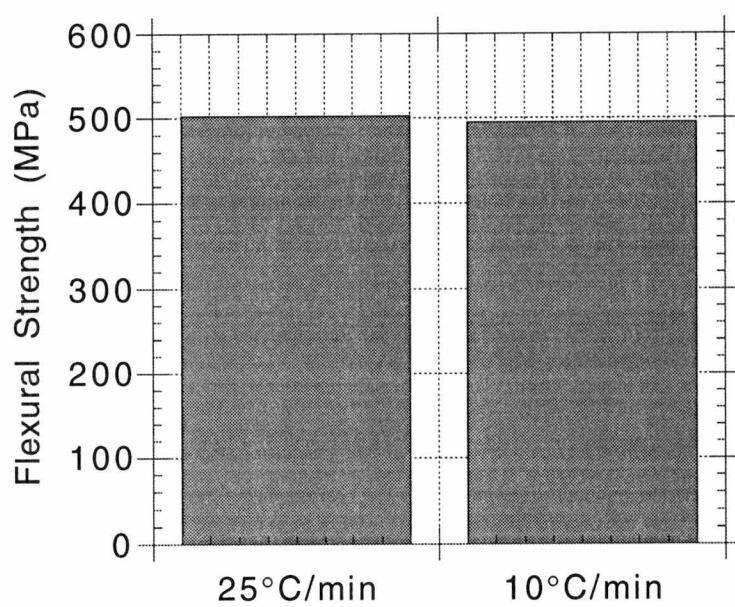


Fig. 4.14. Effect of heating rate on flexural strength of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

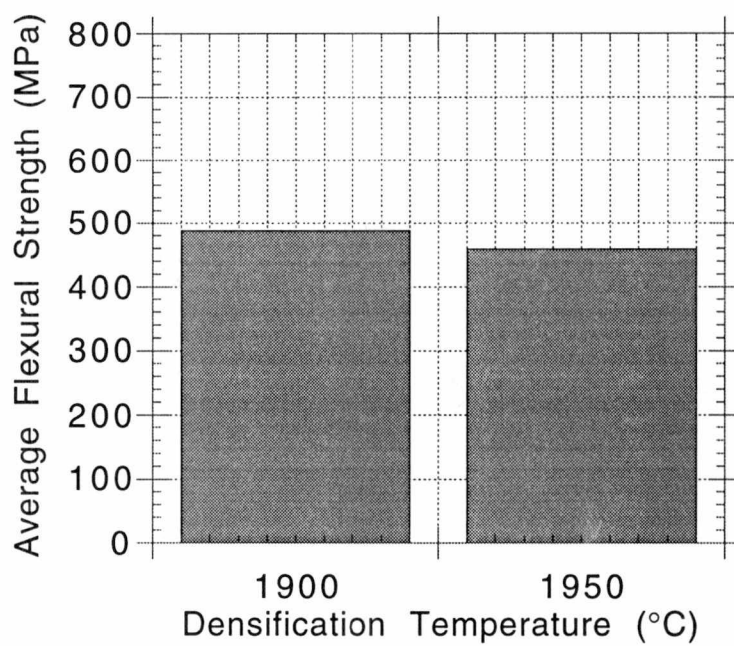


Fig. 4.15. Effect of densification temperature on flexural strength of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

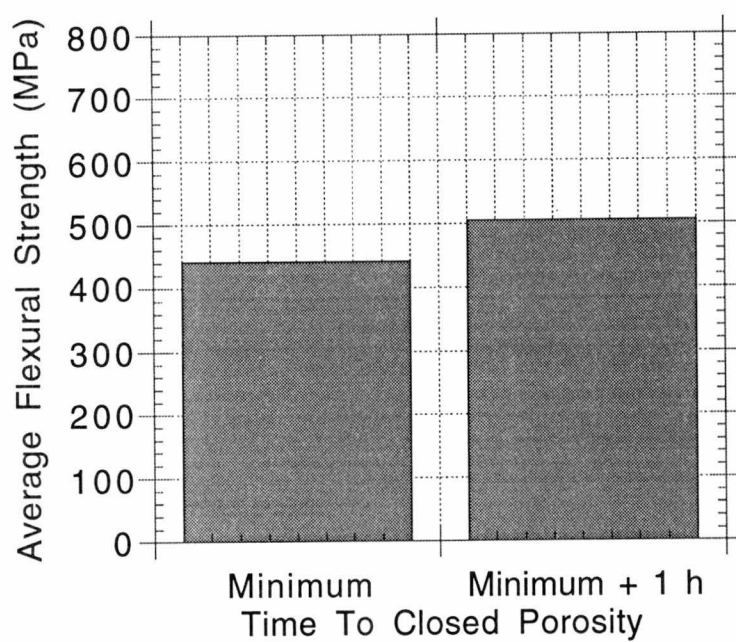


Fig. 4.16. Effect of densification time on flexural strength of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

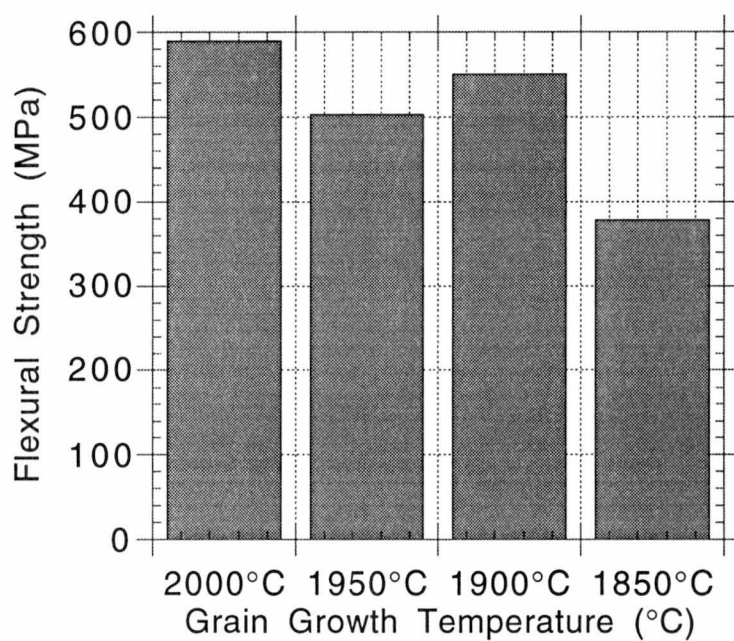


Fig. 4.17. Effect of grain growth temperature on the average flexural strength of gas pressure sintered $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

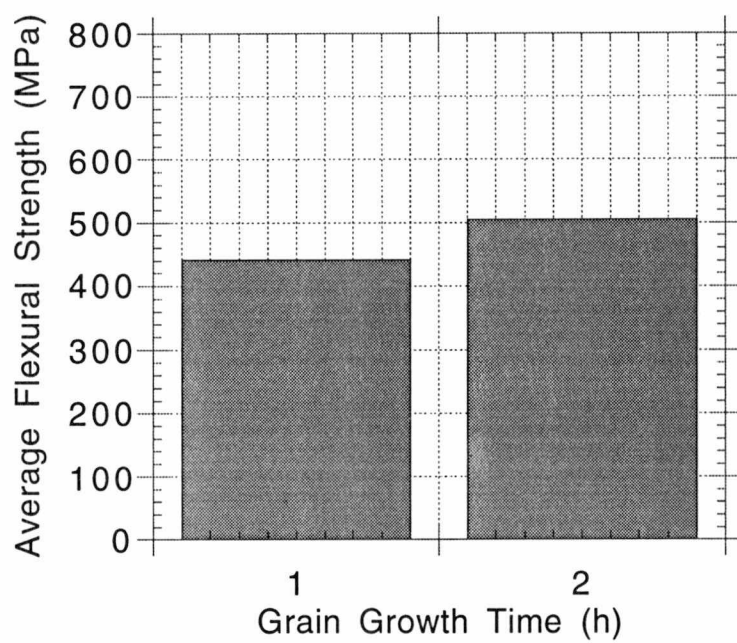


Fig. 4.18. Effect of grain growth time on the average flexural strength of gas pressure sintered $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

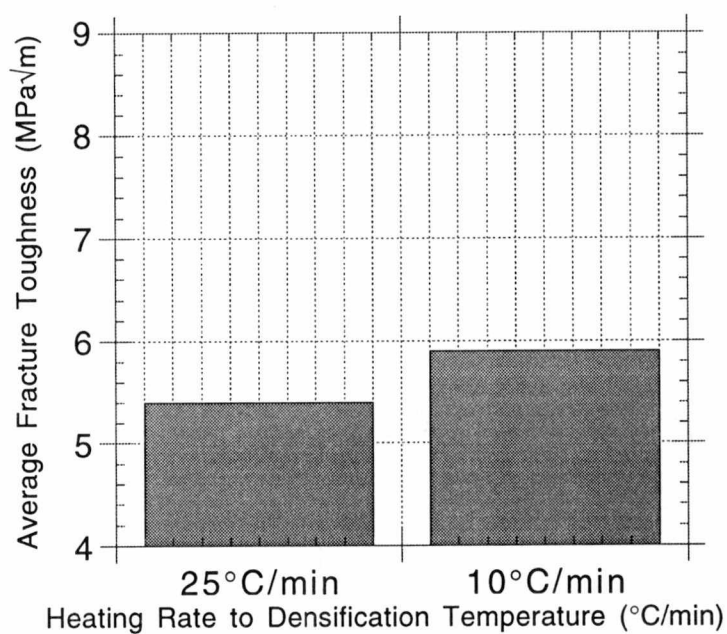


Fig. 4.19. Effect of heating to sintering temperature on the average fracture toughness of gas pressure sintered $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

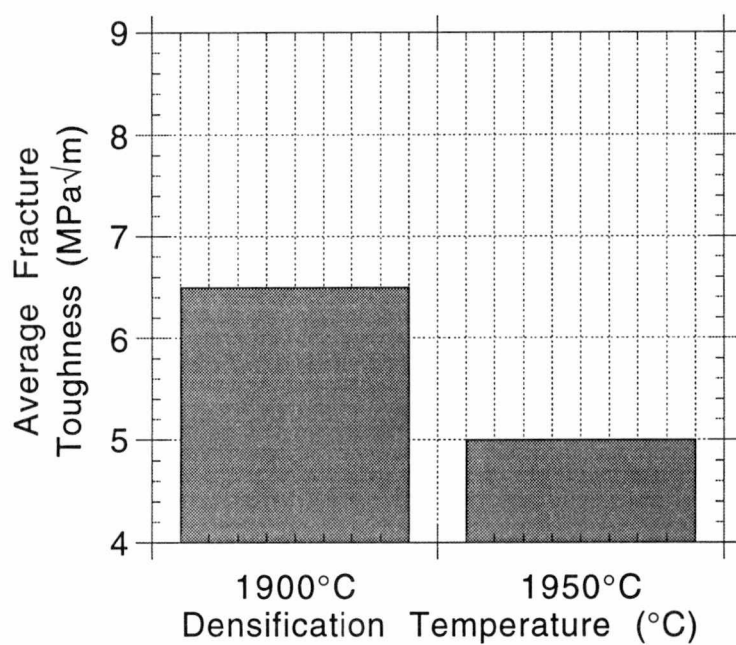


Fig. 4.20. Effect of densification temperature on the average fracture toughness of gas pressure sintered $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

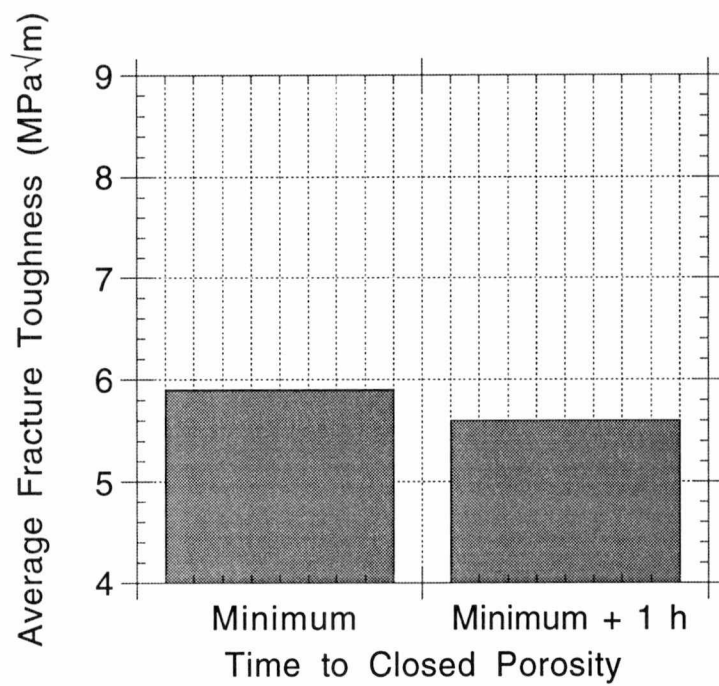


Fig. 4.21. Effect of densification time on the average fracture toughness of gas pressure sintered $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

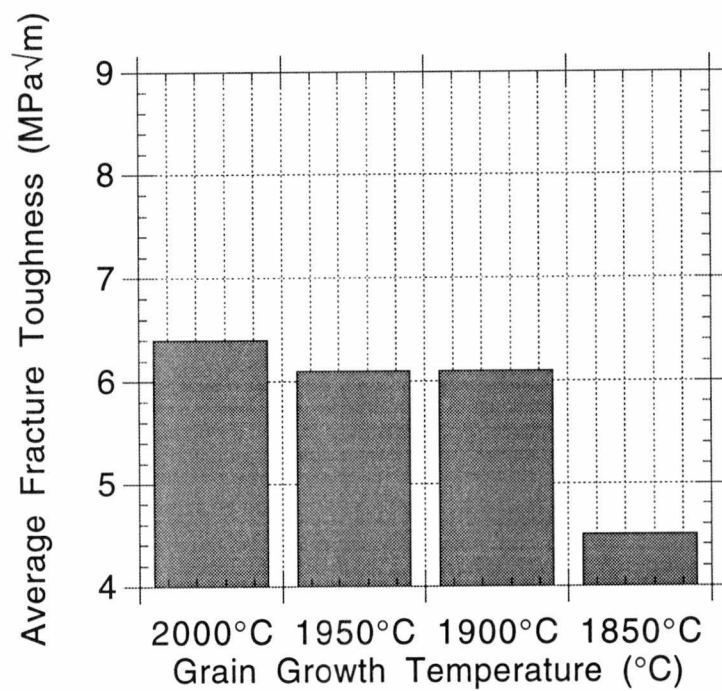


Fig. 4.22. Effect of grain growth temperature on the average fracture toughness of gas pressure sintered $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

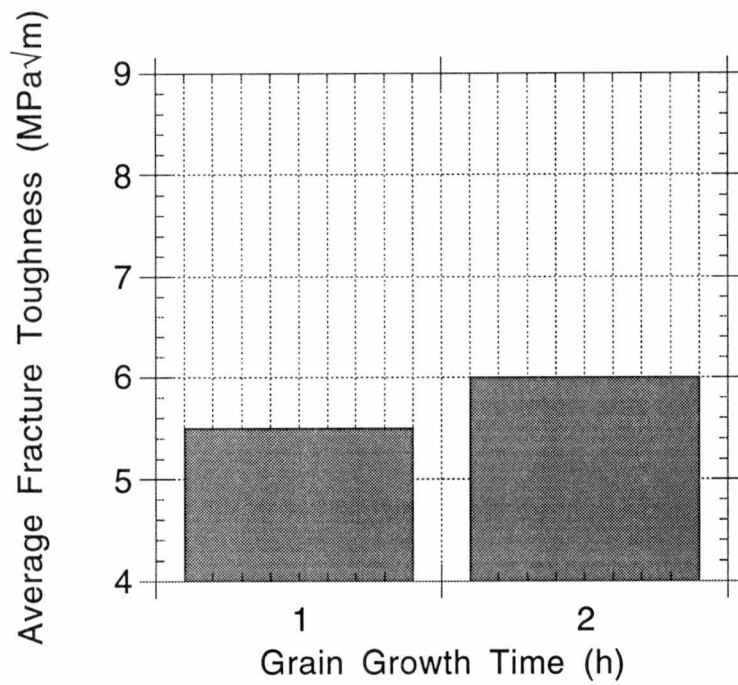


Fig. 4.23. Effect of grain growth time on the average fracture toughness of gas pressure sintered $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

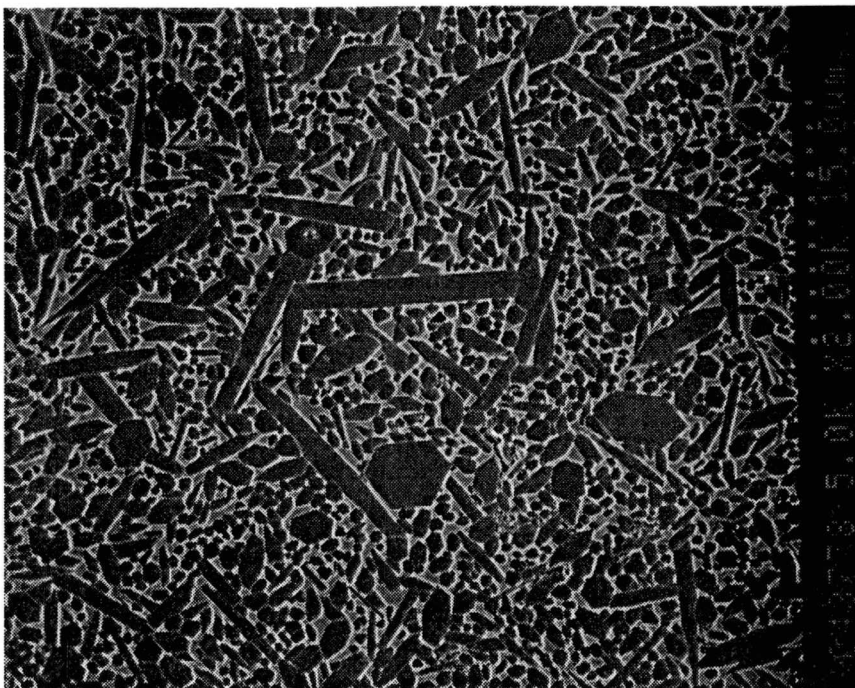
Microstructural Analysis

Microstructural analysis revealed that the lower densification temperature (1900°C) results in generally larger grains with higher aspect ratios as shown in Fig. 4.24. On the surface, this result is contradictory to basically all studies that indicate higher temperatures result in larger grains. However, if one considers the microstructural development process in silicon nitride materials, the larger grains are probably related to the nucleation and growth of the β -Si₃N₄ grains during the early densification stages. Initially, it was believed that the lower densification temperature could result in a slower nucleation rate of the β -Si₃N₄ and thus fewer grains that would be able to grow at the grain growth temperature. However, the lowest temperature in this study (1900°C) was high enough that complete α -to- β transformation takes place in < 15 minutes (as will be shown in Chapter 5). Consequently, it is concluded that the lower densification temperature allowed a few of the largest grains to grow at the expense of the smaller grains. The higher densification temperature resulted in grain growth of even the mid-size grains and an overall smaller and more uniform grain size.

Larger grains were also associated with the higher grain growth temperatures used in the study as shown in Fig. 4.25. This result is fairly obvious and consistent with previous results. High activation energies for crystal growth in the c-axis direction would encourage acicular grain growth at the higher temperatures.

In addition, inner-granular inclusions were observed in several of the samples from the lower grain growth temperatures (Fig. 4.26). These types of inclusions were not observed associated with samples processed at the higher temperatures. Similar inner-granular inclusions have been observed previously and in that case they were attributed to 'trapping'

(a)



(b)

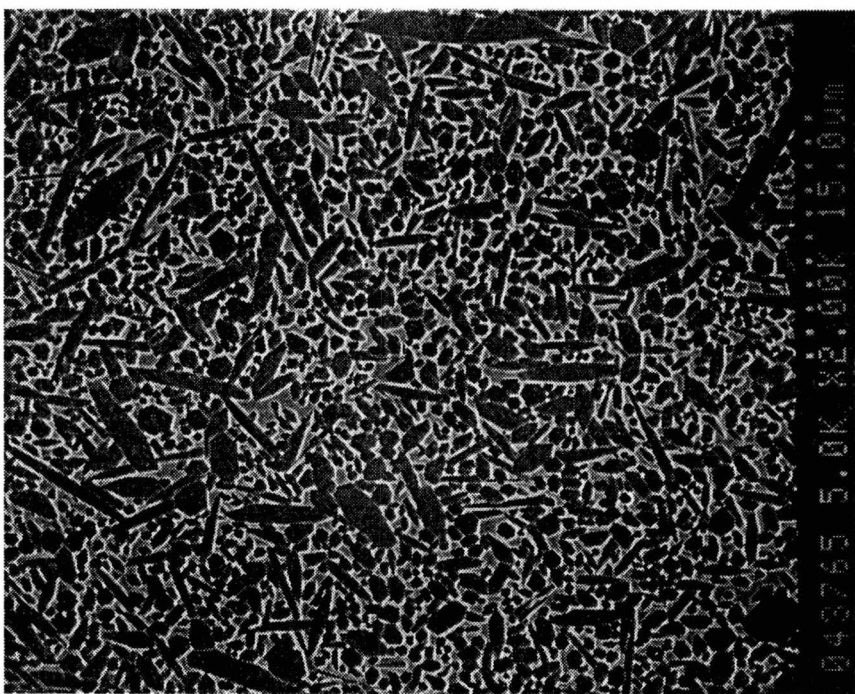


Fig. 4.24. Plasma etched surfaces of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ at the two densification temperatures showing the generally larger grain size for the lower temperature. (a) 1900°C, (b) 1950°C.

(a)



(b)

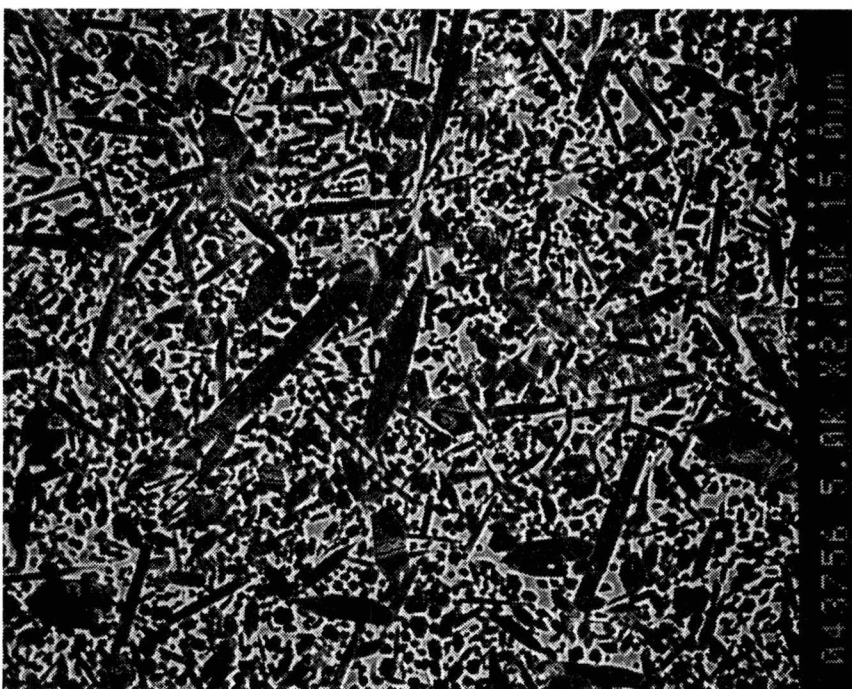
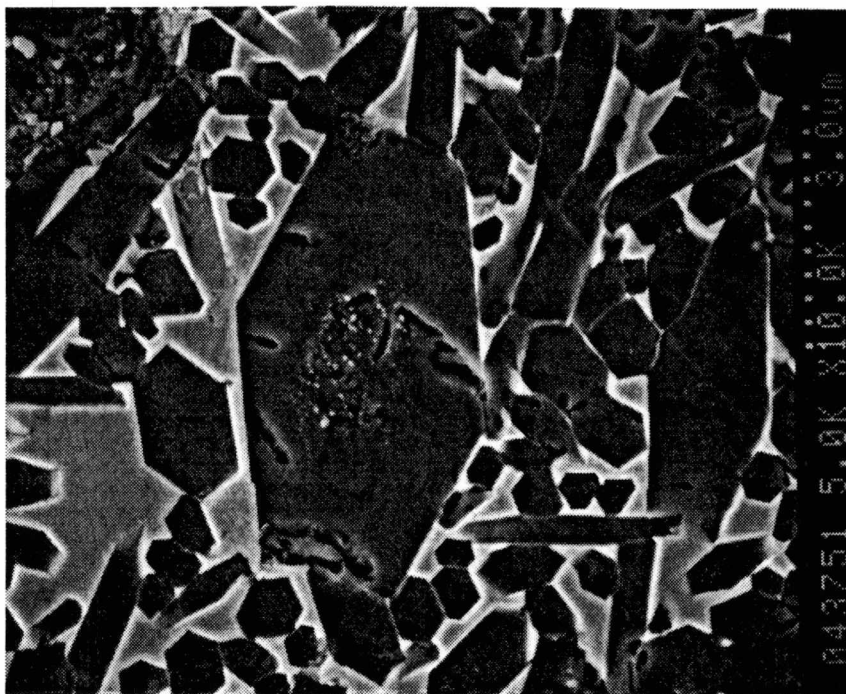


Fig. 4.25. Plasma etched surfaces of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ at two grain growth temperatures showing the generally larger grain size for the higher temperature. (a) 2000°C , (b) 1950°C .

