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DENSIFICATION STUDIES OF SILICON NITRIDE

DISSERTATION

Presented in Partial Fulfillment of the Requirement for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Tai-Il Mah, B.Cer.E., M.Sc.

* * * * * *

The Ohio State University
1976

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I. INTRODUCTION

Over the past two decades, considerable attention has been directed to the study of silicon nitride as a candidate for turbine component material. Above about 1600°C silicon nitride dissociates appreciably, and dense silicon nitride can not be sintered by conventional ceramic methods. When certain additives are mixed with the silicon nitride powder, however, dense bodies can be formed by hot pressing. Magnesium compounds were generally employed as additives and the mechanism of densification appeared to follow the model of reactive liquid sintering. The high temperature strength of hot-pressed silicon nitride with magnesium oxide addition drops drastically above about 1000°C. This phenomenon was explained by a model of interstitial or boundary glassy bonding phase which softened at elevated temperature to permit deformation, probably by grain boundary sliding.

The objective of this investigation was to extend the high strength to higher temperature by recrystallizing the bonding glassy phase.
II. REVIEW OF LITERATURE

A. HISTORICAL BACKGROUND OF SILICON NITRIDE

More than a century ago Deville and Wöhler\(^1\) reported that silicon and nitrogen can combine when heated to a high temperature. Early in this century Weiss and Engelhart\(^2\) studied the reaction between silicon and nitrogen by measuring nitrogen absorption in silicon at temperatures from 1250°C to the melting point of silicon.

In 1925, Friedrich and Sitting\(^3\) heated a mixture of silica and carbon in a stream of nitrogen with a few percent hydrogen at 1500°C and obtained silicon nitride with the composition Si\(_3\)N\(_4\), in accordance with
\[
3\text{SiO}_2 + 6\text{C} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4 + 6\text{CO}
\]
When 10% Fe\(_2\)O\(_3\) was added as a catalyst to the charge, the reaction temperature was reduced to 1250°C - 1300°C. After leaching with concentrated hydrochloric acid, their product was nearly white and crystalline.

In 1930, Hincke and Brantly\(^4\) studied the nitrogen pressure for the reaction Si\(_3\)N\(_4\) \(\rightarrow\) 3Si + 2N\(_2\) at temperatures from 1606°C to 1802°C. They concluded that the dissociation pressure would reach 1 atm at 2250°C from the calculation of the free energy change and heat content.

In the 1950's Leslie, Carroll and Fisher\(^5\) separated from nitride silicon steel, a nitride that they believed to
be $\text{Si}_3\text{N}_4$. They concluded that the nitride was probably orthorhombic from the study of x-ray and electron diffraction patterns.

During 1957 and 1958, a series of papers reported that alpha and beta silicon nitride has hexagonal structure rather than orthorhombic.

B. CRYSTAL STRUCTURE OF SILICON NITRIDE

Since the establishment of the existence of the two forms of alpha and beta silicon nitride, the relationship between these two forms has remained obscure. Researchers have been divided in the interpretation of these forms. One group claimed the alpha and beta silicon nitrides are merely low- and high-temperature forms, while the other group proposed they are 'high oxygen potential' and 'low oxygen potential' modifications.

Relatively high purity silicon nitride powders and thin films have been produced by several chemical reactions such as the nitridation of silicon with nitrogen and the reaction of $\text{SiCl}_4$ or $\text{SiB}_4$ with $\text{NH}_3$ or an $\text{N}_2$-$\text{H}_2$ mixture. Mazdiyasni and Cooke synthesized amorphous $\text{Si}_3\text{N}_4$ from thermal decomposition of silicon diimide, $\text{Si(NH)}_2$, in vacuum. From IR spectra and x-ray diffraction studies performed on the $\text{Si}_3\text{N}_4$, they found it remained amorphous at temperatures up to $1200^\circ\text{C}$ for four hours. However, from $1300^\circ\text{C}$ to $1400^\circ\text{C}$ the powder became alpha silicon nitride and at higher
temperatures it was a mixture of the alpha and beta phases. In order to determine the transformation temperature, they isothermally aged at 50 degrees intervals from 1200° to 1500° C. From x-ray diffraction patterns they found a very slow and continuous transition from the amorphous phase to crystalline alpha silicon nitride at 1200° C for 8 hours or 1300° to 1400° C for 2 hours. At ≈1450° C they found a mixture of mostly beta phase and residual alpha phase. Similar experiments were done by Morgan¹⁴ and he found the amorphous silicon nitride crystallizes to alpha Si₃N₄ at 1490° C.

Wild, Grieveson and Jack¹⁵ studied the crystal structures of alpha and beta germanium and silicon nitride with x-ray powder methods and obtained atomic parameters by least squares computer refinement. They explained the beta silicon nitride as follows:

"The beta structure is a typically covalent solid built up of SiN₄-tetrahedra joined in a three-dimensional network by sharing by corners; two nitrogens (N₂) out of eight in the cell are in special positions at the center of an equilateral triangle of silicons, and each of the other six nitrogens in general positions (N₁) is displaced by only about 0.1 Å from the plane of a less regular triangle of silicons."

The atomic arrangement of beta and alpha silicon nitride proposed by them are shown in Figure 1 and 2 respectively. They also explained the structure of alpha silicon nitride
as follows:

"In the alpha silicon nitride unit cell which contains sites for twenty-eight atoms, Si_{12}N_{16}, there are four different nitrogen atom sites: N1, N2, N3, and N4; and two different silicon atom sites Si1 and Si2. The six nitrogen atoms N1 and the two nitrogen atoms N4 have respectively abnormally high and low occupation numbers. At site N1 has an occupation number greater than unity it can not be occupied solely by nitrogen and must contain a proportion of atoms of higher atomic number, i.e. with a greater x-ray scattering factor. The most likely atom to replace nitrogen is oxygen. The results can then be interpreted in terms of a defect structure with about 25% nitrogen vacancies in site N4, with partial replacement of nitrogen by oxygen in site N1, and with the appropriate number of silicon vacancies to maintain electrical neutrality."

So they suggested that the alpha silicon nitride is really an oxynitride with a limited range of homogeneity Si_{11.4}N_{15.0}^{0.3}-Si_{11.5}N_{15.0}^{0.5} where neutrality is maintained by vacancies in the sites for quadrivalent silicon atoms.

C. MECHANISMS AND PROCESSES OF DENSIFICATION

Wolff and Alcock studied the volatility of Si_{3}N_{4} using the Langmuir method of free evaporation and they suggested from a quantitative interpretation that Si_{3}N_{4} first loses
Figure 1. The atomic arrangement in beta-silicon nitride. From reference 15.

Figure 2. The atomic arrangement in alpha-silicon nitride. From reference 15.
adsorbed gases and then, over longer periods, $N_2$, leaving $Si + Si_3N_4$ (alpha) which, at higher temperatures, goes to $Si(g)$ and $N(g)$. Hoch and co-workers\textsuperscript{17,18}, who studied the vaporization behavior of $Si_3N_4$ at temperatures below the melting point of Si, found that in the decomposition of $Si_3N_4$ pellets according to the reaction, $Si_3N_4(s) \rightarrow 3Si(s) + 2N_2(g)$, the Si content in $Si_3N_4$ increased during heating under vacuum. The compositions of the bulk interiors of the samples and their surface layers did not differ appreciably, however; both regions consisted of two-phase mixtures of $Si + Si_3N_4$. Ryklis et al.,\textsuperscript{19} also showed that $Si_3N_4$ decomposes according to the above equation without forming volatile Si-N species. His conclusions were drawn from the analysis of the vapor over $Si_3N_4$ at $1363^\circ$ to $1945^\circ K$ by mass spectrography, where he found that it dissociated directly to elemental Si and $N_2$ under these conditions.

Batha and Whitney\textsuperscript{20} studied the kinetics of the thermal decomposition of silicon nitride, $Si_3N_4(s) \rightarrow 3Si(l) + 2N_2(g)$, from $1490^\circ$ to $1750^\circ C$ using a static system by measuring the rate of increase in $N_2$ pressure as a function of time. They reported it followed first-order kinetics during the initial stages of dissociation and a process which can be best explained by the Jander solid-state kinetic model in the later stages.

From the above, it is evident that near or above $1600^\circ C$ appreciable dissociation occurs, and dense silicon nitride
can not be sintered by conventional ceramic methods.

Recently there has been considerable work in the area of densification of silicon nitride, which may be divided generally into two categories: so-called reaction-sintering, and hot-pressing of silicon nitride.