(a)



(b)

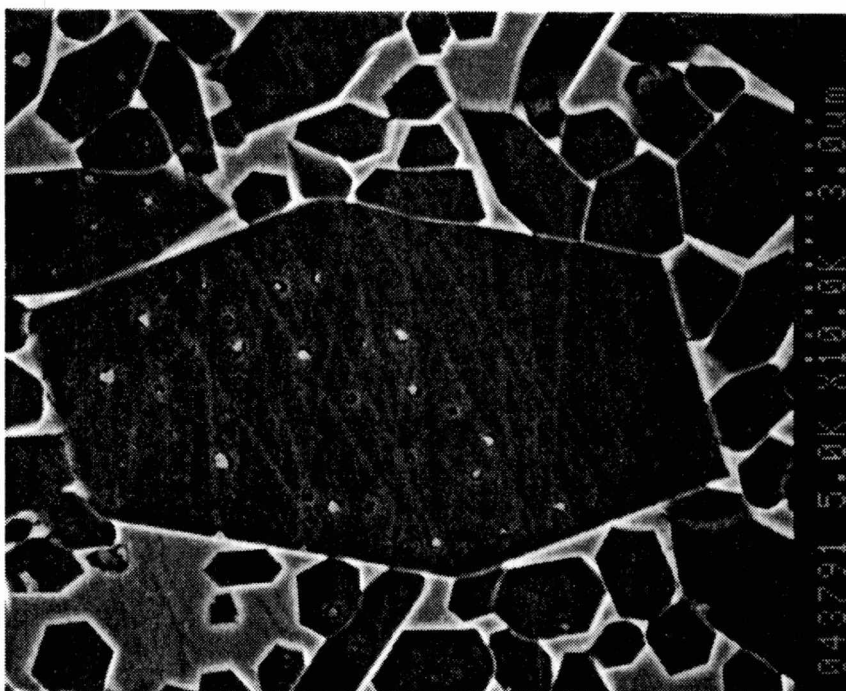


Fig. 4.26. Plasma etched surfaces of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ at the a low grain growth temperature (1900°C) showing some of the innergranular inclusions.

of the liquid phase during grain growth.⁶⁵ It should also be noted that these inclusions were observed in many of the grains from the specimens in the study on physical/compositional gradients presented in Chapter 3. These inclusions may also contribute to a decrease in the flexural strength and fracture toughness. During fracture, the inclusions would act as strength limiting flaws for the individual β - Si_3N_4 grains themselves. As indicated by Equation 1.4, the strength of the bridging grains (squared) is directly related to the increase in observed fracture toughness.

Conclusions

Gas-pressure sintering (GPS) can be used to densify silicon nitride containing a wide variety of sintering additives. Parameters affecting the sintering behavior include densification temperature, densification time, grain growth temperature, grain growth time and heating rates. The Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 samples sintered to high densities at all conditions used in the present study, whereas the Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ samples required the highest temperatures and longest times to achieve densities $\geq 98\%$ T. D.

The main effect on the fracture toughness for Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 samples was the use of a lower densification temperature, which was 1900°C in the present study. For the Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition, fracture toughness was sensitive to and improved by a lower densification temperature (1900°C) and a higher grain growth temperature (2000°C).

For both compositions the lower densification temperature was a significant factor affecting the fracture toughness and promoting a bimodal grain structure. The low significance of the other process parameters implies the microstructure (and therefore properties) are

essentially 'locked-in' during the densification stage and only minor changes can take place afterward. Thus, the microstructural development that occurs during the densification dictates the final properties. The processes occurring during this stage include particle rearrangement, the α -to- β Si_3N_4 phase transformation and the initial β - Si_3N_4 grain growth.

The results indicate that at the lower densification temperature, the α -to- β Si_3N_4 phase transformation and initial grain growth are moderate (in comparison to the other level tested) and the larger β -nuclei are allowed to grow relatively unimpeded during the transformation. A bimodal grain structure is developed in this situation. On the other hand, at the higher densification temperature in this study, the α -to- β Si_3N_4 phase transformation and initial β - Si_3N_4 grain growth are so fast that impingement of the acicular grains occurs. This results in a more uniform, but overall smaller average grain size and lower fracture toughness.

These results were the impetus to perform the study on the β - Si_3N_4 nucleation and initial stage microstructure development that are described in Chapter 4 of this thesis.

CHAPTER V

β - Si_3N_4 NUCLEATION AND INITIAL STAGE MICROSTRUCTURE DEVELOPMENT

As shown before in other research and indicated by the results from Chapters 3 and 4, the microstructure development and therefore, the final properties of silicon nitride are controlled by three basic variables:

1. the starting raw silicon nitride powder
2. the type and quantity of sintering additives
3. the densification conditions

Thus, any study of the microstructure development of silicon nitride needs to be concerned with the parameters associated with these variables.

The results from the study on the effect of sintering parameters on microstructure development during high temperature gas-pressure-sintering (Chapter 4) just presented, showed the densification temperature was a critical factor in affecting the final mechanical properties. The temperature directly influences the microstructure development.

In this step, the major events occurring are the particle rearrangement process and the α -to- β Si_3N_4 transformation. It is just being recognized how important the β -phase nucleation and initial growth stage of microstructure development is to the final properties of the silicon nitride. In fact, the β -phase nucleation and initial growth is probably the major step to producing materials with high fracture toughness.

The microstructure development in this stage of the process is directly related to the kinetics and morphology changes that occur during β -phase nucleation and initial growth. Understanding of the process variables in the initial stage of sintering and their control is essential for obtaining materials with high reliability and superior mechanical properties. Thus, the basic premise of this research topic was to determine the inter-relationships between the raw silicon nitride powders, the sintering additives as the liquid phase forms, β -phase nucleation and the kinetics of the α -to- β transformation. This is an area where there is a large body of fragmented data and observations, however, there is no systematic examination of the system. The purpose of the study was to examine the effects of the silicon nitride powders, the type of sintering additive, β - Si_3N_4 seeds as nucleation sites and process temperature on the initial microstructure development.

Effect of Si_3N_4 Powder Characteristics

As discussed in Chapter 1, there are basically four different methods for producing silicon nitride powders commercially. These are (1) direct nitridation of silicon, (2) carbothermal reduction of silica, (3) gas-phase reaction of SiCl_4 and NH_3 at elevated temperatures, and (4) formation of silicon diimide by liquid-phase reaction of SiCl_4 and NH_3 at low temperatures and its decomposition. Several other methods have been examined and speculated about for producing powders, but the ones listed are the ones most observed in the fabrication of sintered silicon nitride parts.

As discussed in Chapter 1, numerous studies have shown that the silicon nitride powder used in fabrication is an extremely important variable in the microstructural development and final properties of the materials. Most of the early studies of silicon nitride powders were concerned only with either the densification behavior, the final mechanical properties

or the high temperature properties produced by the various grades of powders available. None of the studies have done a comparative assessment of the effects of the raw materials on the microstructural development from a fundamental standpoint. Generally, the previous work found that high starting α - Si_3N_4 contents in the powders are preferable for densification and final material mechanical properties. However, all β -phase starting powders have also been used to produce materials with good mechanical properties.

Examination of the role of powders in the microstructure development is not only an academic exercise, but is of considerable engineering importance. Several studies have shown that the diimide-derived powders generally result in materials with the best mechanical properties. However, these powders are also the most expensive. Thus, there is a desire to use less expensive powders to fabricate materials with good properties. Understanding of the α -to- β Si_3N_4 transformation behavior of the different powders is of importance to the development of cost-effective materials.

Effect of Different Sintering Additives

As mentioned previously, the sintering additives are important in affecting the microstructure development of silicon nitride since they control the eutectic temperature and glass melt viscosity. The additives have also been found to determine the grain growth rate controlling mechanism (either interface or diffusion control). Silicon nitride ceramics are typically sintered using silica-related eutectic liquids in which part of the SiO_2 is derived from surface contamination from the starting Si_3N_4 particles. The additives form sintering liquids with compositions of M-Si-O-N.

Effect of Seeding of the Microstructure

As discussed, silicon nitride gets the excellent properties due to the interlocking morphology of the elongated β -grains. The importance of the initial stage densification and β -phase nucleation steps have also been described.

Like the studies involved with the different silicon nitride powders, the early research on β -seeding were more engineering in nature and primarily examined the effects of β -phase additions on the final properties. The present work examined the effects the β -seeds actually have on the nucleation of additional β -phase, the kinetics of the α -to- β transformation and the overall microstructural development.

To test the effect of raw materials on the initial stage microstructure development, the various powders were mixed with several different sintering additives (to be discussed in the following section). The mixtures were then heated to numerous intermediate temperatures for short to long periods of time. This resulted in partial densification and α -to- β transformation.

The samples were then subjected to x-ray diffraction and the morphology of selected samples was examined by SEM. The rate of transformation was then correlated with the microstructure changes that occurred and differentiations made between the different types of Si_3N_4 powders. It was initially anticipated that the transformation rate kinetics would be similar for the same sintering additives and the pre-exponential rate constant would be a function of the Si_3N_4 particle size. However, this was found to not be the case, and the conditions affecting the α -to- β phase transformation were much more complicated.

Preliminary Study

Several powders were examined in a preliminary research study. These included ones fabricated by direct nitridation of silicon, gas-phase reaction of chlorosilanes and diimide formation and decomposition. They comprise a wide variety of characteristics, such as surface area, particle size, purity, and oxygen content (Table 5.1). All were high in α -phase content.

To assess the effects of these silicon nitride powders on GPS behavior, two compositions were initially chosen that had shown good densification, mechanical properties, and oxidation resistance in previous studies. The intergranular phases chosen were $\text{Y}_2\text{Si}_2\text{O}_7$ (at 5 equivalent % oxygen) and $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

Experimental Design and Conditions

The starting materials consisted of appropriate amounts of Si_3N_4 , La_2O_3 , Y_2O_3 , Yb_2O_3 , or SrO to form the desired intergranular phase.^a The oxygen content of the silicon nitride powders was taken into account in the calculation of the silica addition and milling was done in isopropanol to minimize any oxygen pickup during processing. The powders were turbomilled for ~2 h (1.3 wt.% PVP K-15^b and 1 wt.% Darvan 821A^c were added as dispersants) to fully deagglomerate and mix the various constituents. The mixtures were dried, screened to -100 mesh and isopressed at 207 MPa into discs approximately 7 cm in diameter and 1 cm thick. Binder burnout consisted of a heat-treatment to 600°C in air prior

^a La_2O_3 , Y_2O_3 , Yb_2O_3 ;Molycorp, White Plains, NY; >99.9%; SrO as SrCO_3 ; Mallinckrodt, St. Louis, MO; Reagent Grade

^b GAF Chemicals, Wayne, NJ: Polyvinylpyrrolidone K-15

^c R. T. Vanderbilt, Norwalk, CT

Table 5.1 Characteristics of silicon nitride powders. Manufacturers' reported values.

Manu- facturer	Grade	Fabrication Route	Approx Rel. Cost*	Mean Particle Size (μm)	Surface Area (m^2/g)	α -Phase Content (%)	Oxygen Content (wt. %)	Total Impurity Content (ppm)
Ube	E-10	Diimide	1.9	---	11.7	>95%	1.40	<300
Starck	LC-12SX	Si Nit. ^a	1.5	0.41	19.1	97.5	2.06	<200
Denka	9FW	Si Nit. ^a	1.2	0.80	10.9	92.1	0.98	<0.5 ^b
Starck	LC-10N	Si Nit. ^a	1.2	0.50	13.2	96	1.59	<1000
Starck	GP	Gas Phase	1.7	0.55	10.9	95	1.12	<200
Starck	S 1	Si Nit. ^a	1	0.68	7.4	94.7	1.96	<1000

*Based on purchases of 10 kg. ^aSilicon nitridation.

^bValues in wt. % .

to sintering. A set of samples was also given an oxidation treatment of one hour at 1000°C to increase the oxygen content in the samples.

Sintering was performed in a graphite element furnace with gas overpressure capability. During sintering the samples were covered with a mixture of Si_3N_4 -25% BN-5% Y_2O_3 . Two GPS sintering conditions were examined in the preliminary study: (1) 1850°C for 2 h and 0.3 MPa followed by 1900°C for 2 h and 2 MPa, or (2) 1900°C for 2 h and 0.6 MPa followed by 1950°C for 2 h and 2 MPa. A two-step firing procedure was used to minimize any density gradients across the cross-section of the samples, as this has been known to occur with one-step firing processes. Both GPS runs had a 1 h hold at 1500°C after sintering with no applied overpressure (0.1 MPa) for crystallization of the grain boundary phases. In addition, to examine early stage densification behavior and α -to- β transformation, samples were also heated to either 1700 or 1800°C for 0.25 h at 0.1 MPa pressure and then cooled.

Densities were determined by the Archimedes method. Selected samples of high density were machined into bend bar specimens with nominal dimensions of 3 mm x 4 mm x 50 mm. Flexural strength testing was done in four point bending with inner and outer spans of 20 mm and 40 mm, respectively. Fracture toughness was determined by indentation.

Results of Preliminary Study

The green densities and the early stage densification results are given in Table 5.2. As shown, the nitrided powders had the highest green densities (Fig. 5.1). The densities after heating at 1800°C for 0.25 h were similar for all of the samples (Fig. 5.2). In this region, particle rearrangement is the predominant densification mechanism. Not surprisingly, the

Table 5.2. Summary of results on green densities and early stage densification behavior.

Si_3N_4 Powder	Grain Boundary Phase	Green Density (% T. D.)	Fired Density 1800°C/ 0.25h (% T. D.)	$\beta\text{-Si}_3\text{N}_4$ Content 1700°C	$\beta\text{-Si}_3\text{N}_4$ Content 1800°C
Ube E-10	$\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$	54	77.1	19	58
Starck GP	$\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$	57	73.9	43	96
Starck LC-12	$\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$	64	82.9	27	63
Starck LC-10N	$\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$	65	76.5	37	85
Starck S1	$\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$	59	69.5	26	92
Denka 9FW	$\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$	62	76.4	43	90
Ube E-10	$\text{Y}_2\text{Si}_2\text{O}_7$	53	78.4	10	47
Starck GP	$\text{Y}_2\text{Si}_2\text{O}_7$	54	70.0	20	75
Starck LC-12	$\text{Y}_2\text{Si}_2\text{O}_7$	62	76.9	13	57
Starck LC-10N	$\text{Y}_2\text{Si}_2\text{O}_7$	61	71.3	27	70
Starck S1	$\text{Y}_2\text{Si}_2\text{O}_7$	56	59.9	46	93
Denka 9FW	$\text{Y}_2\text{Si}_2\text{O}_7$	59	70.2	28	78

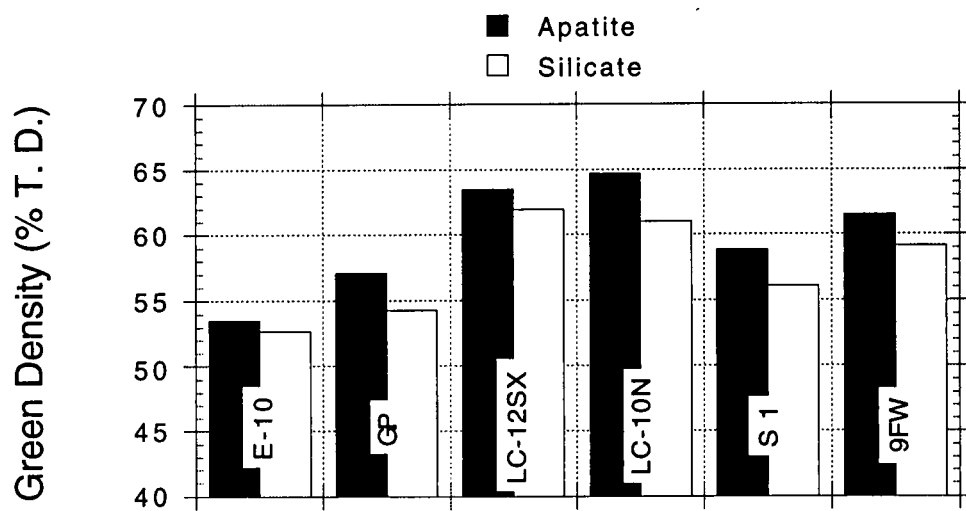


Fig. 5.1. Green densities of compacts from different silicon nitride powders.

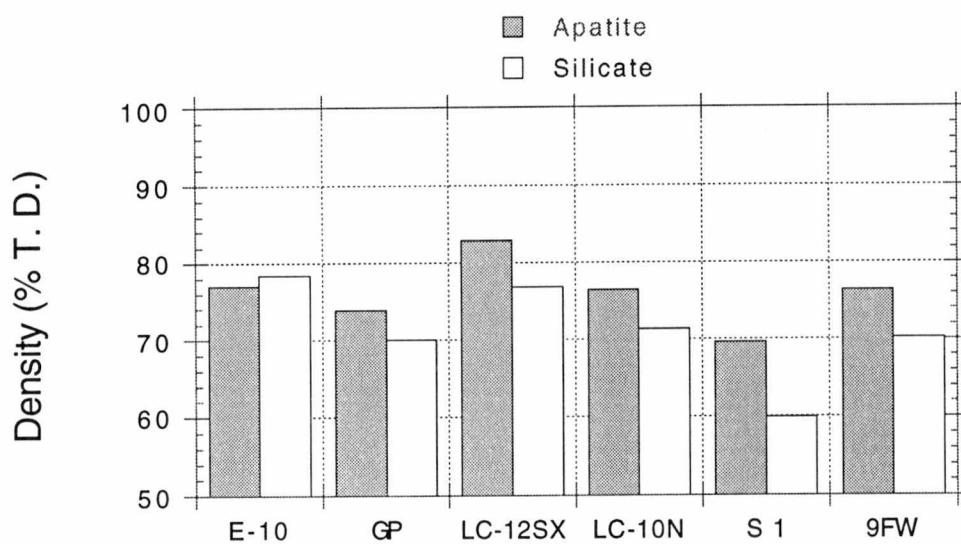


Fig. 5.2. Early stage densification after 1800°C for 15 minutes of compacts from different silicon nitride powders.

low surface area powder (Starck S1) showed the lowest density change. The β - Si_3N_4 content during early stage densification showed significant differences between the Si_3N_4 powders (Figs. 5.3 and 5.4). The diimide derived powder (Ube E-10) showed delayed α/β transformation as compared to the other powders. Conversely, the gas phase derived powder (Starck GP) exhibited nearly complete α/β transformation at 1800°C and this is with a density of ~74% T. D. Thus, there is significant differences between the powders during the initial stage microstructure development.

The densities achieved after GPS are given in Table 5.3. As indicated, the nitrided powders showed the lowest densities, while the diimide and gas-phase powders had the highest densities. The oxidation treatment improved the densification of some of the samples, which is similar to a previous study.^{1,35} The effect of the oxidation treatment on fracture toughness is shown in Fig. 5.5. The oxidation treatment had a significant effect on the fracture toughness for the diimide and gas phase derived powders (Ube E-10 and Starck GP). However, as shown in Fig. 5.6 for the Ube E-10 powder, while the toughness and room temperature flexural strength are improved by increasing the oxygen content, more severe degradation of high temperature strength is evident.

Major Transformation Kinetics Study

All of the earlier results from the previous chapters and the preliminary study of the present chapter indicated that the β -phase nucleation and initial growth is probably the key step to producing materials with high fracture toughness. Consequently, a more detailed study was initiated to the inter-relationships between the raw silicon nitride powders, the sintering additives as the liquid phase forms, β -phase nucleation and the kinetics of the α -to- β transformation.

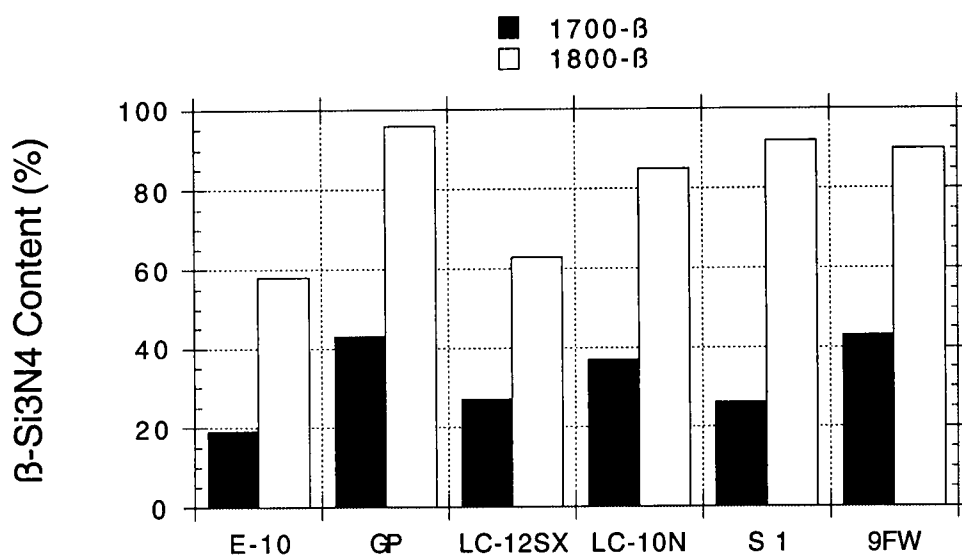


Fig. 5.3. Early stage α -to- β transformation after 1700°C or 1800°C for 15 minutes of compacts from different silicon nitride powders and $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$.

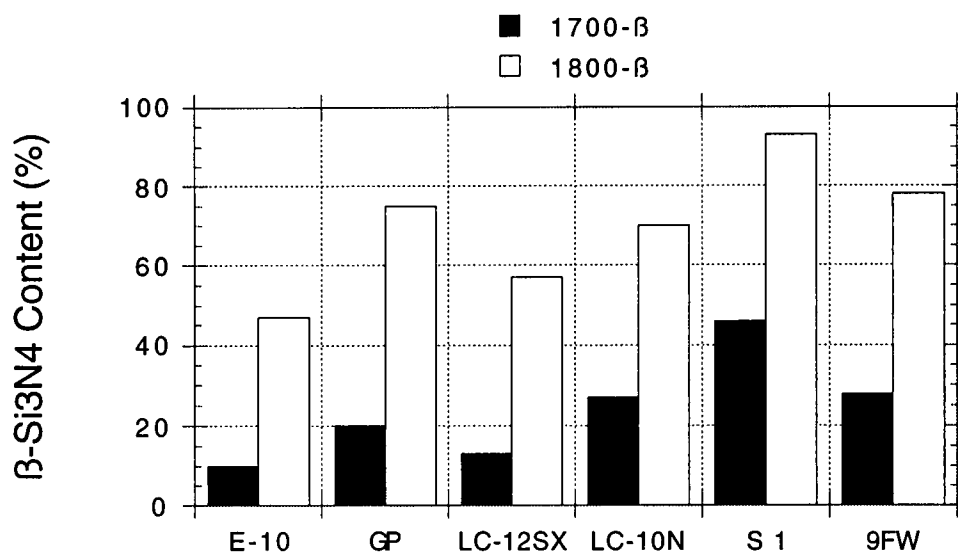


Fig. 5.4. Early stage α -to- β transformation after 1700°C or 1800°C for 15 minutes of compacts from different silicon nitride powders and $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$.

Table 5.3. Summary of results on densification behavior.

Si_3N_4		$\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$			$\text{Y}_2\text{Si}_2\text{O}_7$		
Powder		Intergranular Phase			Intergranular Phase		
		1850/1900	1900/1950	1900/1950 ^a	1850/1900	1900/1950	1900/1950 ^a
Ube E-10		98.2	93.0	98.4	92.0	96.3	97.7
Starck GP		98.3	99.4	98.4	90.8	95.5	91.1
Starck	LC-12SX	86.9	78.4	97.3	84.4	88.3	93.3
Starck LC-10N		86.9	88.3	96.1	77.6	80.7	87.0
Starck S1		82.7	85.7	90.3	66.1	68.7	83.3
Denka 9FW		92.7	98.5	96.6	85.7	88.5	87.7

^a Compacts oxidized at 1000°C for 1 h prior to sintering.

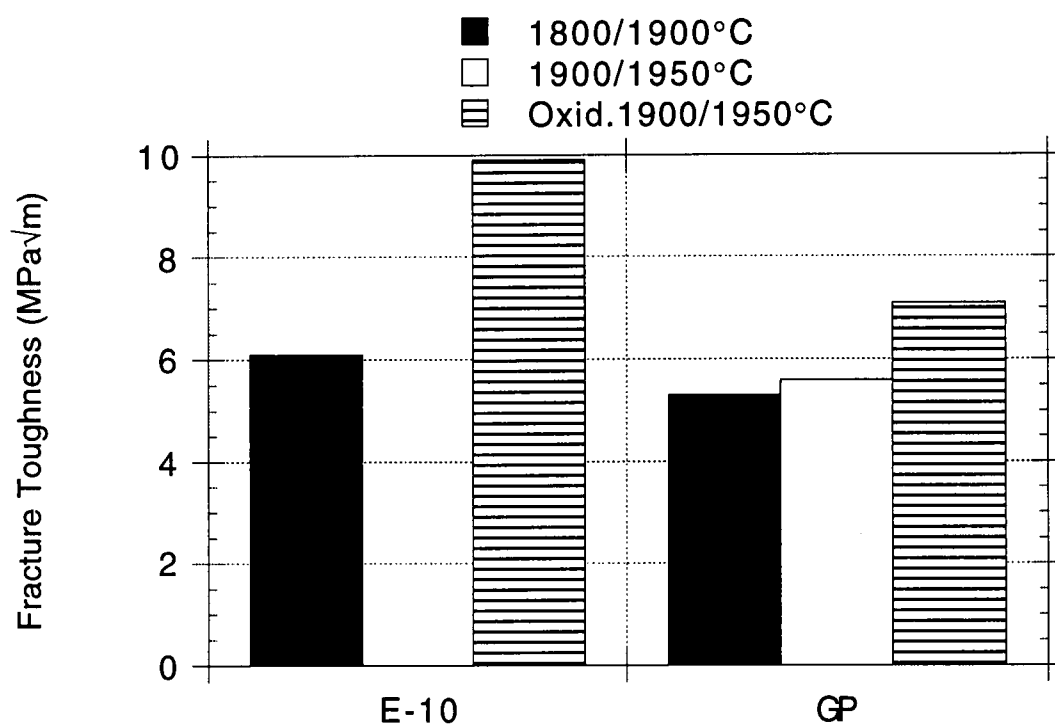


Fig. 5.5. Fracture toughness of gas-pressure sintered $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ as-fabricated and after one hour oxidation treatment at 1000°C.

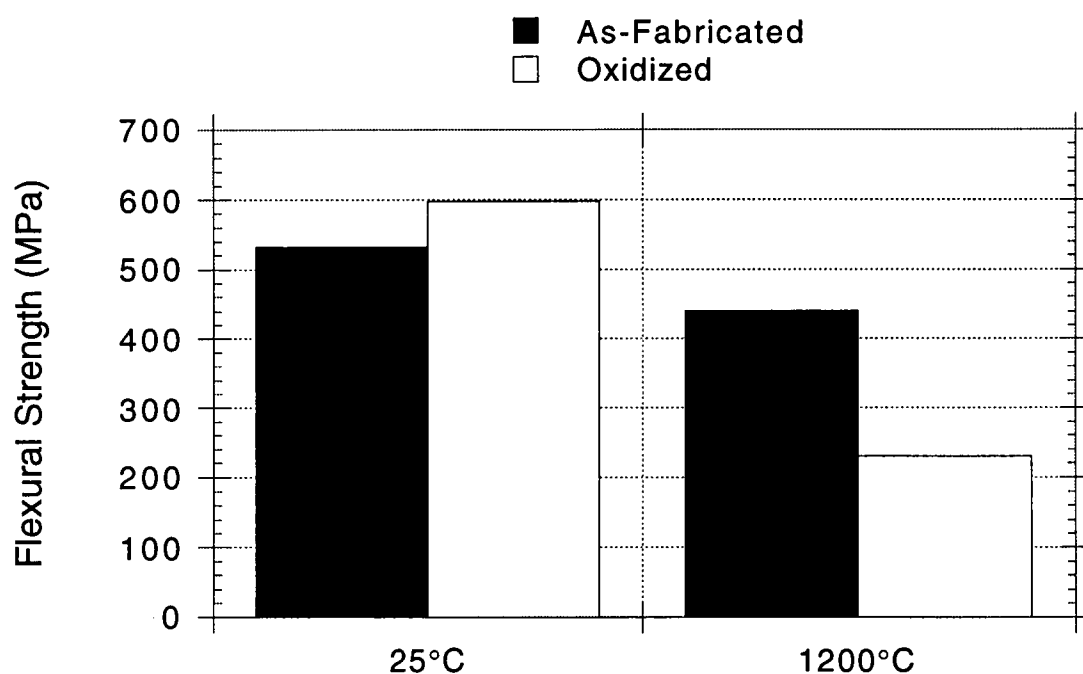


Fig. 5.6. Effect of increasing oxygen content on flexural strength of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (Ube E-10) gas-pressure sintered at 1900°C/2h/0.3 MPa-1950°C/2 h/2 MPa.

Experimental Design and Conditions

Several powders were examined in this research study that comprise a wide variety of characteristics, such as surface area, particle size, purity, and oxygen content (Table 5.4). All are high in α -phase content. To test the effect of raw materials on the initial stage microstructure development, the various powders were mixed with several different sintering additives that give a wide range of liquid properties. The intergranular phases chosen are shown in Table 5.5. The complete experimental matrix is given in Table 5.6.

The Y_2O_3 - Al_2O_3 system (compositions 1 and 2) is one that has been studied extensively and has been used for most of the basic studies on grain growth and densification behavior. It is included here as a defacto standard for comparison with other studies. The choice of two different contents with provide some data on the effect of diffusion in the initial stage sintering process. The benefit of this system is that it offers the greatest latitude in processing parameters, such as powder characteristics and heating schedules, for fabricating silicon nitride materials. Various ratios of the sintering additives have been used and are generally tailored for a particular application and processing sequence.

The Y_2O_3 -MgO system has also been studied previously and has been used to fabricate materials with high fracture toughness. It also represents a system with a lower eutectic temperature than the others.

The $Y_2Si_2O_7$ (at 5 equivalent % oxygen) composition represents a very refractory grain boundary phase. The SiO_2 additions will be used to control the intergranular phases and maintain the composition in an appropriate phase compatibility area, so oxidation problems

Table 5.4. - Characteristics of silicon nitride powders. Manufacturers' reported values.

Manu- facturer*	Grade	Fabrication Route	Mean Particle Size (μm)	Surface Area (m^2/g)	β -Phase Content (%)	Oxygen Content - Bulk/Lattice (wt. %)	Total Impurity Content (ppm)
Ube	E-10	Diimide ^a	0.2	11.7	2.6	1.40/0.63	100
Starck	M 11	Si Nit. ^b	0.55	13.5	7.1	1.78/0.85	400
Starck	GP	Gas Phase ^c	0.55	10.9	3.8	1.12/0.38	100
Dow	EXP	Carb. Red. ^d	0.84	9.3	0.5	1.7/0.91	500
Ube	E-05	Diimide ^a	0.4	5.1	N. D.	1.0/0.66	100
Ube	E-03	Diimide ^a	1.0	3.3	0.8	0.82/0.59	100

^aDiimide decomposition. ^bSilicon nitridation. ^cGas phase reaction ^dCarbothermal reduction.

*Ube, Tokyo, Japan; H. C. Starck, Berlin, Germany; Dow Chemical Co., Midland, MI.

Table 5.5. Sintering additive compositions and approximate eutectic temperatures with silicon nitride and silica.

<u>Composition</u>	<u>Approx. Eutectic Temperature (°C)</u>
1) 6 w/o Y_2O_3 -2 w/o Al_2O_3	1280
2) 9 w/o Y_2O_3 -3 w/o Al_2O_3	1280
3) 6 w/o Y_2O_3 -1 w/o MgO	1200
4) $Y_2Si_2O_7$ (at 5 equivalent % oxygen)	1500
5) $Sr_2La_4Yb_4(SiO_4)_6O_2$ (at 8 equivalent % oxygen)	1400

Table 5.6. - Experimental plan to determine β -nucleation process during initial stage growth.

Sample No.	Si ₃ N ₄ Powder Type	Additive Type	β -Seed Addition
BN-1	Ube E-10	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	0
BN-2	Ube E-03	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	0
BN-3	Starck M11	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	0
BN-4	Starck GP	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	0
BN-5	Dow EXP	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	0
BN-6	Ube E-10	6 w/o Y ₂ O ₃ -1 w/o MgO	0
BN-7	Ube E-03	6 w/o Y ₂ O ₃ -1 w/o MgO	0
BN-8	Starck M11	6 w/o Y ₂ O ₃ -1 w/o MgO	0
BN-9	Starck GP	6 w/o Y ₂ O ₃ -1 w/o MgO	0
BN-10	Dow EXP	6 w/o Y ₂ O ₃ -1 w/o MgO	0
BN-11	Ube E-10	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq.% oxygen)	0
BN-12	Ube E-03	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq.% oxygen)	0
BN-13	Starck M11	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq.% oxygen)	0
BN-14	Starck GP	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq.% oxygen)	0
BN-15	Dow EXP	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq.% oxygen)	0
BN-16	Ube E-10	9 w/o Y ₂ O ₃ -3 w/o Al ₂ O ₃	0
BN-17	Starck M11	9 w/o Y ₂ O ₃ -3 w/o Al ₂ O ₃	0
BN-18	Ube E-10	Y ₂ Si ₂ O ₇ (5 eq.% oxygen)	0
BN-19	Starck M11	Y ₂ Si ₂ O ₇ (5 eq.% oxygen)	0
BN-20	Ube E-05	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	0
BN-21	Ube E-05	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq.% oxygen)	0
BN-22	Ube E-10	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	5 % E10/Pwd
BN-23	Ube E-10	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	5 % E3/Pwd
BN-24	Ube E-10	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	5 % S1/Pwd
BN-25	Ube E-10	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	25 % E10/Pwd
BN-26	Ube E-10	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	25 % E3/Pwd
BN-27	Ube E-10	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	25 % S1/Pwd
BN-28	Starck M11	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	5 % E10/Pwd
BN-29	Starck M11	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	5 % E3/Pwd
BN-30	Starck M11	6 w/o Y ₂ O ₃ -2 w/o Al ₂ O ₃	5 % S1/Pwd
BN-31	Ube E-10	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq.% oxygen)	5 % E10/Pwd
BN-32	Ube E-10	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq.% oxygen)	5 % E3/Pwd
BN-33	Ube E-10	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq.% oxygen)	5 % S1/Pwd

are not encountered. If the rare earth contents are too high without the SiO₂ additions, phases, such as melilite, can be obtained that undergo dramatic volume expansions during oxidation.

Alternate grain boundary phases are also being examined that will aid in densification but be of a transient nature and crystallize into a refractory grain boundary phase. Some possible grain boundary phases include the rare earth-oxide and nitride apatites. These include a wide range of stable apatites of composition A₂B₈(SiO₄)₆O₂ where A is a divalent cation (typically Mg, Mn, Pb, Ca, Sr, Ba) and B is a trivalent cation (typically Y, La, Ce, Nd). An advantage of the nitrogen apatite is that it can oxidize without a large volume expansion.

The Sr₂La₄Yb₄[SiO₄]₆O₂ composition meets the requirements for the formation of the nitrogen apatite as the grain boundary phase. It was included in the present study to examine a system with a very complex intergranular glass phase and its effect on the α-to-β transformation.

The starting materials consisted of appropriate amounts of Si₃N₄, Al₂O₃, La₂O₃, Y₂O₃, Yb₂O₃, or SrO to form the desired intergranular phase.^a The powders were milled for ~8 h (1.3 wt.% PVP^b and 1 wt.% Darvan^c were added as dispersants) to fully deagglomerate and mix the various constituents. The mixtures were dried, screened to -100 mesh and pressed at 100 MPa into discs approximately 2.5 cm in diameter and 3 cm thick.

^a Si₃N₄- Ube, Japan, E10; Al₂O₃- Reynolds, Malakoff, TX, RC-HP DBM; La₂O₃, Y₂O₃, Yb₂O₃- Molycorp, White Plains, NY; >99.9%; SrO as SrCO₃; Mallinckrodt, St. Louis, MO; Reagent Grade

^b GAF Chemicals, Wayne, NJ: Polyvinylpyrrolidone K-15 ^c R. T. Vanderbilt, Norwalk, CT, 821A,

Binder burnout consisted of heating to 600°C in air for 1 h prior to sintering. Heat treatment was performed in a graphite element furnace with heating rates of 20°C/min to the hold temperature under nitrogen gas flow at ambient gas pressure. The heat treatment resulted in partial densification and α -to- β transformation. The samples were then characterized by x-ray diffraction and the morphology examined by SEM.

Fabrication of the β - Si_3N_4 seed

As described in the Chapter 2, β - Si_3N_4 seed was produced by heating various combinations of Si_3N_4 powders and Y_2O_3 as shown in Table 5.7. Scanning electron microscopy photographs of the β -phase seed powders are shown in Figs. 5.7 through 5.11. As shown, several different β - Si_3N_4 morphologies were produced. In addition, a commercially produced β - Si_3N_4 powder was as a seed material in some of tests.

Powder mixtures were made with different starting α/β - Si_3N_4 ratios and sintering additives as shown in Table 5.8. The samples were sintered by GPS using optimized densification parameters that were developed for high toughness materials from Chapter 4. The densification results are shown in Table 5.9. These samples were machined into test bars for mechanical property testing.

As shown in Table 5.9, high densities were achieved for all of the samples containing up to 50% β - Si_3N_4 . The lowest densities were observed for samples containing the Shin-etsu β - Si_3N_4 and the material with the Y_2O_3 - SiO_2 plus the β - Si_3N_4 .

Table 5.7. Fabrication of β - Si_3N_4 seed.

β - Si_3N_4 Fabrication ID	Seed Powder	Starting Si_3N_4	Y_2O_3 Addition	β - Si_3N_4 Content (%)
E-10 (Nitrate)	Ube E-10		0.7 wt.% (as nitrate)	93
E-10 (Powder)	Ube E-10		1 wt.% (powder)	100
E-03 (Powder)	Ube E-03		1 wt.% (powder)	78
S1 (Powder)	Starck S1		1 wt.% (powder)	100



Fig. 5.7. SEM of β -Si₃N₄ seed material E10/Nit.

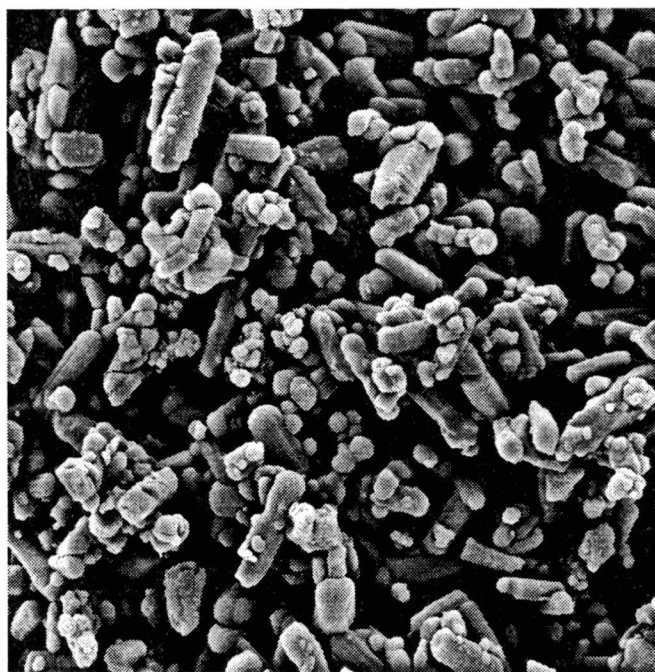


Fig. 5.8. SEM of β -Si₃N₄ seed material E10/Pwd.

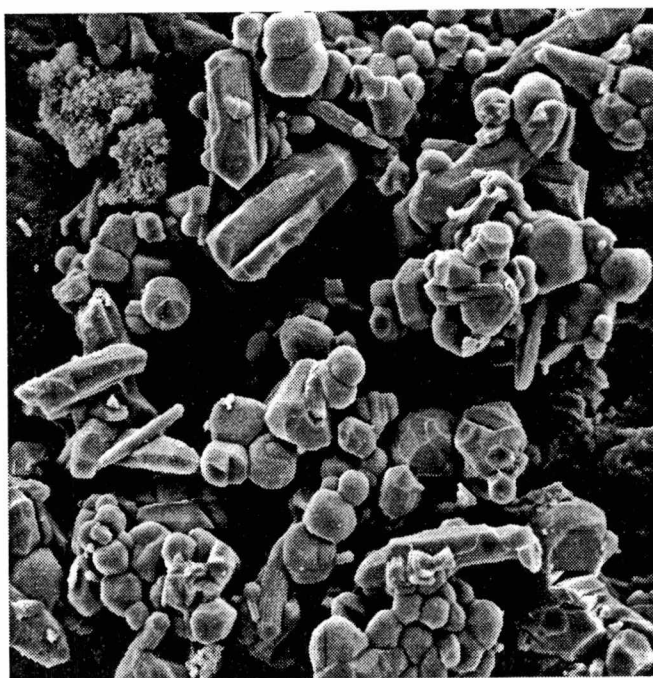


Fig. 5.9. SEM of β -Si₃N₄ seed material E3/Pwd.

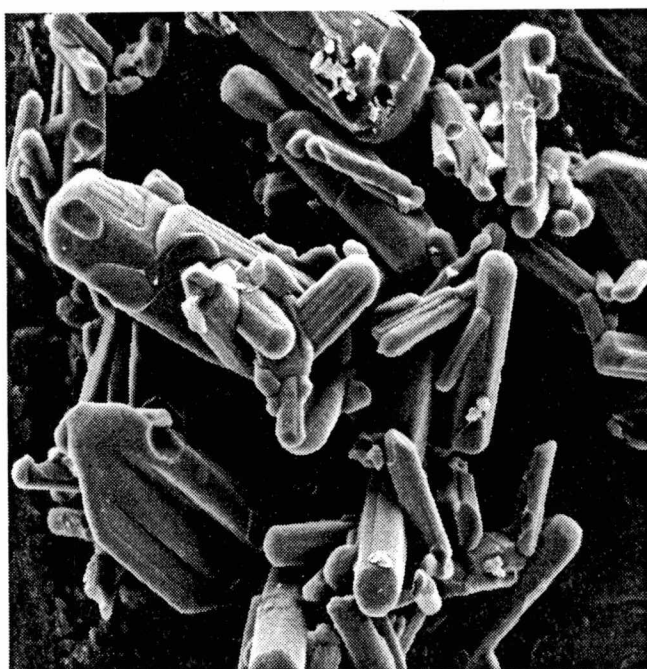


Fig. 5.10. SEM of β -Si₃N₄ seed material S1/Pwd.

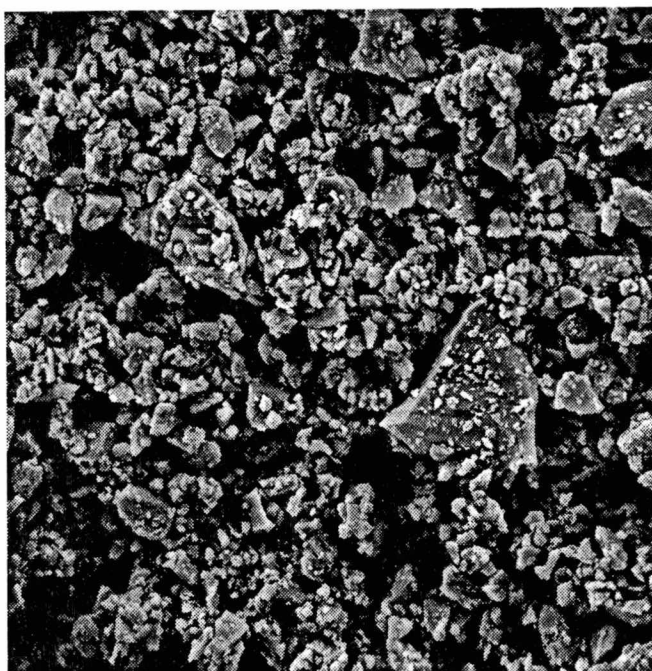


Fig. 5.11. SEM of β -Si₃N₄ seed material Shin-etsu.

Table 5.8. Test matrix to determine effects of β -Si₃N₄ content.

Test No.	Grain Boundary Phase Composition	Rare Earth Addition	β -Si ₃ N ₄ Content (%)	β -Si ₃ N ₄ Source	Seed
MR-1	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	0	--	
MR-2	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	25	E-10 (Nitrate)	
MR-3	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	25	E-10 (Powder)	
MR-4	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	25	E-03 (Powder)	
MR-5	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	25	S1 (Powder)	
MR-6	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	25	Shin-Etsu	
MR-7	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	50	E-10 (Nitrate)	
MR-8	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	5	E-10 (Nitrate)	
MR-9	Y ₂ Si ₂ O ₇ (5 eq. % ox.)	Powder	0	--	
MR-10	Y ₂ Si ₂ O ₇ (5 eq. % ox.)	Powder	25	E-10 (Nitrate)	
MR-11	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	50	E-10 (Powder)	
MR-12	Sr ₂ La ₄ Yb ₄ (SiO ₄) ₆ O ₂ (8 eq % ox)	Powder	5	E-10 (Powder)	

Table 5.9. Summary of results on densification of samples gas pressure sintered at 1900°C/1950°C.

Sample No.	Weight (%)	Loss	Density (g/cm ³)	Density (% T. D.)
MR-1	5.4		3.50	99.5
MR-2	4.5		3.53	100.3
MR-3	4.1		3.54	100.5
MR-4	4.3		3.53	100.4
MR-5	3.7		3.54	100.5
MR-6	4.3		3.31	94.0
MR-7	2.7		3.52	99.9
MR-8	3.4		3.51	99.6
MR-9	1.3		3.22	96.1
MR-10	2.0		3.11	92.9
MR-11	4.8		3.52	100.0
MR-12	4.2		3.50	99.4

Results on β - Si_3N_4 Transformation Kinetics

After heating to the intermediate sintering temperatures, the samples were analyzed by x-ray diffraction. For selected samples, the morphology was examined by SEM. Raw data results obtained on the β -phase contents as a function of the heating temperature and time are shown in Tables 5.10 through 5.12.

As indicated, the transformation rates at 1700°C and 1800°C were so fast that for most of the powders of interest, the conversion was completed after only 15-30 minutes. From this data, the transformation rates could be correlated with Si_3N_4 powder type, sintering additive type, sintering additive amount, Si_3N_4 powder surface area, β - Si_3N_4 seed type and β - Si_3N_4 seed amount.

Kinetic Analysis of Transformation

The formal theory of nucleation and growth processes are a derivation of kinetic law that follows a Jonhson-Mehl-Avrami type equation as follows:^{202,203}

$$X = 1 - \exp[-(\pi/3)Iu^3t^4] \quad [\text{Eq. 5.1}]$$

where X = fraction transformed

I = nucleation rate

u = growth rate

t = time

Table 5.10 Summary of results on β -Si₃N₄ contents after heating to intermediate temperatures (1500°C and 1600°C) and times.