A reaction sintered silicon nitride part is now produced via the following general steps of process: the silicon powder is first formed by ordinary forming methods such as die pressing, slip casting, isostatic pressing, extruding etc.; the blank then goes through the part-nitriding process; after machining, the part-nitrided part is subjected to the final nitriding stage and final machining process. The reaction sintering mechanism is a very complex one due to many factors such as the ppm range of oxygen and water vapor in the nitriding gas which affect the crystal structure of silicon nitride, nitriding time and temperature effect, impurity of silicon and particle size of silicon, etc.. From the consecutive study for the nitridation kinetics of silicon, Messier et al. found that in moderately "oxidizing" atmospheres ($O_2$ concentration < 10 ppm), the kinetics of nitridation are retarded by the $SiO_2$ film that forms around either individual grains or the entire specimen. They also concluded that the kinetics of the reaction of $Si$ powder compacts and $N_2$ to form a mixture of alpha and beta $Si_3N_4$ are parabolic only in the later stages of reaction at 1300°C to 1400°C. Atkinson et al. suggested
from their study, however, that alpha silicon nitride powder, dispersed in the silicon powder, catalyzes the reaction between the silicon and nitrogen. Also a surface layer of silica on the alpha powder particles might be the catalyst. They also studied the effect of silicon particle size and speculated from their experiments that the rate-determining step in the reaction-sintering of silicon compacts up to 5 cm diameter is the reaction between silicon and nitrogen, and that the permeation of nitrogen through the compact is a relatively unimportant factor. Of course the silicon particle size determined the overall reaction rate, thus the gas-particle reaction is seen to be the rate-determining step. The exact role of the impurities such as Fe on nitridation of silicon is not clearly understood. Previous study of the investigator\textsuperscript{27} showed that alpha silicon nitride whiskers formed by the VLS mechanism, i.e. SiO (g) and N\textsubscript{2} are present as gaseous reactant and Fe as the liquid transport medium. Messier and Wong\textsuperscript{24} suggested the similar conclusion as the liquid phase promotes the formation of both forms of silicon nitride by a mechanism similar to the VLS one but not involving whisker growth. Dalgleish and Pratt\textsuperscript{26} studied the microstructure of reaction-sintered silicon nitride at different nitriding temperatures and concluded that the early stages of nitridation lead mainly to the formation of the background matte. At temperatures below the melting-point of silicon the pores of the silicon
compact become filled with needles. Continued reaction increases the number and thickness of the needles which grow together and generate the fine-grained matrix. At the same time small areas of silicon are converted to granular Si$_3$N$_4$. When the temperature of nitridation is increased above the melting-point of silicon there is increased formation of beta silicon nitride as crystallites grow into the molten silicon held within the alpha matrix. Prolonged reaction above the melting-point of silicon results in the conversion of residual silicon to granular silicon nitride and densification of the background matte, until the formation of the two-phase structure, discrete beta Si$_3$N$_4$ grains surrounded by a dense matte of alpha Si$_3$N$_4$, is complete.

Deeley et al. were the first to densify silicon nitride powder by using hot-pressing additives. They studied more than twenty different kinds of additives in varying amounts. After hot-pressing between 1800° to 1850°C, they reported a magnesium compound (either MgO or Mg$_3$N$_2$) is most effective as an additive which yields high density and high flexural strength. Following this initial work, Lumby and Coe improved the processing variables to achieve reproducible flexural strength values 100,000 psi. More recently Wild et al. studied the role of magnesia in hot-pressed silicon nitride and suggested the possible reactions which take place while hot-pressing as follows:

"1) at 1000°C the Mg(OH)$_2$ decomposes to give MgO and
water vapor;

2) between 1000°C and 1400°C the MgO reacts with surface silica to form forsterite (Mg$_2$SiO$_4$);

3) above 1400°C the forsterite begins to react with alpha silicon 'nitride' (Si$_{11.5}$N$_{15}$O$_{0.5}$) to form enstatite (MgSiO$_3$) and beta silicon nitride (Si$_3$N$_4$). The equation for the reaction is $4 \text{Si}_{11.5}\text{N}_{15}\text{O}_{0.5} + \text{Mg}_2\text{SiO}_4 \rightarrow 15 \text{Si}_3\text{N}_4 + 2 \text{MgSiO}_3$;

4) in the MgO-SiO$_2$ system there is a liquidus region between 1500°C and 1600°C and at approximately the enstatite composition. This liquid phase acts as a flux and plasticizing agent, thus facilitating the removal of pores within the compact and enabling very rapid densification;

5) above 1600°C the material becomes fully dense, all the alpha is converted to beta and the forsterite lines disappear from the diffraction pattern;

6) on cooling, the magnesium silicate remains as a vitreous phase and is therefore not observed on x-ray photographs of the hot-pressed material, which show only lines due to beta silicon nitride;