Sample ID	1500°C			1600°C		
	BN-x-5	BN-x-9	BN-x-10	BN-x-1	BN-x-11	BN-x-4
Time(min)	60	180	360	15	30	60
BN-1	9.8%	23.4%	46.6%	25.7%	43.6%	59.5%
BN-2	0.0%	0.6%	1.8%	1.4%	2.1%	3.5%
BN-3	21.5%	37.0%	58.2%	36.9%	52.4%	64.6%
BN-4	14.5%	31.9%	53.7%	31.3%	53.1%	67.9%
BN-5	2.9%	4.4%	7.9%	4.8%	2.3%	13.9%
BN-6	12.0%	17.6%	26.7%	25.9%	44.3%	54.8%
BN-7	3.3%	3.6%	6.7%	3.5%	6.8%	9.7%
BN-8	31.0%	53.6%	74.2%	45.8%	73.8%	85.2%
BN-9	16.8%	34.8%	59.0%	35.1%	65.4%	75.8%
BN-10	4.3%	6.2%	8.4%	7.7%	19.1%	16.4%
BN-11	11.9%	7.6%	11.8%	20.4%	21.8%	30.9%
BN-12	0.0%	0.0%	2.8%	1.1%	0.9%	1.5%
BN-13	17.4%	27.5%	37.7%	41.9%	49.0%	63.4%
BN-14	11.8%	13.6%	20.0%	25.8%	31.6%	42.4%
BN-15	3.9%	2.2%	2.5%	3.7%	4.1%	4.5%
BN-16	8.9%	20.4%	35.1%	26.7%	34.2%	48.4%
BN-17	20.7%	34.8%	49.9%	36.9%	54.5%	67.6%
BN-18	3.3%	3.1%	3.6%	1.5%	9.3%	13.9%
BN-19	9.8%	8.7%	11.0%	25.5%	24.6%	30.8%
BN-20		9.2%	15.8%	4.7%		12.4%
BN-21		2.2%	2.7%	1.1%		2.9%

Table 5.11 - Summary of results on β -Si₃N₄ contents after heating to intermediate temperatures (1700°C and 1800°C) and times.

Sample ID	1700°C		1800°C	
	BN-x-2	BN-x-6	BN-x-7	BN-x-8
Time(min)	15	60	15	60
BN-1	88.5%	100.0%	100.0%	100.0%
BN-2	7.5%	15.9%	26.6%	75.2%
BN-3	93.4%	100.0%	100.0%	100.0%
BN-4	98.8%	100.0%	100.0%	100.0%
BN-5	31.0%	49.4%	64.3%	96.1%
BN-6	86.6%	100.0%	100.0%	99.3%
BN-7	15.5%	36.6%	47.8%	98.9%
BN-8	100.0%	100.0%	100.0%	100.0%
BN-9	100.0%	100.0%	100.0%	100.0%
BN-10	32.5%	56.5%	69.7%	100.0%
BN-11	56.9%	79.0%	95.9%	100.0%
BN-12	5.8%	8.9%	15.2%	38.9%
BN-13	91.2%	100.0%	100.0%	100.0%
BN-14	73.0%	97.5%	100.0%	100.0%
BN-15	17.0%	25.6%	37.2%	78.3%
BN-16	81.9%	97.8%	100.0%	100.0%
BN-17	92.9%	100.0%	100.0%	100.0%
BN-18	40.5%	77.2%	97.4%	99.6%
BN-19	61.6%	78.5%	98.4%	100.0%
BN-20	24.0%	51.0%	---	99.0%
BN-21	12.3%	30.9%	---	84.6%

Table 5.12 - Summary of results on amount of α -to- β Si_3N_4 conversion that occurred after heating to an intermediate temperature (1500°C) and times. These samples contained an initial β -phase content which were not included in the conversion calculations. The values shown are for the fraction of initial α -phase transformed to β -phase.

1500°C

Sample ID	BN-x-9	BN-x-10	Initial β -Phase	Initial β -Phase
Time (min)	180	360	Content (%)	Addition
BN-22	38.2%	65.8%	7.4	5 % E10/Pwd
BN-23	31.5%	56.6%	4.2	5 % E3/Pwd
BN-24	40.1%	67.8%	7.0	5 % S1/Pwd
BN-25	71.2%	94.4%	26.9	25 % E10/Pwd
BN-26	32.8%	66.4%	10.7	25 % E3/Pwd
BN-27	74.4%	95.7%	24.8	25 % S1/Pwd
BN-28	39.4%	56.2%	11.7	5 % E10/Pwd
BN-29	34.0%	52.0%	8.5	5 % E3/Pwd
BN-30	39.2%	55.6%	11.3	5 % S1/Pwd
BN-31	16.0%	22.8%	7.4	5 % E10/Pwd
BN-32	8.6%	16.3%	4.2	5 % E3/Pwd
BN-33	16.1%	24.4%	7.0	5 % S1/Pwd

These studies have typically been used quite successfully in the study of phase changes, such as crystallization, or the decomposition of solids.²⁰⁴ When multiple crystals nucleate and grow, it is generally found that the fraction of material transformed is described by a simplified general rate expression of the above Johnson-Mehl-Avrami-type function:

$$X(t) = 1 - \exp[-K^m t^n] \quad [\text{Eq. 5.2}]$$

Johnson and Mehl developed an equation with $m=n$, whereas Avrami used a simpler version with $m=1$. The K coefficient represents an effective, common reaction rate into which both the nucleation rate and growth rate are combined. Rearranging, the following form of the equation is used in practice to experimentally determine the coefficients:

$$-Kt^n = \ln(1 - X) \quad [\text{Eq. 5.3}]$$

The exponential growth described by equation 5.1 is valid for linear growth under most circumstances and approximately valid for the early stages of diffusion controlled growth. In classical studies, the transformed volume as a function of time gives a characteristic sigmoidal or S-curve shape typical for many transformations based on nucleation and growth mechanisms. Experimentally, the values of n are determined from the experimental data and a plot of $\ln(-\ln(1-X))$ versus $\ln t$, where the slope is n and the y-intercept is K .

The K coefficient can be related to several thermodynamic and kinetic variables, such as free energy of formation for the phase change and atomic diffusivities. It is usually assigned as Arrhenian temperature dependence according to the following:

$$K = K_0 \exp(-E/kT) \quad [\text{Eq.5.4}]$$

For the most part, the nucleation rate is minimal and the growth rate has the major impact on the value of K . In practice, it is observed that the crystal growth rate is relatively constant at a given temperature, but the nucleation rate is not and it generally decays exponentially with time.

Experimentally, it has been found that n values vary from ~ 1 to 4. If there is no change in the nucleation mechanism, n is considered independent of temperature, however, K is dependent on nucleation and growth rates and is therefore highly dependent on temperature. Some work in interpretation of the n values has been done in metal systems, however a clear interpretation of the experimental meaning of n is difficult.^{205,206} Previous work on the interpretation of n values is summarized in Table 5.13 for various situations.²⁰⁶

For interface-controlled or diffusion-controlled growth with the crystal growth rate independent of time, the exponent n assumes the values of 1, 2 and 3 for one-, two- and three-dimensional growth, respectively. While many situations have been studied, experimental determinations of the n value are not typically sufficient to deduce the growth habit by themselves.

The Avrami-type function has been applied to the nucleation and growth of crystals from the liquid in other glass systems.²⁰⁷⁻²⁰⁹ Consequently, it was the initial step for analysis of the β -phase nucleation and growth study in the present work.

Table 5.13 Time exponent, n , for various nucleation and growth situations.

n	Conditions
$3+1=4$	Constant V , spherical growth from sporadic nuclei ($I^* \propto t^3$)
$3+0=3$	Constant V , spherical growth from instantaneous nuclei
$2+1=3$	Constant V , disk-like growth from sporadic nuclei
$2+0=2$	Constant V , disk-like growth from sporadic nuclei
$1+1=2$	Constant V , rod-like growth from sporadic nuclei
$1+0=1$	Constant V , rod-like growth from instantaneous nuclei

Effect of Silicon Nitride Powder Type

A plot of the $\ln(-\ln(1-X))$ versus $\ln t$ is shown in Fig. 5.12. As indicated, the data fit well and were analyzed with a linear equation as shown in the figure. The n and K coefficients for the transformation behavior of several of the compositions were calculated in a similar manner and are given in Table 5.14. As shown, the n values at 1500°C were ~ 1 for all of the different Si_3N_4 powders, sintering additives and β -seed additions. At 1600°C, the n values were slightly less than 1. According to Table 5.13, these types of n values < 1 indicate growth of elongated grains or thickening of plates from pre-existing nuclei after grain impingement. These conditions are relatively close to the situation involved with the α -to- β transformation.

The n values on the order of 1 indicate the reaction rates (%/min) were linear with respect to time and follow a relationship:

$$\frac{d\beta}{dt} = kX \quad [\text{Eq. 5.5}]$$

Linear kinetics for the α -to- β transformation in the range of 10-80% conversion have been observed previously.²¹⁰⁻²¹³ Consequently, further analysis was done using the linear kinetics model.

The α -to- β transformation behavior for the various powder types as a function of time is shown in Figs. 5.13 and 5.14 for $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Yb}_2\text{O}_3\text{-La}_2\text{O}_3\text{-SrO}$ sintering additive systems. The data were fitted with a linear equation which is also shown in the figures. As indicated, the fits for a linear reaction were quite reasonable.

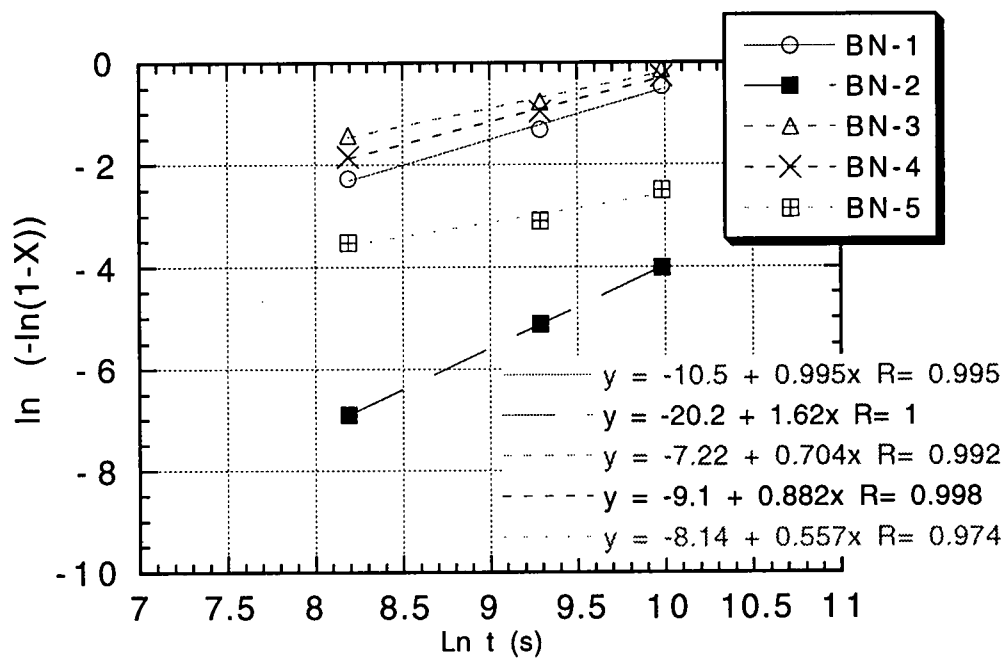


Fig. 5.12. Kinetic analysis of α -to- β Si_3N_4 transformation behavior for samples BN-1 through BN-5 at 1500°C . The sintering additive was 6% Y_2O_3 -2% Al_2O_3 .

Table 5.14. Avrami coefficients of n and K for transformation kinetics.

Sample	1500°C		1600°C	
	n	K	n	K
BN-1	0.99	2.9E-05	0.75	2.3E-03
BN-2	1.22	8.7E-08	0.67	1.4E-04
BN-3	0.70	7.3E-04	0.59	8.7E-03
BN-4	0.88	1.1E-04	0.80	1.7E-03
BN-5	0.55	3.1E-04	0.81	1.3E-04
BN-6	0.48	2.4E-03	0.89	4.5E-04
BN-7	0.38	1.3E-03	0.75	2.2E-04
BN-8	0.72	1.0E-03	0.85	1.3E-03
BN-9	0.87	1.4E-04	0.92	6.8E-04
BN-10	0.38	1.9E-03	0.91	1.0E-04
BN-11	0.49	8.9E-04	0.78	2.8E-04
BN-12	1.83	2.7E-10	0.81	2.0E-05
BN-13	0.50	3.0E-03	0.72	1.3E-03
BN-14	0.30	1.0E-02	0.79	4.8E-04
BN-15	0.53	1.3E-04	0.74	3.1E-05
BN-16	0.85	8.8E-05	0.54	7.5E-03
BN-17	0.61	1.6E-03	0.64	5.9E-03
BN-18	0.34	1.3E-03	1.64	2.8E-07
BN-19	0.26	8.5E-03	0.36	1.9E-02
BN-20	1.22	1.0E-06	--	--
BN-21	0.57	9.7E-05	--	--
BN-22	1.07	1.0E-05	--	--
BN-23	1.05	9.4E-06	--	--
BN-24	1.07	1.2E-05	--	--
BN-25	1.16	1.7E-05	--	--
BN-26	0.99	5.3E-07	--	--
BN-27	1.18	1.8E-05	--	--
BN-28	1.01	6.2E-04	--	--
BN-29	1.02	2.0E-04	--	--
BN-30	1.01	6.8E-04	--	--
BN-31	0.90	8.5E-04	--	--
BN-32	0.90	9.0E-06	--	--
BN-33	0.92	3.3E-04	--	--

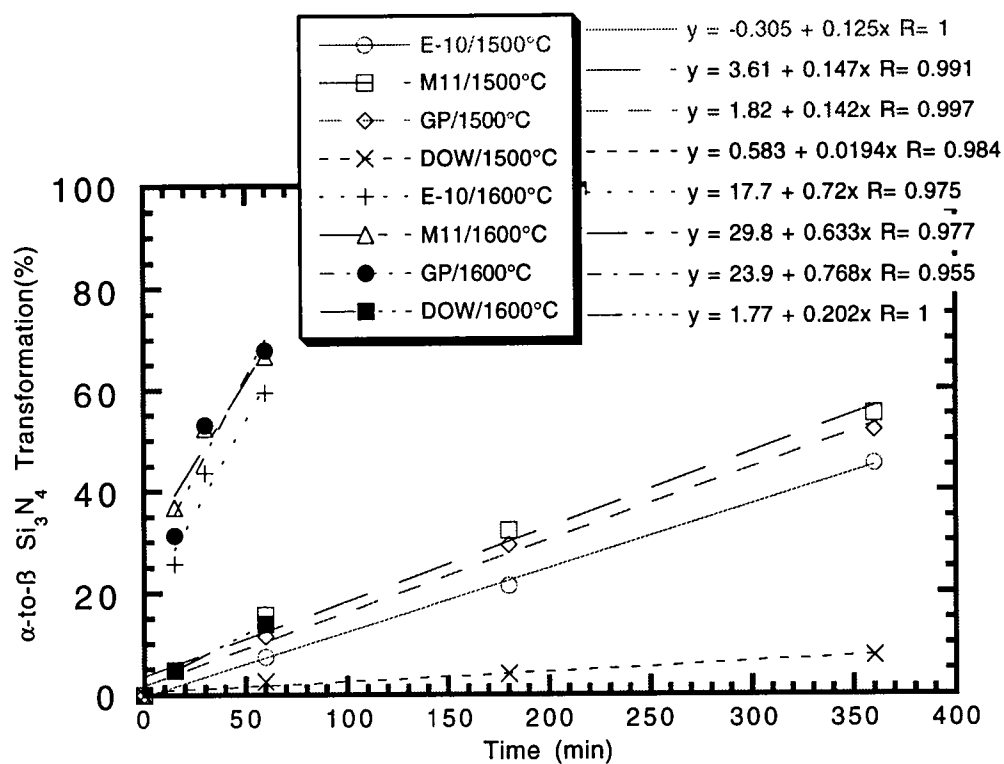


Fig. 5.13. α -to- β Si_3N_4 transformation as a function of time for the various silicon nitride powders at 1500°C and 1600°C. The sintering additive was 6% Y_2O_3 -2% Al_2O_3 .

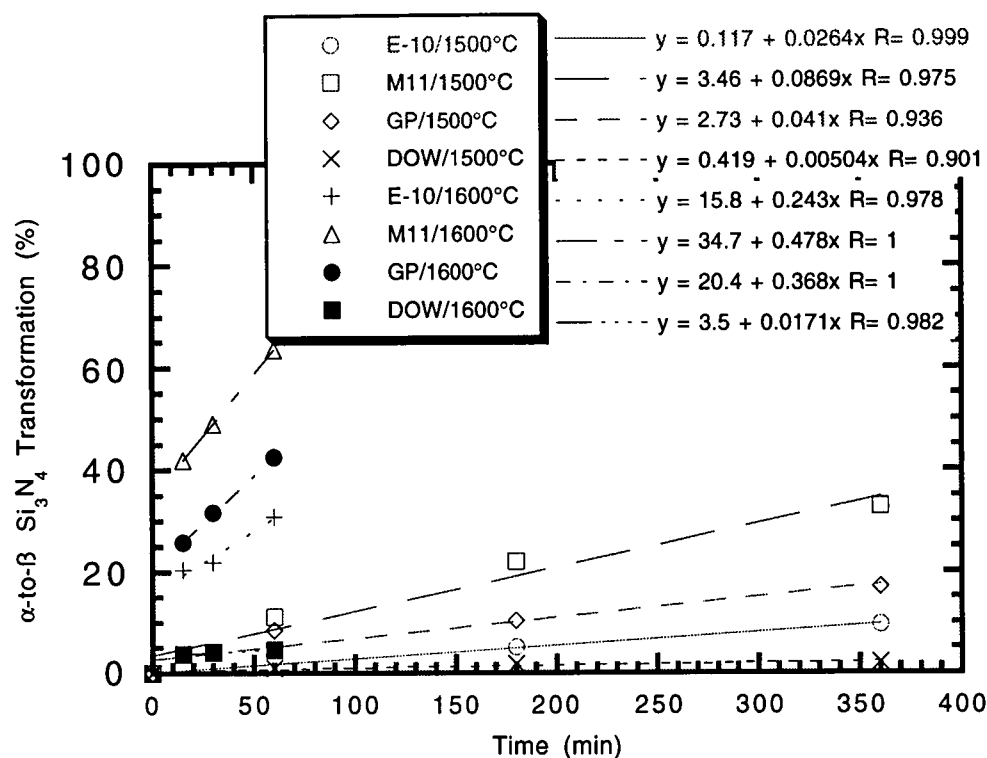


Fig. 5.14. α -to- β Si_3N_4 transformation as a function of time for the various silicon nitride powders at 1500°C and 1600°C. The sintering additive was Yb_2O_3 - La_2O_3 - SrO .

The α -to- β Si_3N_4 transformation rates for the different types of Si_3N_4 powders with different sintering additive types is summarized in Figs. 5.15 and 5.16. As shown, the linear kinetics for the different powders exhibit quite different transformation behavior. For both of the sintering additive types shown, the Starck M11 Si_3N_4 powder generally exhibited the highest transformation rate, while the Dow EXP Si_3N_4 powder had the slowest.

As will be shown later, the differences in the transformation rates are significantly dependent on the powder surface area and initial β - Si_3N_4 content. In addition, other factors could possibly be involved, such as the lattice oxygen content and the carbon content, which could affect the Si_3N_4 dissolution rate.

Effect of Sintering Additive Type

The effect of different sintering additive types on the transformation rate was shown in Figs. 5.17 through 5.20 for Ube E-10, Starck M11, Starck GP and Dow EXP Si_3N_4 powders, respectively. The data were fitted with a linear equation which is also shown in the figures. As indicated, linear rate kinetics fit the data well for the various additives.

The Y_2O_3 - Al_2O_3 (YA) and Y_2O_3 - MgO (YM) based materials had the highest transformation rates. These additives also typically would have the lowest liquid phase viscosities during sintering which would tend to enhance the transformation rate.^{214,215} The diffusivity of species in the liquid glass phase has been found to follow the Stokes-Einstein relationship, so the lower viscosities result in higher diffusion rates.^{216,217}

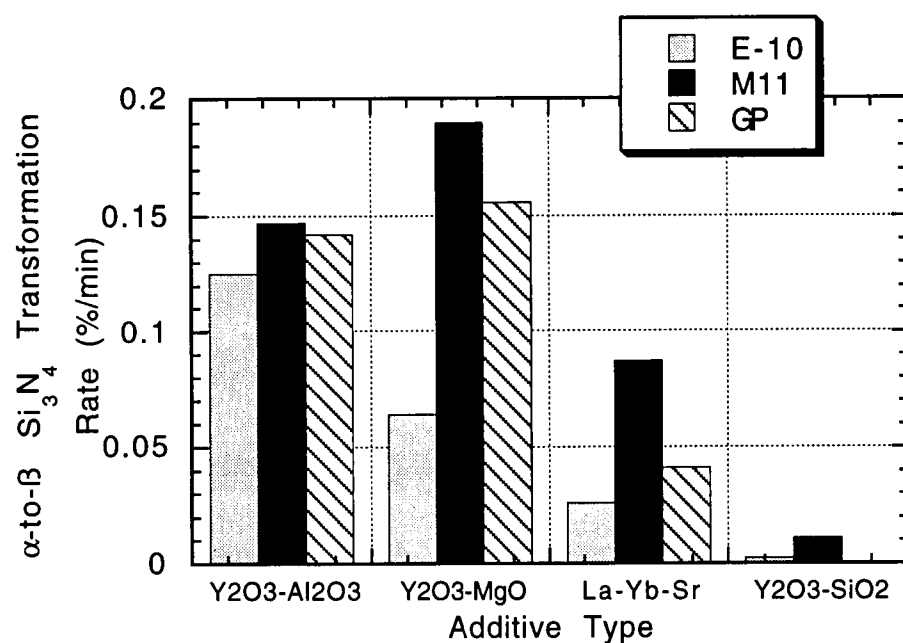


Fig. 5.15. α -to- β Si_3N_4 transformation rate for the various types of sintering additives with the E-10, M11 and GP silicon nitride powders at 1500°C.

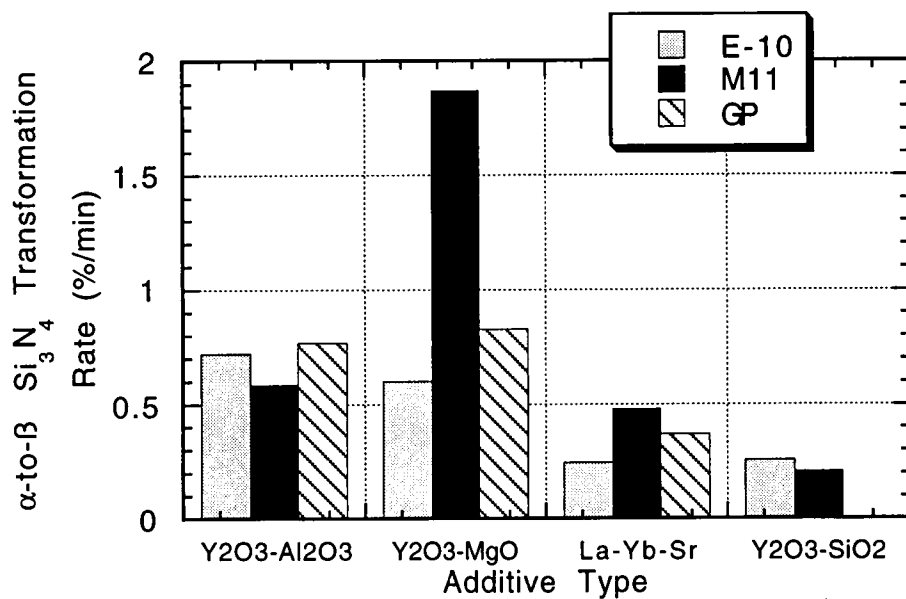


Fig. 5.16. α -to- β Si_3N_4 transformation rate for the various types of sintering additives with the E-10, M11 and GP silicon nitride powders at 1600°C.

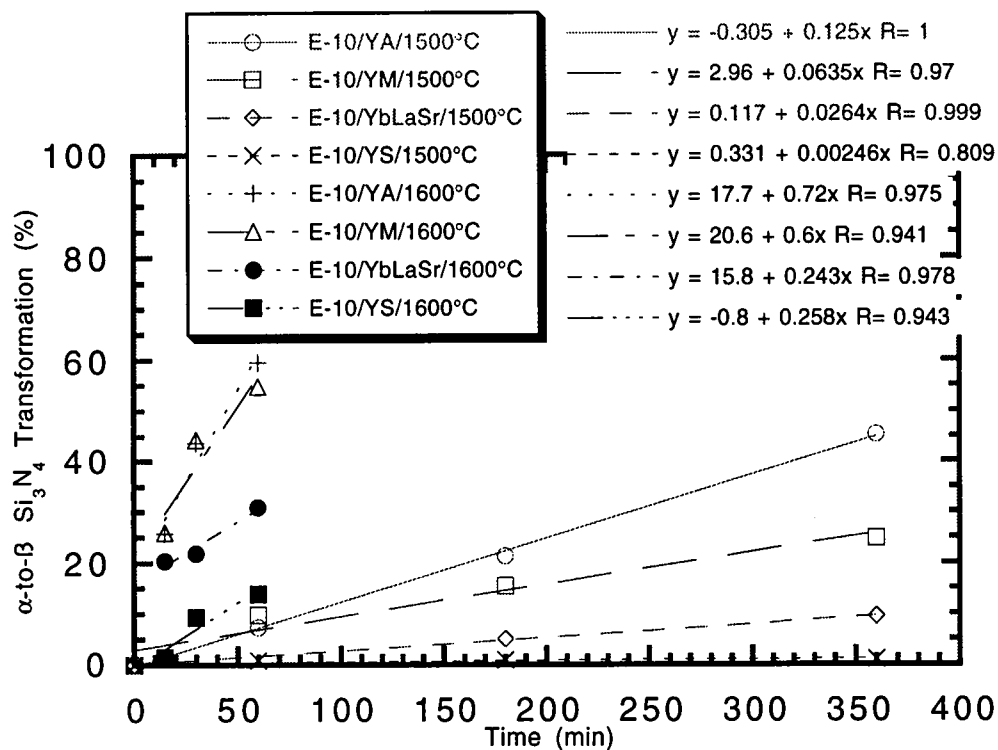


Fig. 5.17. α -to- β Si_3N_4 transformation as a function of time for the various types of sintering additives at 1500°C and 1600°C. The silicon nitride powder was Ube E-10.

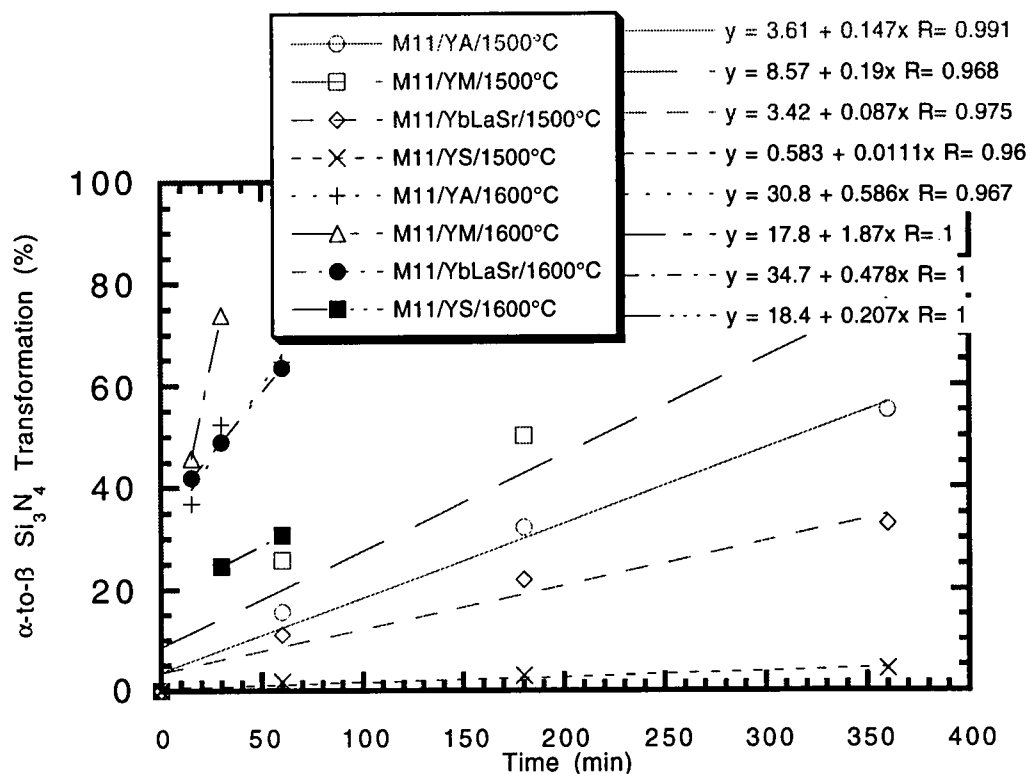


Fig. 5.18. α -to- β Si_3N_4 transformation as a function of time for the various types of sintering additives at 1500°C and 1600°C. The silicon nitride powder was Starck M11.

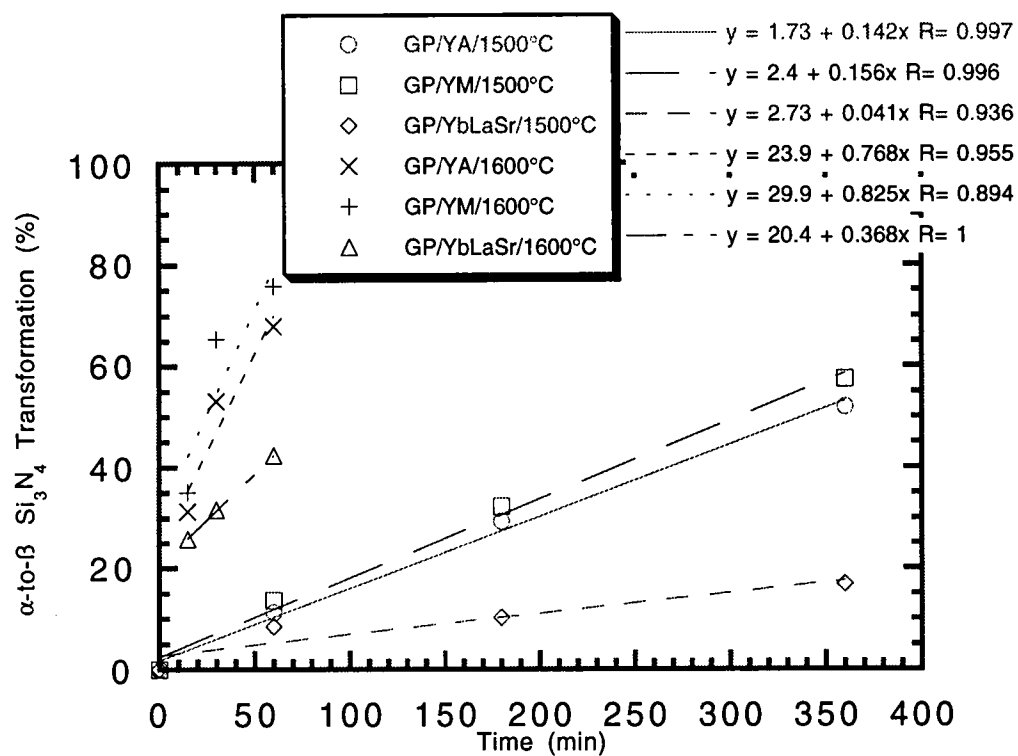


Fig. 5.19. α -to- β Si_3N_4 transformation as a function of time for the various types of sintering additives at 1500°C and 1600°C. The silicon nitride powder was Starck GP.

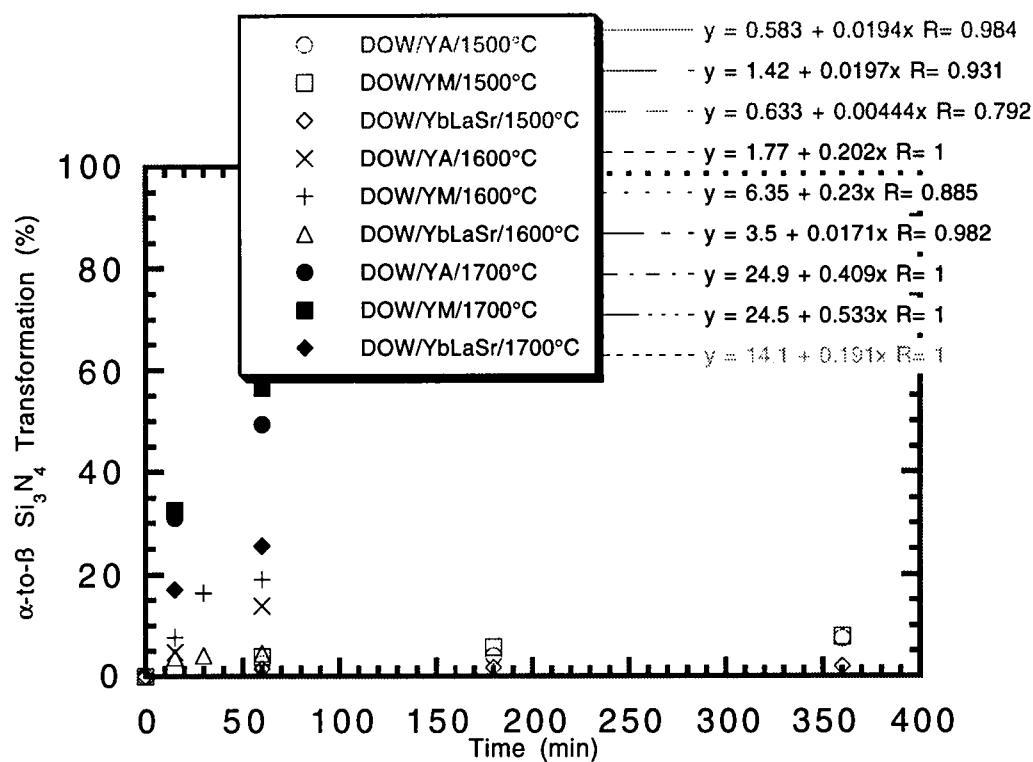


Fig. 5.20. α -to- β Si_3N_4 transformation as a function of time for the various types of sintering additives at 1500°C and 1600°C. The silicon nitride powder was Dow EXP.

It was observed that molecular transport in simple liquids is empirically described by the Stokes-Einstein equation:

$$D = \left(\frac{k}{3\pi a_o} \right) \frac{T}{\Phi} \quad [\text{Eq. 5.6}]$$

where Φ = viscosity

D = diffusion coefficient

a_o = molecular diameter

k = Boltzman's constant

T = Temperature

The Y_2O_3 - SiO_2 (YS) additive system would have the highest liquid phase viscosity and indeed, the slowest transformation rate is observed with these materials. The Yb_2O_3 - La_2O_3 - SrO (YbLaSr) system was intermediate in transformation kinetics compared to the other systems.

The sintering additives also increase the nitrogen solubility of the liquid phase and therefore, increase the nitrogen availability. Silica, SiO_2 , alone has a small nitrogen solubility of approximately 7 atom. %. However, silica in combination with additives, such as Y, Al and Mg increases the nitrogen solubility up to as high as 20 atom. %.¹⁹³ Thus, the α -to- β transformation is facilitated by the use of sintering additives.

Effect of Sintering Additive Amount

Results on the transformation rate with different sintering additive amounts are summarized in Figs. 5.21 and 5.22. Generally, the larger amount of sintering additive resulted in a slower transformation rate. If the additional sintering additive increases the liquid volume, a slower transformation rate would tend to indicate a diffusion controlled process for the α -to- β transformation as compared to an interface controlled transformation. Previous results had indicated that grain growth in the Y-A system was diffusion controlled.²¹⁸ These results indicate that the α -to- β transformation is also a diffusion controlled mechanism.

Effect of β - Si_3N_4 Seed on the α -to- β Transformation

The different Si_3N_4 powders all contained different amounts of initial β -phase. To determine the effect of the initial β nuclei on the transformation behavior, several samples were fabricated with different amounts of β -seeds in addition to what was initially present in the as-received powders. The β -seed types and their fabrication were described previously.

The effect of the β - Si_3N_4 seed additions on the transformation behavior is shown in Figs. 5.23 and 5.24. The data is for one sintering additive type although the other systems exhibited similar behavior. As indicated, the β -seed additions actually increase the α -to- β transformation rate as shown in Fig. 5.25 and a linear relationship appears to also exist between the transformation rate and the amount of initial β -seeding. Such behavior of higher transformation rates with β -seeding has been observed previously, but the linear relationship was unknown.²¹⁹⁻²²¹

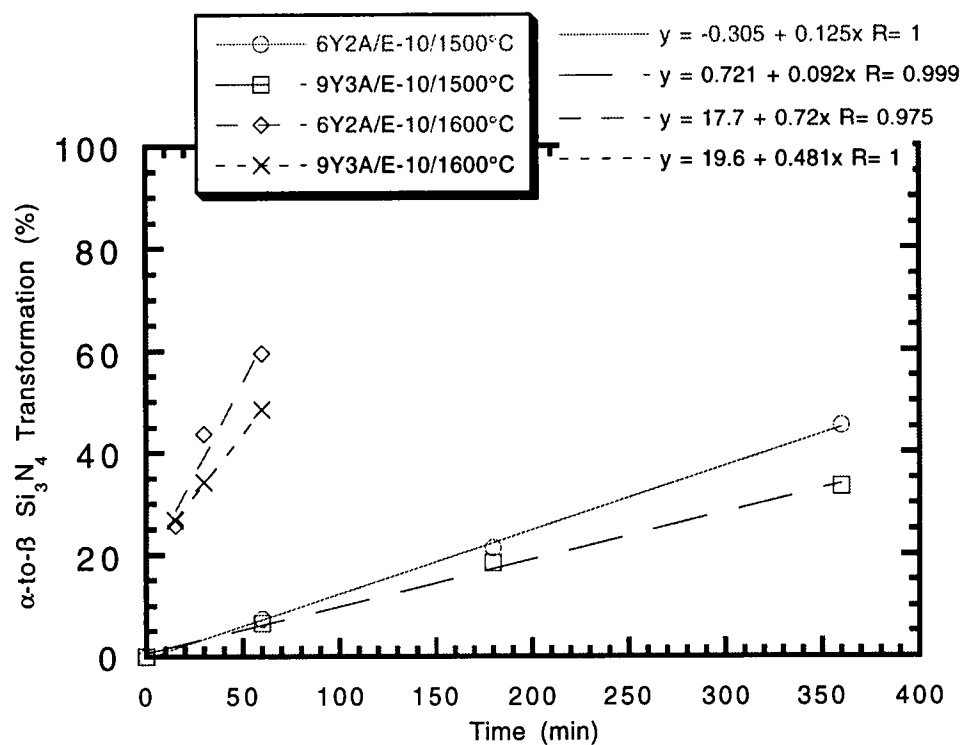


Fig. 5.21. α -to- β Si_3N_4 transformation as a function of time for different amounts of sintering additive at 1500°C and 1600°C . The sintering additive was either 6% Y_2O_3 -2% Al_2O_3 or 9% Y_2O_3 -3% Al_2O_3 . The silicon nitride powder was Ube E-10.

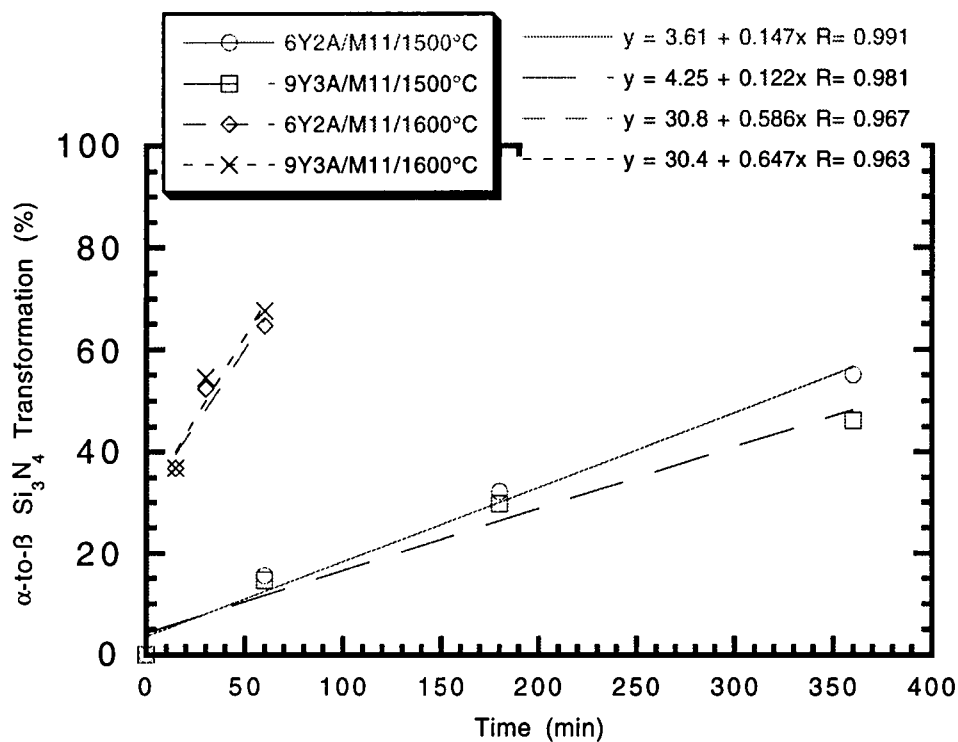


Fig. 5.22. α -to- β Si_3N_4 transformation as a function of time for different amounts of sintering additive at 1500°C and 1600°C. The sintering additive was either 6% Y_2O_3 -2% Al_2O_3 or 9% Y_2O_3 -3% Al_2O_3 . The silicon nitride powder was Starck M11.

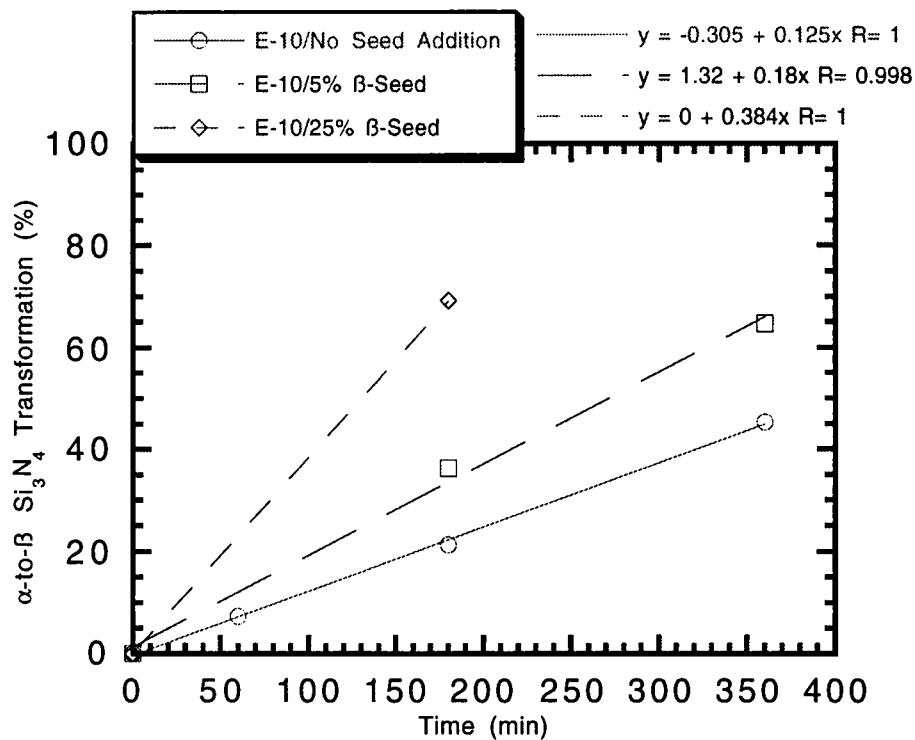


Fig. 5.23. α -to- β Si_3N_4 transformation as a function of time for different amounts of β - Si_3N_4 seed at 1500°C and 1600°C . The sintering additive was 6% Y_2O_3 -2% Al_2O_3 . The silicon nitride powder was Ube E-10 and the β -seed was fabricated from Ube E-10 powder.

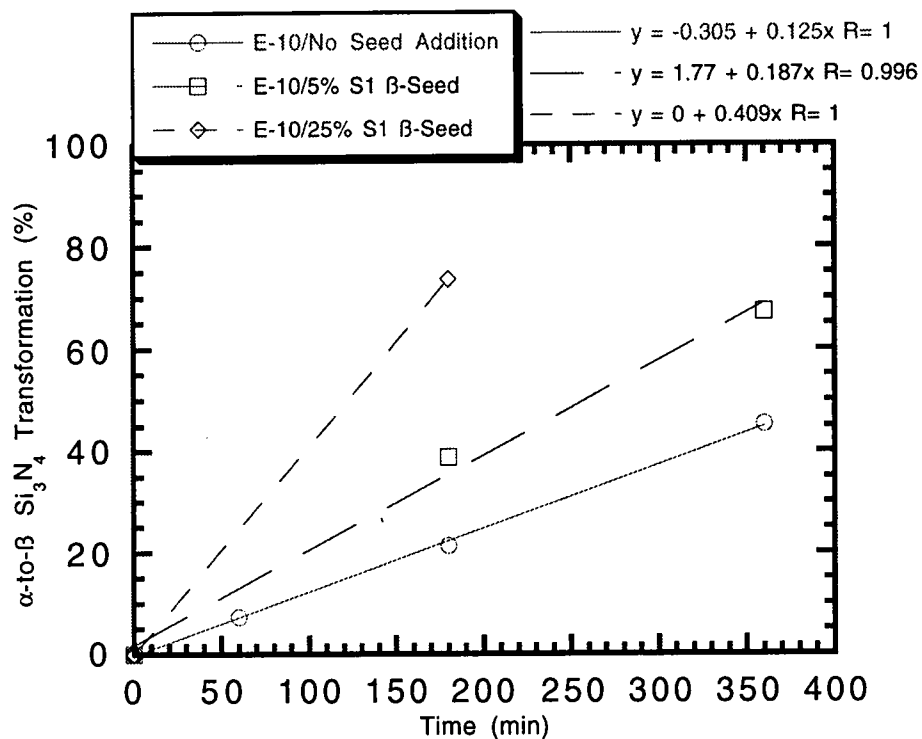


Fig. 5.24. α -to- β Si_3N_4 transformation as a function of time for different amounts of β - Si_3N_4 seed at 1500°C and 1600°C. The sintering additive was 6% Y_2O_3 -2% Al_2O_3 . The silicon nitride powder was Ube E-10 and the β -seed was fabricated from Starck S1 powder.

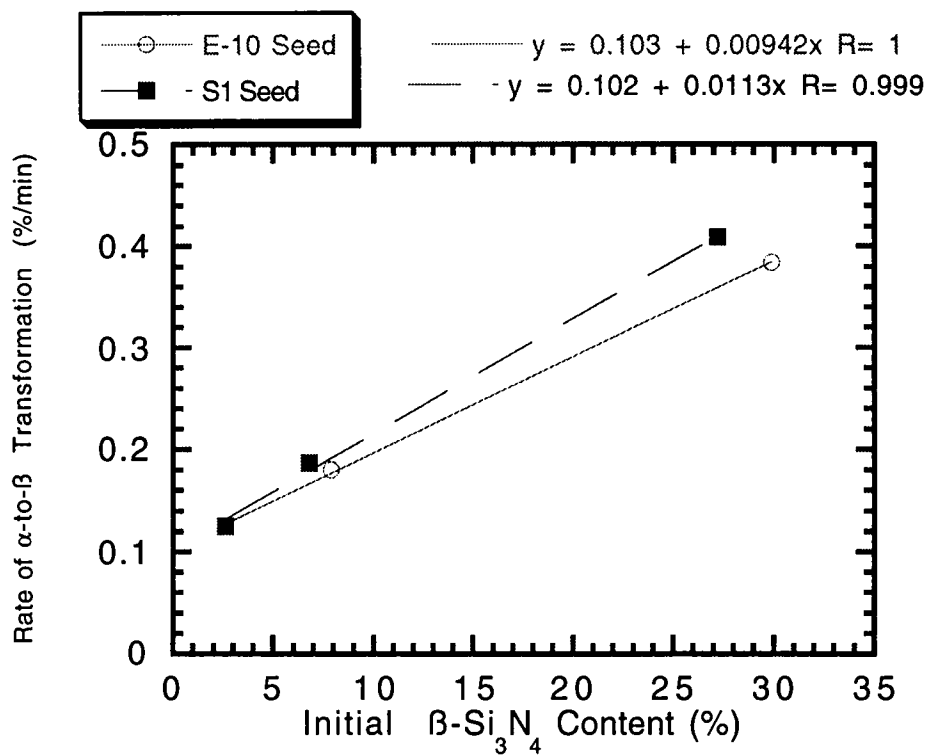


Fig. 5.25. α -to- β Si_3N_4 transformation rate as a function of initial β - Si_3N_4 content for two types of seed. The silicon nitride powder was Ube E-10, the sintering additive was 6% Y_2O_3 -2% Al_2O_3 and the tests were at 1500°C.

The increase in the α -to- β transformation rate with the addition of β -seeds is dependent on one of two possibilities. Referring to Fig. 5.26, if one assumes an equilibrium composition of the liquid phase at temperature in terms of its Si and N solubilities, then the increase in transformation rate is due to either (1) an increase in α -phase dissolution rate or (2) an increase in the β -phase precipitation rate. Since the addition of the β -seed can only influence the precipitation rate, that is the only explanation. This would explain the small difference in transformation rates between the types of β -seed as shown in Fig. 5.25. In that case, the S1 seed material had a slightly higher surface area which would increase the precipitation rate. Recently, it has been speculated that the transformation rate is a function of the β -seed nuclei density and surface area.²²²

The increase in phase transformation rates with seeding is not unique to silicon nitride materials. Earlier studies found that seeding of boehmite (AlOOH) with fine particles of α - Al_2O_3 increased the kinetics of the transformation and there was a decrease in the transformation temperature.^{223,224} These studies also found that by modifying the intermediate pore structure during seeding by the appropriate heat treatment, denser materials with more uniform microstructures could be produced.

Effect of Si_3N_4 Powder Surface Area Characteristics

The effect of silicon nitride powder surface area on the transformation rate is given in Figs 5.27 and 5.28. Not surprisingly, the silicon nitride powder with the highest surface area exhibits the highest transformation rate. All these powders used for the surface area comparison were fabricated by the diimide process.

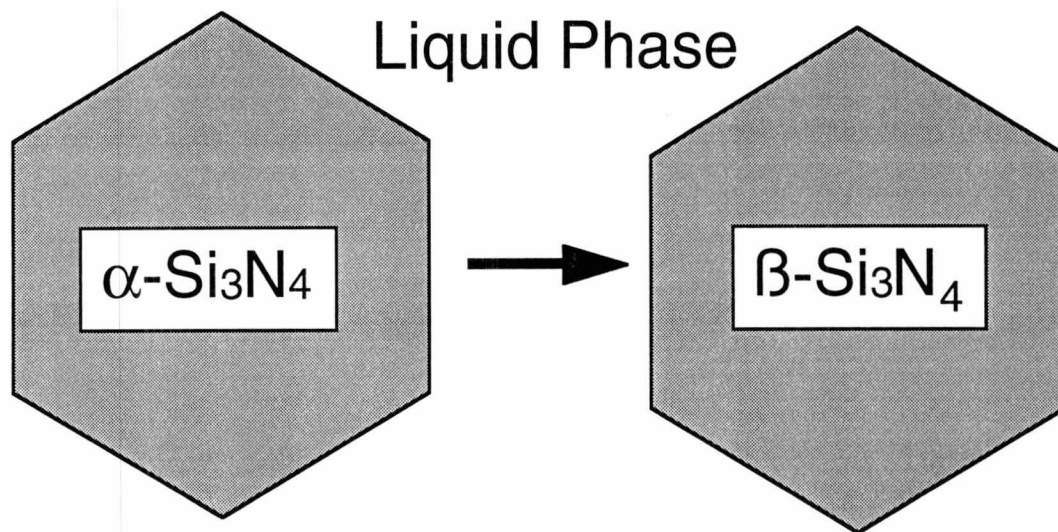


Fig. 5.26. Schematic representation of α -phase dissolution and β -phase precipitation.

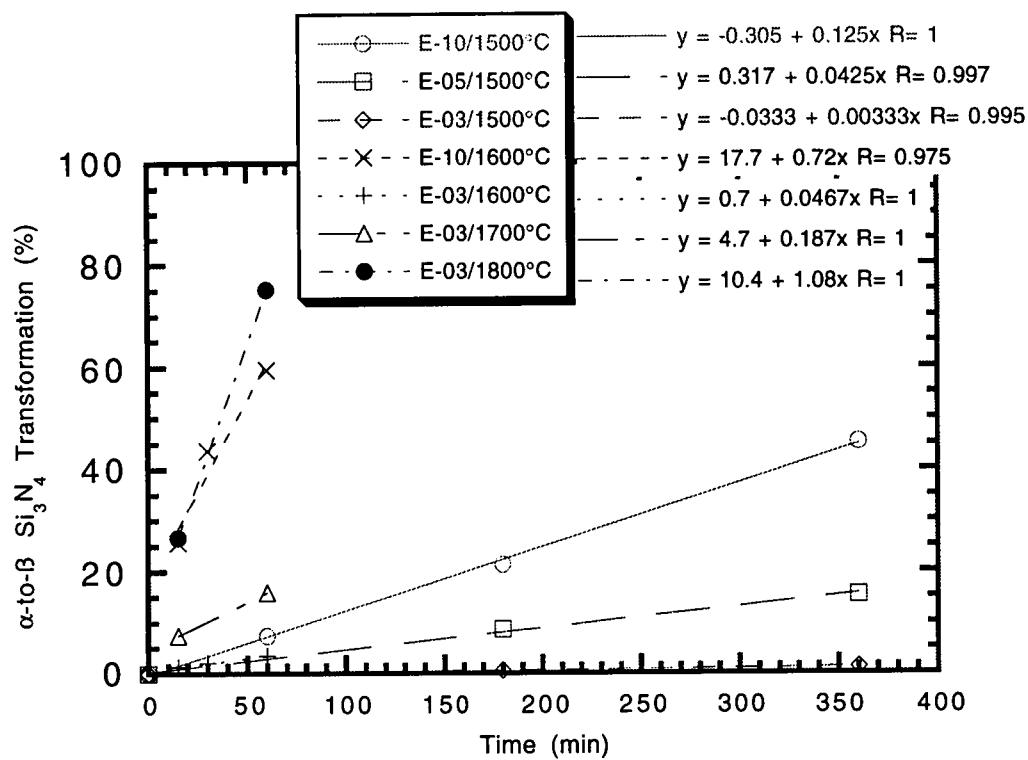


Fig. 5.27. α -to- β Si_3N_4 transformation as a function of time for the similar silicon nitride powders with different surface areas at 1500°C and 1600°C. The sintering additive was 6% Y_2O_3 -2% Al_2O_3 .

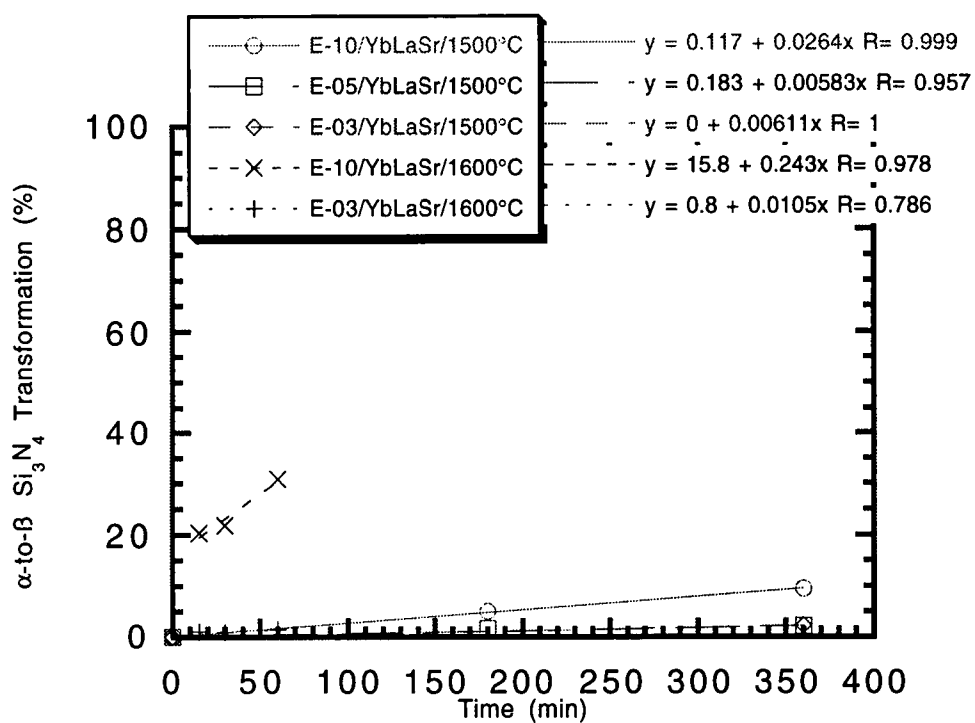


Fig. 5.28. α -to- β Si_3N_4 transformation as a function of time for the similar silicon nitride powders with different surface areas at 1500°C and 1600°C. The sintering additive was $\text{Yb}_2\text{O}_3\text{-La}_2\text{O}_3\text{-SrO}$.

As noted above, it was generally observed that the highest surface area silicon nitride powders exhibited the highest transformation rates. The appropriate relationship between the transformation rate and surface area was estimated by examining the behavior of powders made by the same process.

To insure and reinforce the idea that powders made by the same process indeed behave in a similar fashion, an Arrhenius plot of α -to- β Si_3N_4 transformation rate as a function of inverse temperature ($1/T$) for the silicon nitride powders was made (Fig. 5.29). In this case, the sintering additive for these samples was 6% Y_2O_3 -2% Al_2O_3 . The activation energies for the powders are nearly identical in the range of 539-556 kJ/mol. These values are similar to previous studies on silicon nitride transformation rate kinetics.²¹⁹⁻²²¹ Since all of the powders were fabricated by the diimide process they should have similar initial lattice oxygen contents and carbon contents and small differences in total oxygen content and initial β contents. So the only significant difference in the transformation rate is attributable to the surface area variation. A plot of the transformation rate as a function of silicon nitride powder surface area for the diimide powders is shown in Figs. 5.30 and 5.31. As indicated, there appears to be a linear relationship between the rate and the surface area for the data at 1500°C and 1600°C.

Effect of Powder Lattice Oxygen and Carbon Contents

The results have established that the α -to- β transformation kinetics for a particular sintering additive type are related to the initial β content and the powder surface area. Empirically, these effects have been derived from many previous studies. However, these factors alone do not explain all the differences in transformation behavior between the powders. In particular, the powder fabricated by carbothermal reduction (Dow EXP) displays a

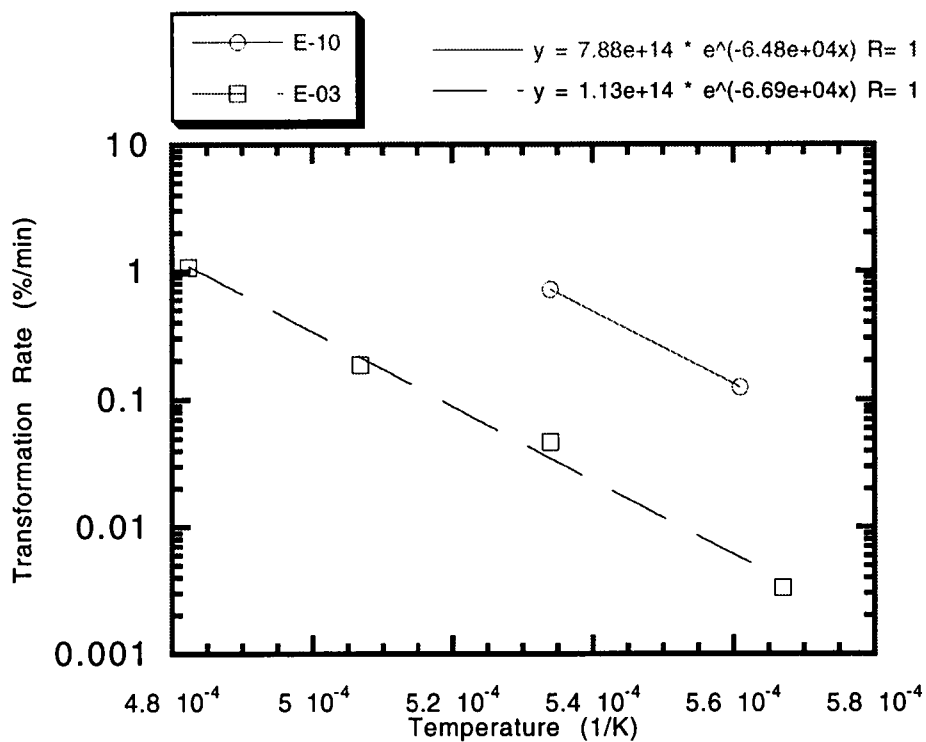


Fig. 5.29. Arrhenius plot of α -to- β Si_3N_4 transformation rate as a function of inverse temperature ($1/T$) for two silicon nitride powders (Ube E-10 and Ube E-03). The sintering additive was 6% Y_2O_3 -2% Al_2O_3 .

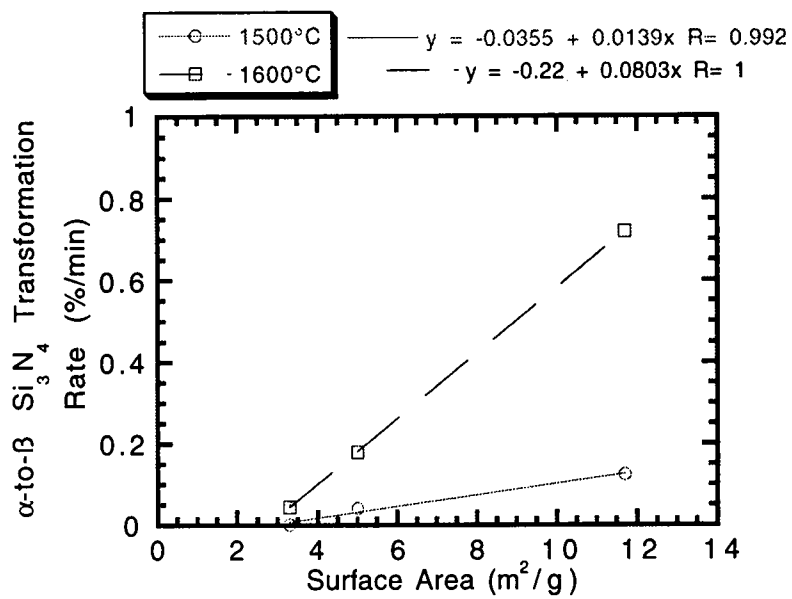


Fig. 5.30. α -to- β Si_3N_4 transformation rate as a function of starting silicon nitride surface area for the various silicon nitride powders made by the diimide process (Ube E-10, E-05 and E-03) at 1500°C and 1600°C. The sintering additive was 6% Y_2O_3 -2% Al_2O_3 .

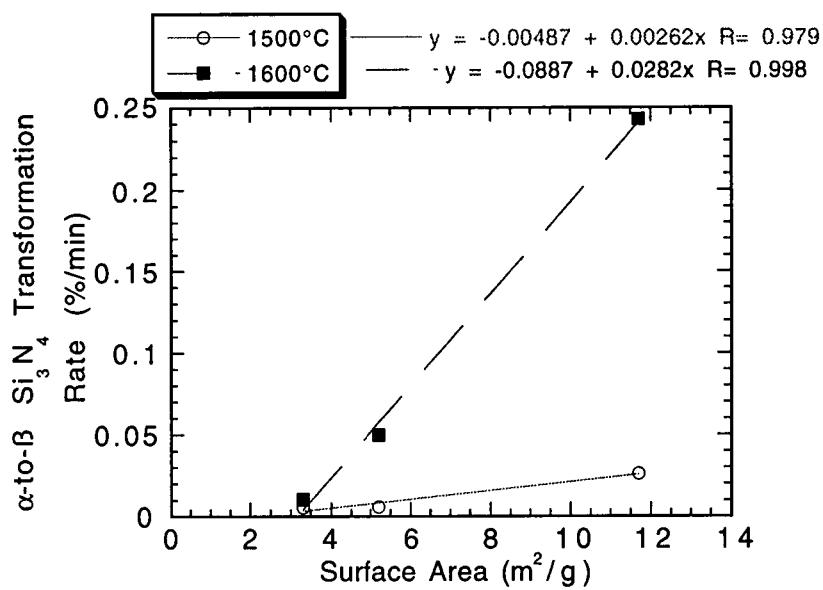


Fig. 5.31. α -to- β Si_3N_4 transformation rate as a function of starting silicon nitride surface area for the various silicon nitride powders made by the diimide process (Ube E-10, E-05 and E-03) at 1500°C and 1600°C. The sintering additive was Yb_2O_3 - La_2O_3 - SrO .

significantly slower transformation rate than would be predicted based on the initial β content and surface area. The difference is believed to be associated with the dissolution or melting behavior of the starting α -phase powder in the liquid phase upon which the transformation kinetics are directly dependent.

For the α -to- β transformation to occur, the liquid must dissolve substantial quantities of nitrogen. Because of its lower concentration in the liquid, nitrogen availability is the limiting species in the transformation and grain growth. The primary source of nitrogen is the dissolution of the Si_3N_4 particles. This is especially true at low overpressures of nitrogen. Since diffusion through the liquid is governed by its viscosity, for a given sintering additive system, the transformation rate should be dependent on the dissolution rate of the Si_3N_4 particles.

Possible influences on the dissolution behavior would include impurities (such as metallic cations, carbon and oxygen) and the bond strength in the crystal structure. In examining the data, the lower purity Si_3N_4 powders did exhibit the lower transformation rates. However, impurities, such as Ca and Fe would tend to increase the melting rate, not decrease it. Related work observed that impurities actually increased the dissolution rate of SiO_2 into the melt.²²⁵ In addition, the results from the preliminary study did not show a slower transformation rate for the low purity powder (Denka 9FW) in comparison to the other powders. Therefore, metallic cation impurities are not believed to be the cause for the slower transformation rate of the carbothermally derived powder.

The carbon content of the Si_3N_4 was taken from the data supplied with the powders from the manufacturers. The rates were normalized to a surface area of $11 \text{ m}^2/\text{g}$ and an initial β -phase content of 2.5 % so the different powders could be compared on an equal basis.

Figure 5.32 shows the normalized transformation rate as a function of the carbon content. While Fig. 5.32 shows there is a definite trend to higher rates at the low carbon contents, the relationship is indeterminate at the higher carbon contents. An explanation for this is that the transformation rate is probably dependent on the form in which the carbon is present. At the low carbon contents (<0.2 wt. %), the carbon is associated within the α - Si_3N_4 structure. Consequently, it would have a direct effect on the dissolution rate of the particles. However, at the high carbon contents of the carbothermally produced powders, the carbon may be present in other forms, such as SiC or even free carbon. These forms would not directly affect the dissolution kinetics of the α -phase and the overall α -to- β transformation. In addition, the solubility of carbon in oxynitride glass melts is low. This would also reduce the dissolution of the α -phase containing lattice carbon and increase its stability.

An examination of the effect of the lattice oxygen content on the α -to- β transformation can be done in a similar manner. However, the lattice oxygen content of the powders must be determined. The total oxygen content of the Si_3N_4 was taken from the data supplied with the powders from the manufacturers. The oxygen content of silicon nitride particles is distributed between the surface layer and the bulk oxygen content according to the following relationship:

$$C_{\text{Total}} = C_o + C_b \quad [\text{Eq. 5.7}]$$

Previous studies on Si_3N_4 powders have shown amorphous oxide layers on the surfaces of the particles.²²⁶⁻²³⁰ Direct observations by TEM indicated these layers were 3-5 nm thick.^{5,30,5,31} Other studies, using XPS techniques, determined the layers were 0.1-1 nm thick if a 'pure' SiO_2 composition was assumed or 0.3-3 nm thick if a Si_2ON_2 composition

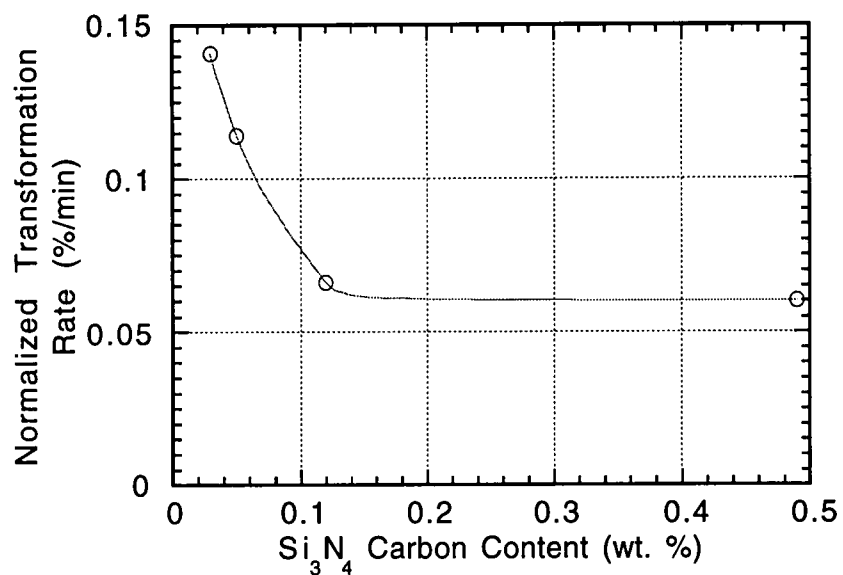


Fig. 5.32. Normalized α -to- β Si_3N_4 transformation rate as a function of starting silicon nitride carbon content at 1500°C . The sintering additive was 6% Y_2O_3 -2% Al_2O_3 . The transformation rates were normalized to a powder surface area of $11 \text{ m}^2/\text{g}$ and an initial β -phase content of 2.5 %.

was assumed.²²⁶⁻²³² XPS analysis of the bond energies for the Si 2p electron peaks indicate the surfaces are intermediate between SiO₂ and Si₂ON₂.²³³

Greil and coworkers determined that a linear relationship exists between the surface oxide concentration (calculated from XPS results) and the isoelectric point (pH_{iep}, point of zero charge) of silicon nitride in aqueous suspensions for several commercial powders.^{228,229} Isoelectric points are commonly used in ceramic processing to describe the surface charge characteristics of particles in contact with a liquid. When a powder is dispersed in a liquid medium, surface charges are established and under an electric field these surface charges cause the particles to move. When the electrophoretic mobility of a particle is zero, the particle is said to have an isoelectric point (I_{ep}) or point of zero charge. In ceramics, the isoelectric point is usually described as a function of pH.

The empirically derived relationship between isoelectric point and surface oxygen content on silicon nitride powders is shown below:

$$C_0^s = S_v[0.0161(9.3 - pH_{iep})] \quad [\text{Eq. 5.8}]$$

, where C₀^s = Surface oxygen concentration (wt. %)

S_v = Surface area of the powder (m²/g)

pH_{iep} = isoelectric point pH

This behavior was explained by using a two-site surface dissociation model with appropriate values of the dissociation constants for the acidic silanol and basic amine groups. Similar correlations have been observed in other studies.²³⁰ The isoelectric point

of the powders used in this study were obtained from the literature.²³¹⁻²⁴⁴ The lattice oxygen contents were then calculated using the equations above.

The relationship between the lattice oxygen content and the transformation rate is shown in Fig. 5.33. As indicated, the transformation rate is observed to decrease with increasing lattice oxygen. Melting involves the breaking of bonds as the material enters the liquid phase.

The melting point or phase transition from solid-to-liquid is a well defined parameter in materials science. However, the actual atomistic mechanisms involved are not entirely understood.^{245,246} This is in contrast to the solidification phase transition from liquid-to-solid where there is an enormous body of data describing the process, mechanisms and kinetics. For materials, melting is equivalent to an increase in the vacancy concentration of up to 10% as the phase transition proceeds. The liquid melt can be considered an array of voids and small regions of disordered crystal and in the case of normal glass melts, the materials are believed to be composed of SiO_4 tetrahedra. In particular, for oxynitride melts in silicon nitride ceramics, the liquid is thought to be comprised of $\text{Si}(\text{O},\text{N})_4$ tetrahedral structural units consisting mainly of $\text{Si}(\text{O})_4$, $\text{Si}(\text{O}_3\text{N})$ and $\text{Si}(\text{O}_2\text{N}_2)$ groups with a small concentration of $\text{Si}(\text{ON}_3)$.²¹⁵ During melting the change from the long-range crystallographic order existing in the close-packed lattice to one of small regions of disordered clusters has been proposed to be associated with the generation of dislocation cascades.^{5,44} However, to date no definitive explanation of the melting mechanism has been put forth. Normally, it has been assumed that the α -phase and β -phase both melt at the same rate in an oxynitride melt.^{222,247}

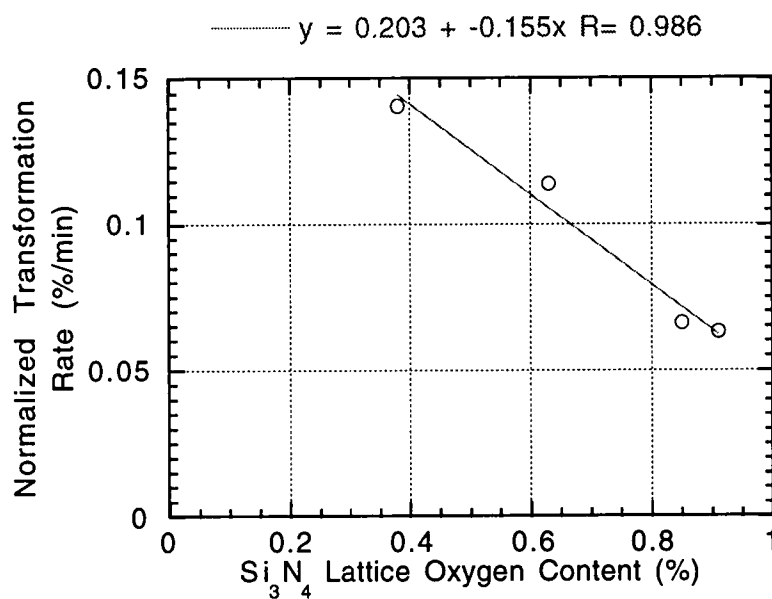


Fig. 5.33. Normalized α -to- β Si_3N_4 transformation rate as a function of starting silicon nitride lattice oxygen content at 1500°C . The sintering additive was 6% Y_2O_3 -2% Al_2O_3 . The transformation rates were normalized to a powder surface area of $11 \text{ m}^2/\text{g}$ and an initial β -phase content of 2.5 %.

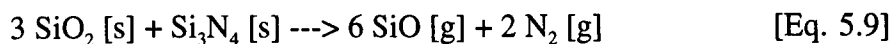
As mentioned previously, the α - and β - phase structures have similar crystal structures and densities and the first-order bonding is the same in each case. The α -phase is considered to be the low temperature phase and the β - the high temperature polymorph. Early studies reported oxygen in the lattice has been reported to stabilize the α -phase, however, this fact is disputed.²⁴⁸⁻²⁵⁰ The oxygen solubility in silicon nitride is reported to be on the order of 0.8-1.4 wt. %.²²⁸

From all the data, it may be concluded that the effect of the lattice oxygen and carbon contents on the Si_3N_4 dissolution behavior may be associated with the differences in the bond strengths: Si-N of 335 kJ/mol, Si-O of 452 kJ/mol and Si-C of 318 kJ/mol.²⁵¹ The high lattice oxygen contents and the strengths of the Si-O bond could contribute to a decrease in the melting kinetics of the α - Si_3N_4 and a decrease in the overall transformation kinetics.

Because the nature of the reaction, production of silicon nitride by carbothermal reduction is susceptible to incorporating significant amounts of oxygen in the crystal lattice of the particles. This is especially true for large scale quantities where the local CO gas partial pressure can build-up (>0.345 ATM at $T < 1435^\circ\text{C}$) and make SiO_2 stable.²⁵² Such fabrication considerations are probably why the Dow EXP powder is so high in lattice oxygen content.

This increase in stability of the α -phase by lattice oxygen may be the major cause for the slow α/β transformation rates for the high lattice oxygen silicon nitride powder.

Oxygen in the bulk silicon nitride lattice has also been found to contribute to gas evolution as the α/β transformation takes place according to the following reaction:



Such a reaction may explain some of the ‘de-sintering’ phenomenon observed when densifying carbothermally produced powder under one atmosphere of nitrogen.^{253,254}

Microstructure Examination

Selected samples of materials heated to intermediate temperatures were broken and the fracture surfaces examined by SEM. This type of method is commonly used to examine the grain structure. The morphological changes that occurred during the initial stage α -to- β transformation and densification were observed. The specimens were selected to ascertain the effects of the different Si_3N_4 powders or the different sintering additive compositions on the morphology changes. The changes that occurred could only be analyzed qualitatively by these methods.

The fracture surfaces of samples fabricated with Ube E-10 Si_3N_4 and sintering additives of 6% Y_2O_3 -2% Al_2O_3 , Yb_2O_3 - La_2O_3 - SrO and 6% Y_2O_3 -1% MgO are shown in Figs. 5.34, 5.35 and 5.36, respectively. As shown, obvious differentiations between the different sintering additives is difficult at best.

The morphology changes accompanying the transformation of specimens containing Dow EXP Si_3N_4 powder and 6% Y_2O_3 -2% Al_2O_3 are shown in Fig. 5.37. Because there are few acicular grains present it is evident that little transformation has occurred after 15 minutes at 1600°C. The fracture surface of the material after 1800°C indicates a very wide range in the grain diameters that takes place with this Si_3N_4 powder.

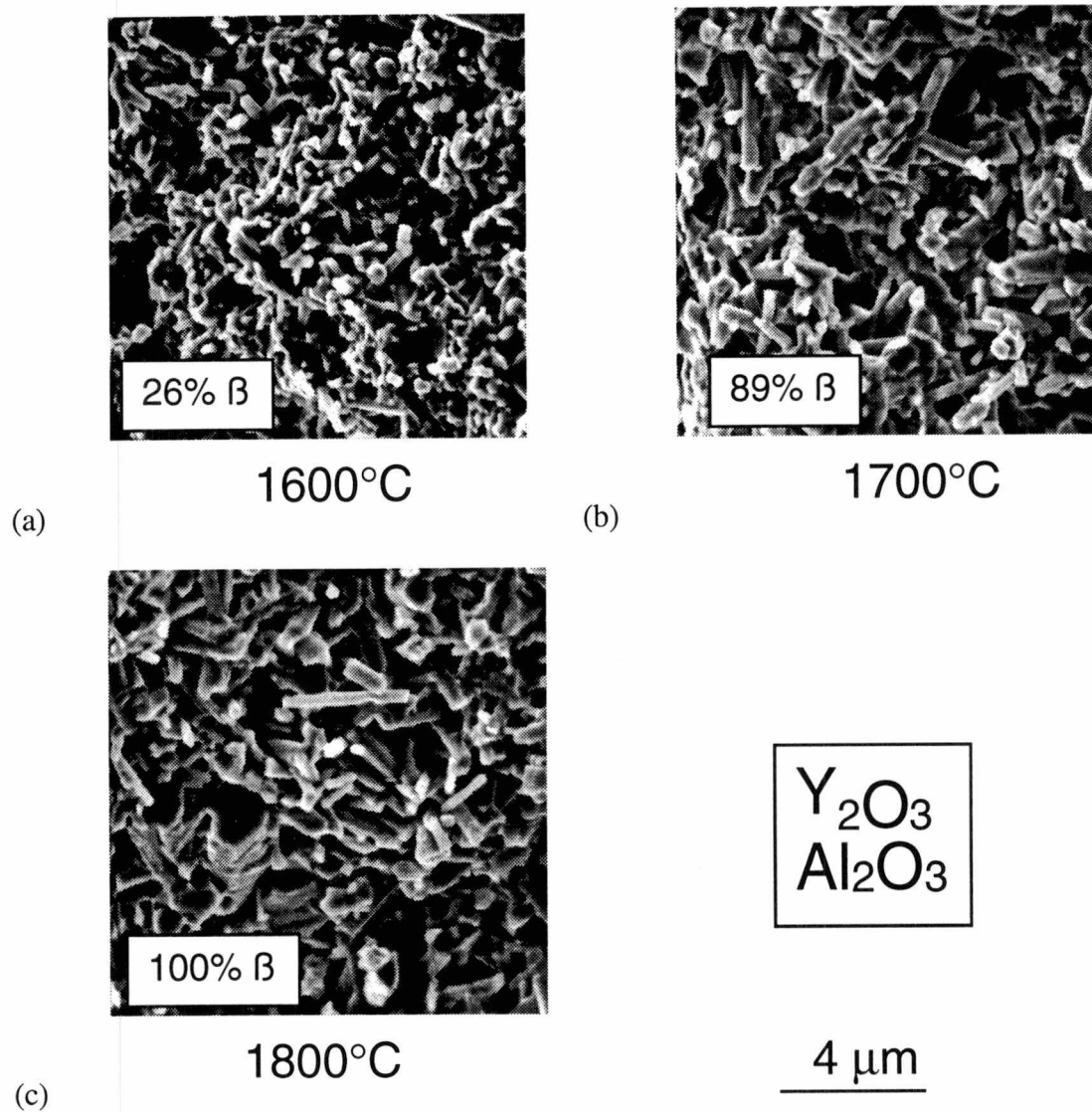


Fig. 5.34. Fracture surface of samples heated to intermediate temperature as shown for 15 minutes. (a) 1600°C, (b) 1700°C, and (c) 1800°C. Powder was Ube E-10. Sintering additive was 6% Y_2O_3 -2% Al_2O_3 . β - Si_3N_4 content shown on photographs.

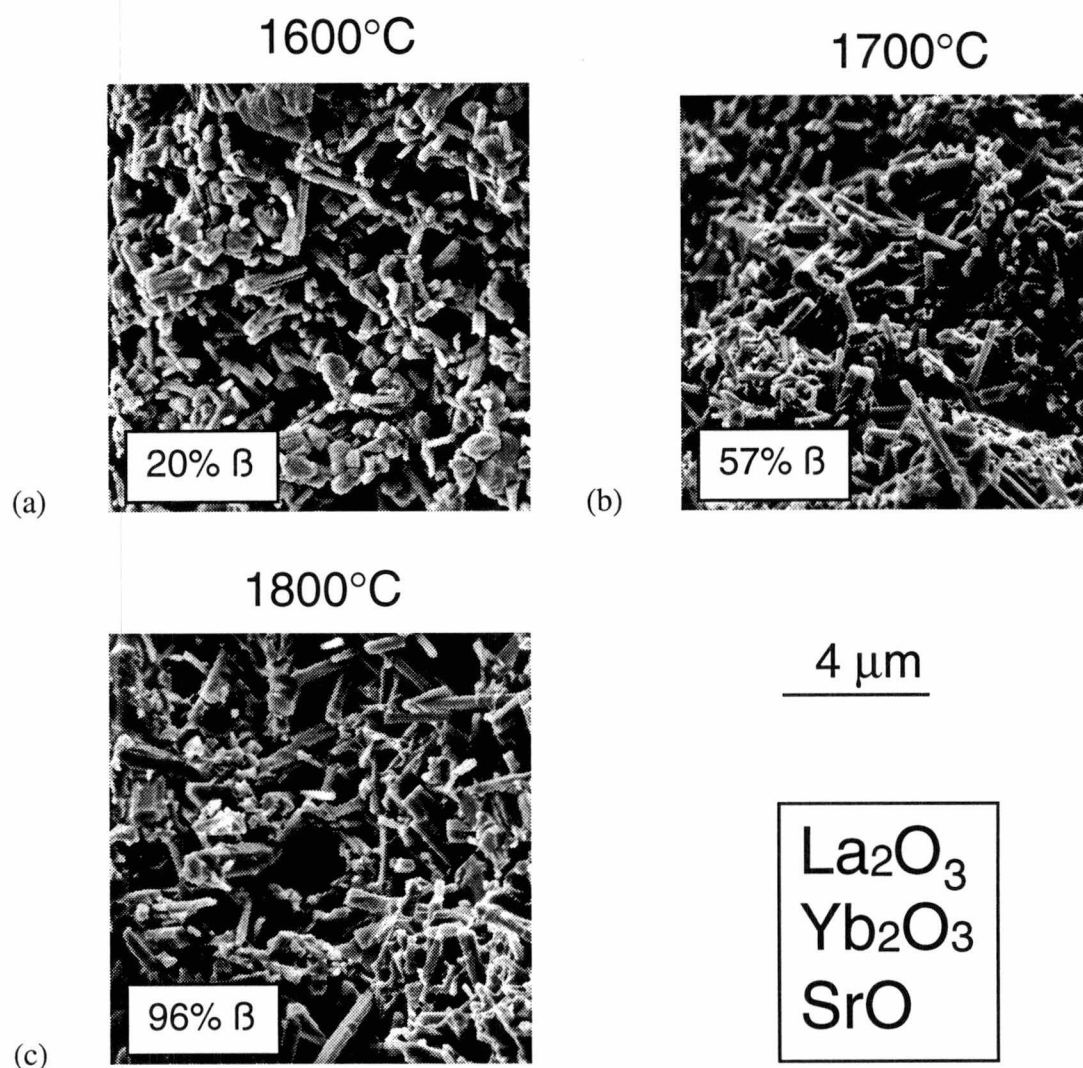
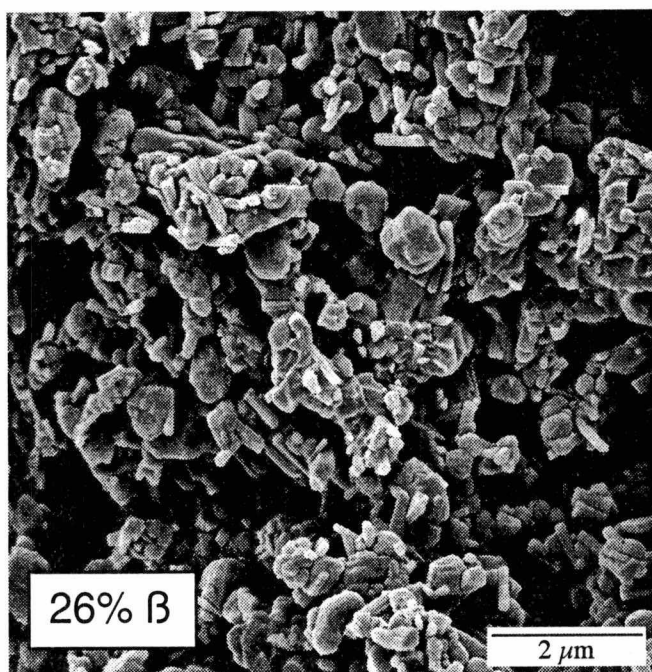


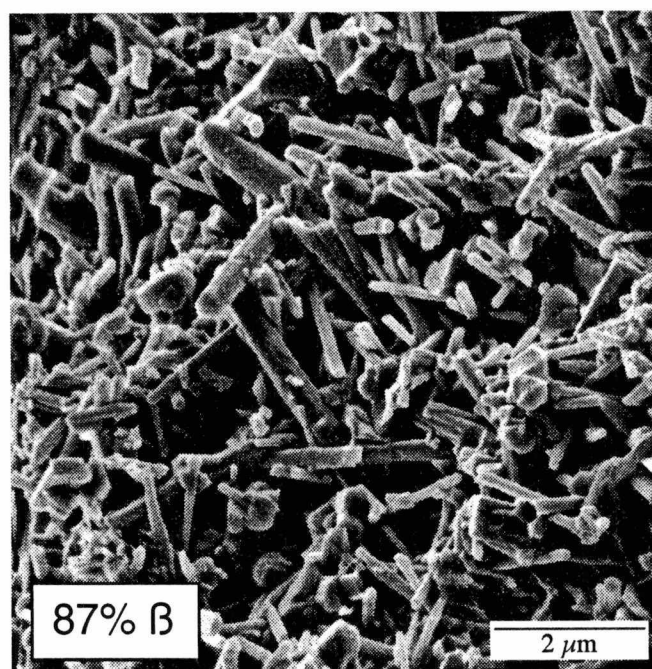
Fig. 5.35. Fracture surface of samples heated to intermediate temperature as shown for 15 minutes. (a) 1600°C, (b) 1700°C, and (c) 1800°C. Powder was Ube E-10. Sintering additive was $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$. β - Si_3N_4 content shown on photographs.

1600°C



(a)

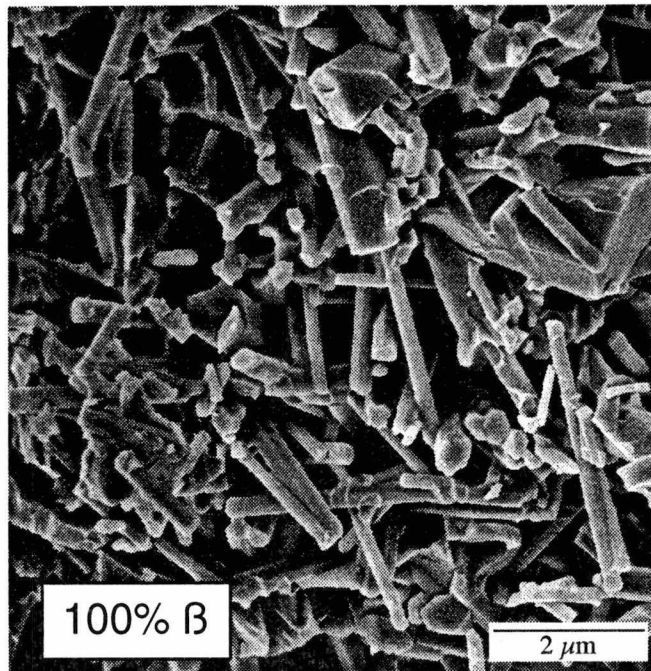
1700°C



(b)

Fig. 5.36. Fracture surface of samples heated to intermediate temperature as shown for 15 minutes. (a) 1600°C, (b) 1700°C, and (c) 1800°C. Powder was Ube E-10. Sintering additive was 6% Y_2O_3 -1% MgO . β - Si_3N_4 content shown on photographs.

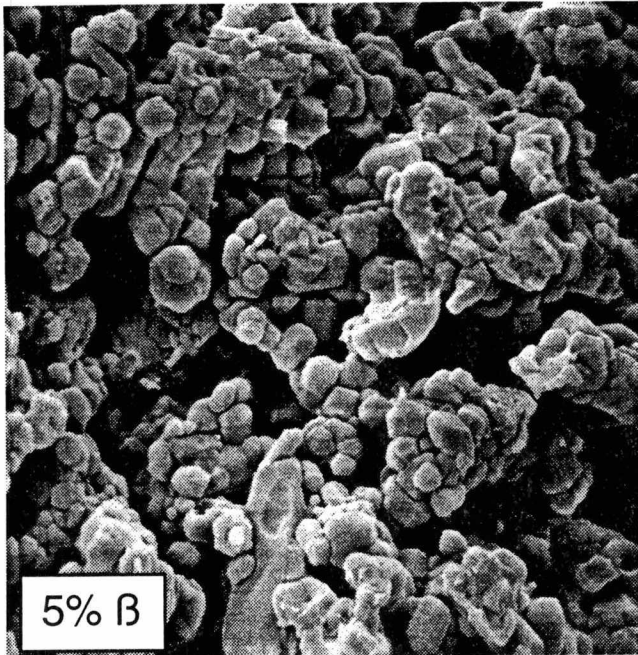
1800°C



(c)

Fig. 5.36. (Continued) Fracture surface of samples heated to intermediate temperature as shown for 15 minutes. (a) 1600°C, (b) 1700°C, and (c) 1800°C. Powder was Ube E-10. Sintering additive was 6% Y_2O_3 -1% MgO . β - Si_3N_4 content shown on photographs.

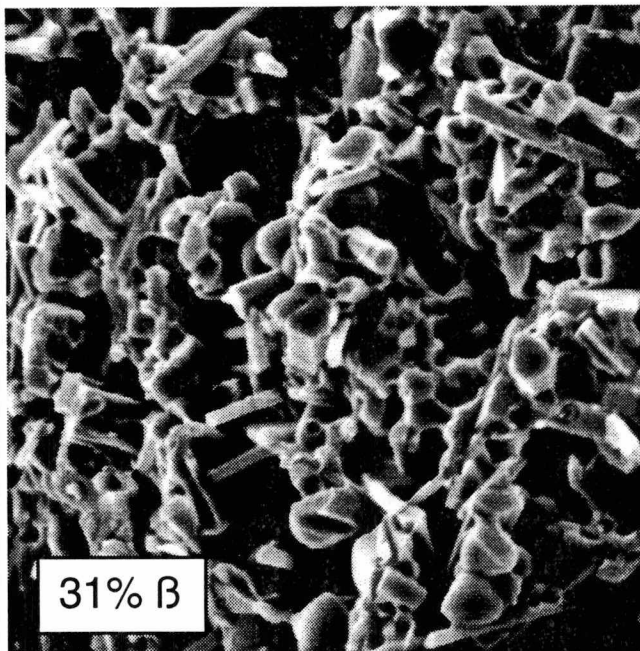
1600°C



(a)

4 μm

1700°C

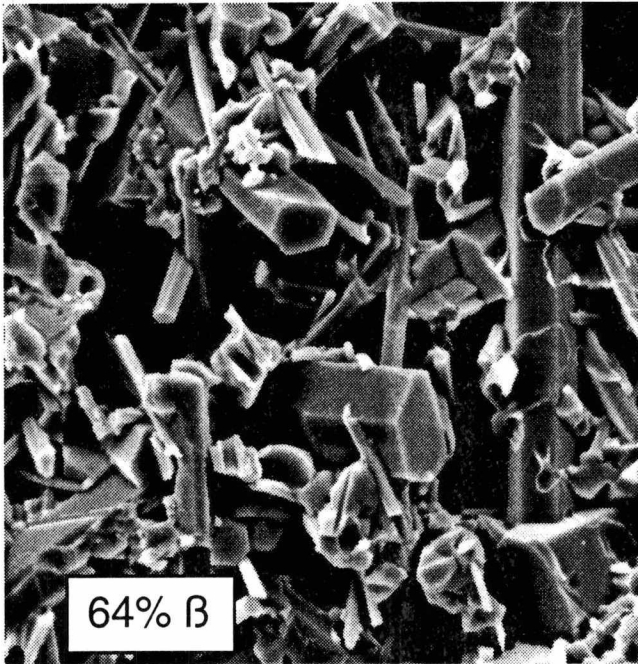


(b)

4 μm

Fig. 5.37. Fracture surface of samples heated to intermediate temperature as shown for 15 minutes. (a) 1600°C, (b) 1700°C, and (c) 1800°C. Powder was Dow EXP. Sintering additive was 6% Y_2O_3 -2% Al_2O_3 . β - Si_3N_4 content shown on photographs.

1800°C



(c)

4 μm

Fig. 5.37. (Continued) Fracture surface of samples heated to intermediate temperature as shown for 15 minutes. (a) 1600°C, (b) 1700°C, and (c) 1800°C. Powder was Dow EXP. Sintering additive was 6% Y_2O_3 -2% Al_2O_3 . β - Si_3N_4 content shown on photographs.

Quantitative Analysis of Initial Stage β - Si_3N_4 Grain Growth

As described in Chapter 2, selected samples were subjected to dissolution of the intergranular phase and collected. These grains were analyzed for length and diameter by SEM and the aspect ratio (length/diameter) was calculated. The samples were selected to determine the effects on the initial stage β - Si_3N_4 grain growth of the Si_3N_4 powder type, the sintering additive composition, the liquid phase volume content and time. All of the samples were high in β - Si_3N_4 content (95-100%). This was intended to eliminate any misinterpretations in dimensions that would be caused by the inability to distinguish between the α - and β -phases in the SEM after dissolution into individual grains.

The effect of the powder type on the initial stage β - Si_3N_4 grain growth (1800°C for 15 minutes) is shown in Fig. 5.38. The comparison indicates that the Starck M11 powder has a shorter length, but higher aspect ratio. This says that overall, the β - grains were much thinner in diameter than those developed in the Ube E-10 powder. Such a situation is related to the high initial β -content of the M11 powder and its higher transformation rate. Those factors would contribute to highly acicular growth of many grains during the initial grain growth stage.

The differences in the sintering additive composition on the initial stage β - Si_3N_4 grain growth is illustrated in Fig. 5.39. As shown, the higher viscosity liquid phase (Yb_2O_3 - La_2O_3 - SrO) results in larger average diameter and aspect ratios in comparison to the lower viscosity liquid (Y_2O_3 - Al_2O_3 system). It had been previously shown that the Yb_2O_3 - La_2O_3 - SrO system had a slower transformation rate and this apparently encouraged grain growth in the c-axis direction of fewer grains. The Y_2O_3 - Al_2O_3 composition, on the other hand, exhibited a higher transformation rate and this causes grain growth of many β - Si_3N_4 grains

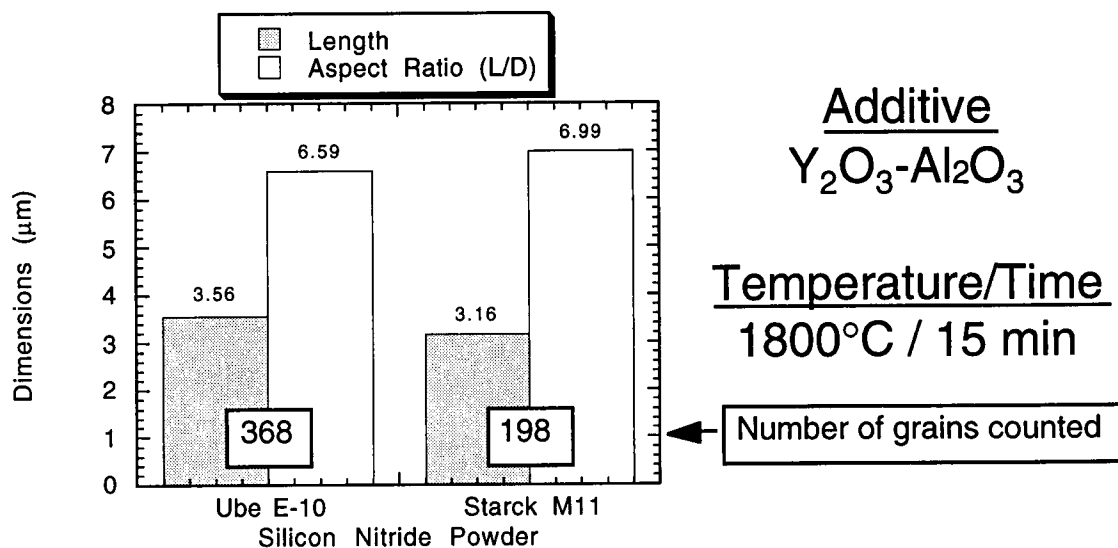


Fig. 5.38. Effect of silicon nitride powder type on initial stage β - Si_3N_4 grain growth. Powders were either Ube E-10 or Starck M11 as indicated. Heating time was $1800^{\circ}C$ for 15 minutes. Sintering additive composition was 6% Y_2O_3 -2% Al_2O_3 .

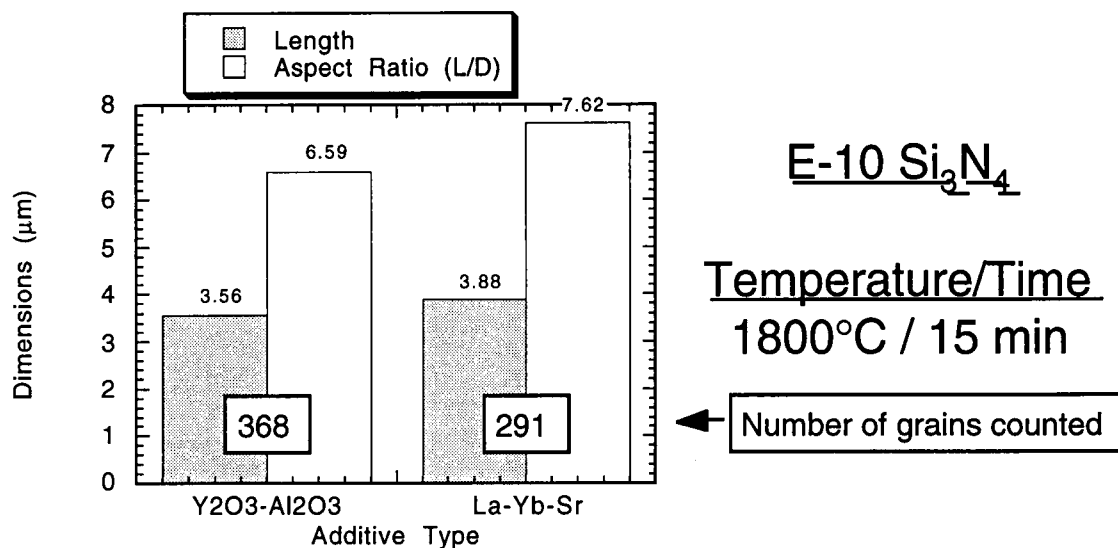


Fig. 5.39. Effect of sintering additive composition on initial stage β -Si₃N₄ grain growth. Powder was Ube E-10. Heating time was 1800°C for 15 minutes. Sintering additive composition was either 6% Y₂O₃-2% Al₂O₃ or Sr₂La₄Yb₄(SiO₄)₆O₂.

and impingement. The impingement of similar sized grains would tend to limit grain growth in both diameter and length. The higher viscosity liquid phase encourages acicular growth of $\beta\text{-Si}_3\text{N}_4$ grains because it decreases diffusivity for nitrogen and silicon and consequently, growth in diameter (the [210] direction) is limited by solute deficiency.

The effect of the liquid phase volume content on the initial stage $\beta\text{-Si}_3\text{N}_4$ grain growth is shown in Fig. 5.40. As indicated, increased additive volume content results in a decrease in grain dimensions both in length and aspect ratio. Previously, the larger volume content had been shown to have a slower transformation rate indicating a diffusion controlled process. The smaller grain dimensions also suggest a diffusion controlled mechanism for the grain growth. However, the increase in additive content can also contribute to a time delay in the α -to- β transformation and decrease the grain size in that way. This is because more of the $\alpha\text{-Si}_3\text{N}_4$ must be dissolved prior to the liquid phase reaching Si and N saturation. Thus, grain growth is slowed in comparison to the lower additive content materials.

Like most materials, as silicon nitrides are held at elevated temperatures, grain growth naturally occurs. The effect of the high temperature hold time on the grain development is shown in Fig. 5.41 for high viscosity liquid phase compositions ($\text{Yb}_2\text{O}_3\text{-La}_2\text{O}_3\text{-SrO}$ system). As indicated, the average grain lengths and aspect ratios increase with time (up to 60 min. in this case) which is what one would expect. While these relatively short times indicate increasing aspect ratios with time, previous results have shown long hold times to result in coarsening of the microstructures and a decrease in the average aspect ratio.^{1,16}

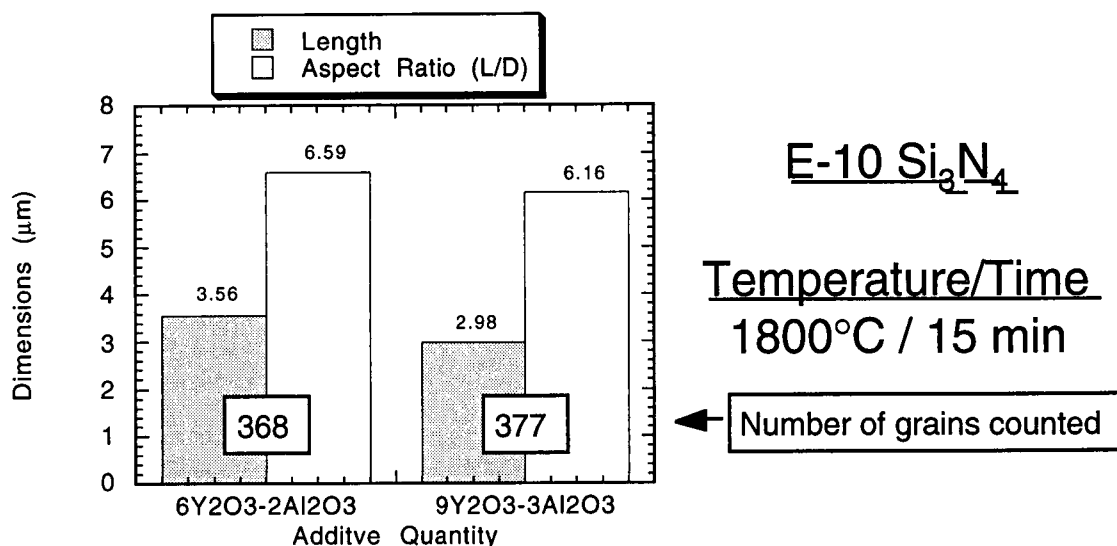


Fig. 5.40. Effect of sintering additive volume content on initial stage $\beta\text{-Si}_3\text{N}_4$ grain growth. Powder was Ube E-10. Heating time was 1800°C for 15 minutes. Sintering additive composition was either 6% Y_2O_3 -2% Al_2O_3 or 9% Y_2O_3 -3% Al_2O_3 .

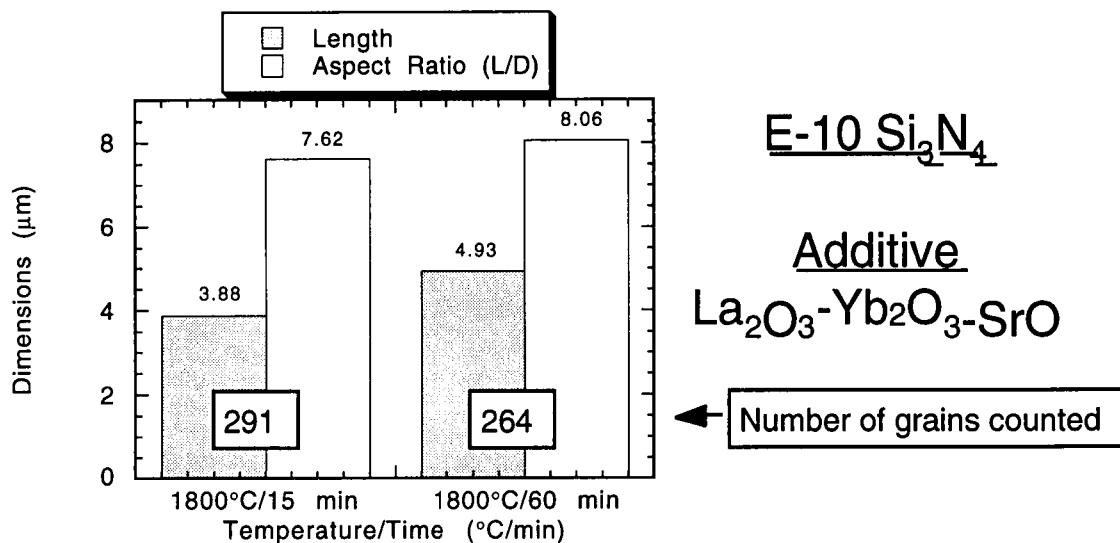


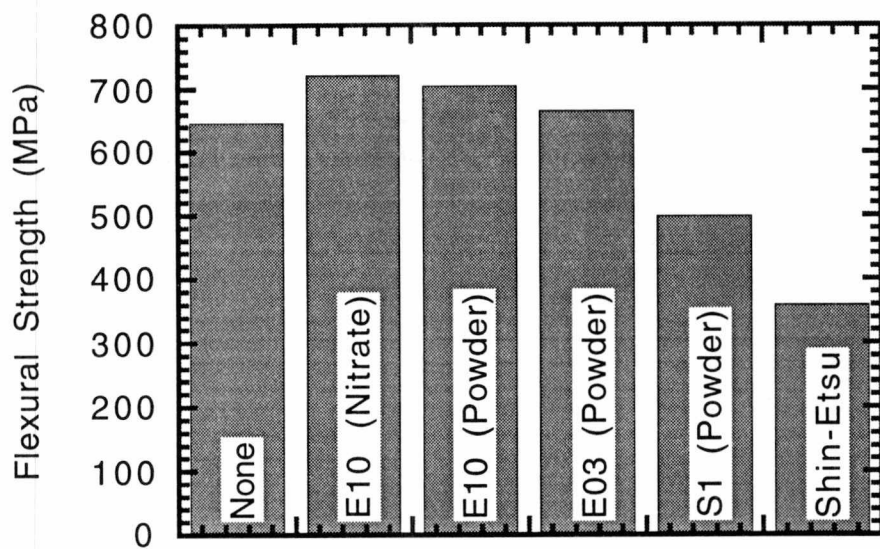
Fig. 5.41. Effect of sintering time on initial stage $\beta\text{-Si}_3\text{N}_4$ grain growth. Powder was Ube E-10. Heating was at 1800 $^{\circ}\text{C}$ for either 15 or 60 minutes. Sintering additive composition was $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$.

Results of β -phase Seeding on Mechanical Properties

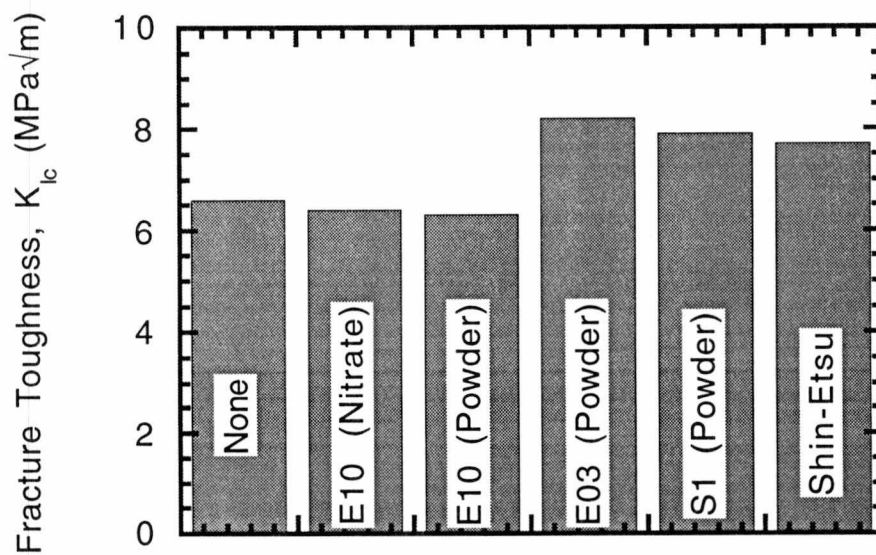
The effect of the type of β - Si_3N_4 seed on flexural strength and fracture toughness are illustrated in Fig. 5.42. The seeds fabricated by the reaction of either yttrium nitrate or Y_2O_3 powder and Ube E-10 Si_3N_4 developed materials with the highest flexural strength. However, the fracture toughness of these materials (at the 25% addition level) showed no improvement over the baseline composition having no β -seed addition. High observed fracture toughness are usually associated with bimodal microstructures of high aspect ratio grains. The β -seeds made with Ube E-10 Si_3N_4 were similar in size to the α -phase powder and during the initial stage liquid formation these seeds may have had dissolution rates similar or higher than the α -phase powder. In that case, the β -seeds would have a minor contribution to the β -nucleation and result in the development of a uniform grain size. This may explain the improved strengths with no increase in toughness, but microstructure analysis will be done to confirm this.

In contrast, the β -seeds made with the Ube E-03 or Starck S1 Si_3N_4 (and Y_2O_3 powder) were generally larger than the starting α -phase powder. This resulted in materials with similar or slightly lower strengths, but significantly higher fracture toughness as shown in Fig. 5.42. The microstructures are believed to be more bimodal in grain size which would result in the increased fracture toughness. In the case of the samples made with the β -seed from Shin-Etsu, the low strengths are attributable to the poor densification exhibited by these materials. The higher toughness is probably due to a combination of some large β - Si_3N_4 particles in the powder and the low density.

The effects of the β -seed content on flexural strength and fracture toughness are summarized in Fig. 5.43. As indicated, improvements in strength were observed with the

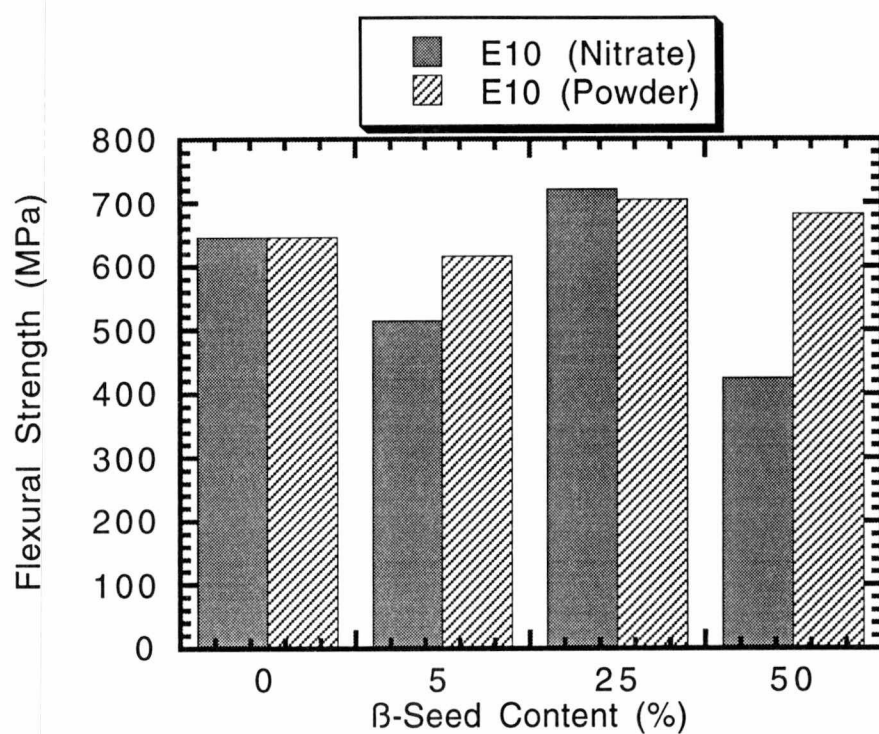


(a)

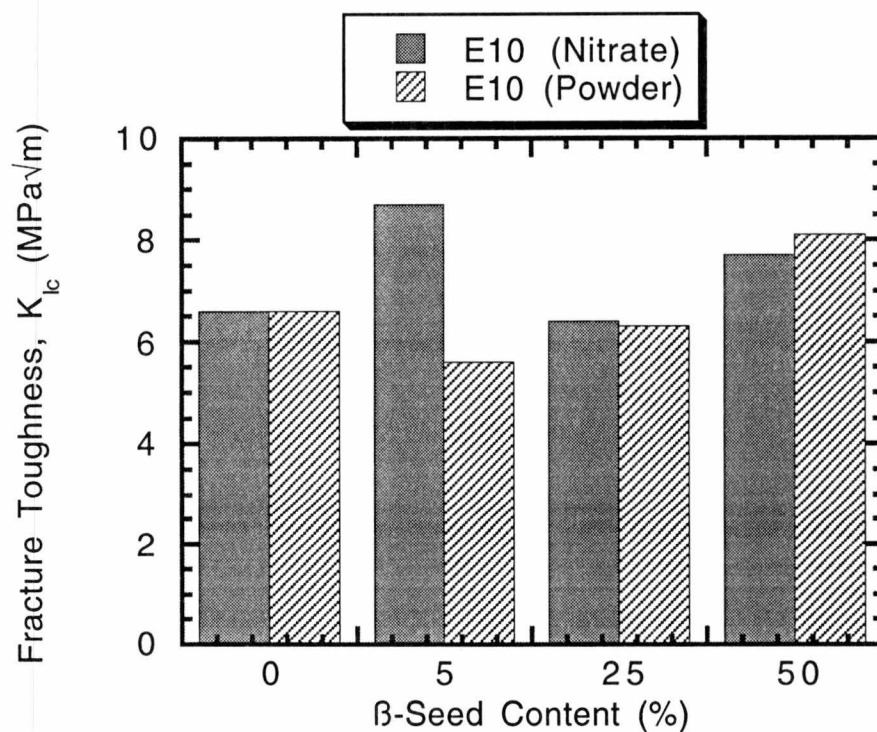


(b)

Fig. 5.42. Effect of β -seed type on the (a) flexural strength and (b) fracture toughness for gas-pressure sintered silicon nitride with $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition.



(a)



(b)

Fig. 5.43. Effect of β -seed content on the (a) flexural strength and (b) fracture toughness for gas-pressure sintered silicon nitride with $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition.

addition of 25% β -seed. At the other two additive levels (5 and 50%) generally lower strengths were obtained, however, the results were mixed. The fracture toughness also showed no definite trend. Higher toughnesses were observed with 50% β -seed additions, while the other additive levels showed no consistent improvements. Microstructural analysis will be used to explain the results.

Conclusions

The kinetics of the α -to- β Si_3N_4 transformation are dependent on several characteristics of the starting silicon nitride powder. Most important, are the silicon nitride powder surface area and initial β - Si_3N_4 content which both tend to increase the transformation rate. The transformation rates were found to follow a linear relationship depending on the surface area and initial β -phase content. The addition of the β -seed are believed to increase the precipitation rate of the β - Si_3N_4 because of the increased β -phase surface area. Consequently, the dissolution rate of the α -phase is also increased and the overall α -to- β Si_3N_4 transformation rate.

Other factors, such as increasing lattice oxygen or carbon contents within the β - Si_3N_4 powder particles, appear to contribute to decreasing the transformation rate. This is due to the high bond strength of the Si-O bond and the stability it gives to decreasing the melting kinetics. The lattice carbon content decreases the α -phase melting rate because of its low solubility in the liquid silicate melt. Although linear expressions were observed to occur, the limited amount of data demands that additional experimental evidence is needed to confirm such a linear relationship.

The glass phase from the sintering additives was also found to affect the α -to- β Si_3N_4 transformation rate. For higher viscosity and more refractory additives, the result is a decrease in the transformation rate. Such relationship have been observed in previous studies. In addition, larger volumes of the glass phase were observed to decrease the transformation rate. This indicates the α -to- β Si_3N_4 transformation is a diffusion controlled mechanism. The growth morphology of the β - Si_3N_4 grains during the initial stage growth is also affected by the Si_3N_4 powder and sintering additives. More acicular grains were developed from nitrided Si_3N_4 powders, high viscosity glass melts and lower quantities of glass.

CHAPTER VI

SUMMARY

Three inter-related aspects in the fabrication of silicon nitride ceramics were performed for the thesis work. The topics included: (1) an analysis of the composition and physical gradients in bulk silicon nitride, (2) the effect of sintering parameters on microstructure development during the high-temperature sintering stage and the resulting mechanical properties, and (3) an investigation of β -Si₃N₄ nucleation and initial stage microstructure development.

Parameters affecting the formation of composition and physical gradients in bulk silicon nitride include the packing powder composition, crucible type, sintering temperature, nitrogen pressure, sintering time, use of barrier/protective coatings, and setter type. Optimum conditions for densification, minimization of weight loss and minimization of reaction layer thickness depend mainly on the sample composition. During high temperature GPS processing, chemical and physical gradients develop from the exposed surfaces to the interior regions. The gradients are due to the furnace conditions and the environment adjacent to the samples. The experimental results indicate that oxygen diffusion and volatilization occurs from the exposed specimen surfaces. This phenomenon results in high nitrogen contents in the near-surface region and suggests that the gradient layers are formed by compositional changes across phase fields. The formation of nitrogen-rich phases, such as melilite, occurs on the as-sintered surfaces. Since nitrogen availability in the liquid is the limiting species for grain growth, the higher nitrogen concentration leads to the appearance of large grains near the surfaces compared to those developed in the bulk of the materials. Along with the compositional gradients, mechanical property differences also exist between the as-sintered surfaces and the bulk materials. In

some cases, high fracture toughness was observed in the near-surface regions. This was more evident when sintering parameters that promoted high weight losses (i.e. no packing powder, graphite crucibles, high temperatures and low nitrogen pressures) were used. In addition, the strengths of as-sintered surfaces of $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ were observed to be reduced by more than 30% compared to the bulk material.

Gas-pressure sintering (GPS) was used to densify silicon nitride containing a wide variety of sintering additives. Parameters affecting the sintering behavior were found to include densification temperature, densification time, grain growth temperature, grain growth time and heating rates. Samples of $\text{Si}_3\text{N}_4\text{-6\% Y}_2\text{O}_3\text{-2\% Al}_2\text{O}_3$ composition sintered to high densities at all conditions used in the present study, whereas samples of $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition required the highest temperatures and longest times to achieve densities $\geq 98\%$ T. D. The main effect on the fracture toughness for samples of $\text{Si}_3\text{N}_4\text{-6\% Y}_2\text{O}_3\text{-2\% Al}_2\text{O}_3$ was found to be the use of a lower densification temperature, which was 1900°C in the present study. For the $\text{Si}_3\text{N}_4\text{-Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ composition, fracture toughness was sensitive to and improved by a lower densification temperature (1900°C) and a higher grain growth temperature (2000°C). For both compositions the lower densification temperature was a significant factor affecting the fracture toughness and promoting a bimodal grain structure. The low significance of the other process parameters implies the microstructure (and therefore properties) are essentially 'locked-in' during the densification stage and only minor changes can take place afterward. Thus, the microstructural development that occurs during the densification dictates the final properties.

The kinetics of the α -to- β Si_3N_4 transformation are dependent on several characteristics of the starting silicon nitride powder. Most importantly, are the silicon nitride powder surface

area and initial β - Si_3N_4 content which both tend to increase the transformation rate. Other factors, such as lattice oxygen or carbon contents, appear to contribute to decreasing the transformation rate because they inhibit melting of the α - Si_3N_4 into the liquid phase.. In addition, the glass phase from the sintering additives also affects the transformation rate with higher viscosity and more refractory additives resulting in a decrease in the transformation rate. Larger volumes of the glass phase were observed to decrease the transformation rate. More acicular β - Si_3N_4 grains were developed during the initial stage growth from nitrided Si_3N_4 powders, high viscosity glass melts and lower quantities of glass.

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VITA

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He is married to Criste Tiegs and has two children, John and Jeremy.