7) the crystallographic transformation of alpha silicon 'nitride' is a grain refinement process which produces very fine grained beta Si$_3$N$_4$. The small grain size and zero porosity gives the material extremely high room temperature strength.
they aged a specimen hot-pressed at 1700°C with 10 wt% MgO addition at 1350°C for 24 hours in an evacuated silica tube to confirm that enstatite is present. From x-ray photographs they found only beta $\text{Si}_3\text{N}_4$ before ageing but after ageing crystalline enstatite (MgSiO$_3$) and silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) were present as well as beta $\text{Si}_3\text{N}_4$. The similar study done by Lange and Terwilliger disprove the hypothesis of Wild et al. that the change of alpha phase to beta phase silicon nitride is a necessary part of the densification process. They reported that the silicon nitride powder containing 90% 'beta phase' can be densified completely. Weston and Carruthers also studied the kinetics of the densification process and concluded that alpha silicon nitride can be hot-pressed to near theoretical density at temperatures above 1550°C without significant conversion to the beta form. From a measured surface area of $14.8 \text{ m}^2\text{g}^{-1}$ for the alpha silicon nitride powder, they calculated that complete reaction with a layer of amorphous silica 2.5 um thick is sufficient to convert 5% MgO completely to 12.5% of liquid of eutectic composition. They also concluded that most of the alpha beta conversion, which undoubtedly occurs during the lengthy hot-pressing cycle normally used, takes place after theoretical density is reached.

D. **Strength**

There have been several publications which report the
modulus of rupture of reaction-sintered silicon nitride between room temperature and about 1500°C. Thompson and Pratt measured the variation of the transverse rupture strength with temperature in four-point bending for a series of specimens of alpha Si$_3$N$_4$ of 2.6 g/cm$^3$ density. Between room temperature and 1200°C the strength is essentially constant at $13 \pm 2 \times 10^3$ psi. Above 1200°C the strength fluctuates, and ultimately falls to a value of $6 \pm 1 \times 10^3$ psi at 1590°C. According to Parr and May who measured transverse rupture strength versus temperature by three-point bending (2.6 g/cm$^3$ density), the room temperature strength was $25 \times 10^3$ psi, increased slightly to $27 \times 10^3$ psi at 1000°C, peaked at 1300°C with $35 \times 10^3$ psi, and dropped to $29 \times 10^3$ psi at 1500°C. Meanwhile Evans and Davidge studied the temperature-dependence of the strength of reaction-sintered silicon nitride of two densities 2.55 g/cm$^3$ and 2.13 g/cm$^3$. Their tests were performed in a purified argon atmosphere by three-point bending test. Low density samples showed $15 \times 10^3$ psi room temperature strength and unvaried to 1400°C. High density samples showed high strength of $40 \times 10^3$ psi and decreased linearly by a slight amount, until at 1800°C it was $32 \times 10^3$ psi where the material begins to sublime. Therefore they concluded that the strength of reaction sintered silicon nitride varies little with temperature. Similar densities samples (2.22 and 2.63 g/cm$^3$) were tested by Lloyd and the room temperature
strength of the less dense material was $15 \times 10^3$ psi and the denser material $28 \times 10^3$ psi. The strength of both materials was observed to rise with increasing temperature up to $1400^\circ C$, the low density form doubling its strength in this temperature range. Noakes and Pratt$^{37}$ found a peak at $1200^\circ C$ similar to that reported by Parr and May$^{34}$. Their four-point bend tested samples had room temperature strength of $20 \times 10^3$ psi which remained to $1000^\circ C$, then peaked at $1200^\circ C$ with $30 \times 10^3$ psi, and dropped to $15 \times 10^3$ psi at $1500^\circ C$. They compared their results with that of Evans and Davidge$^{36}$ and concluded that the strength of reaction-sintered silicon nitride is determined by the size of the largest pores arising from the production schedule. The control of this schedule should enable a range of strengths to be developed from the same starting material over the temperature range $0^\circ - 1200^\circ C$. They also pointed out that in their material and that of Thompson and Pratt$^{33}$ the oxygen content is sufficiently high for a glassy phase to be present in the intergranular regions. This accounts for the rapid softening at high temperature while the material used by Evans and Davidge$^{36}$ contained little or no oxygen. They suggested the importance of controlling the oxygen content of the nitride where strength and creep resistance at temperature above $1200^\circ C$ are required.

For the case of hot-pressed silicon nitride, the temperature dependence of strength is quite different from that of reaction-sintered silicon nitride. Lloyd$^{35}$ studied two
different sets of hot-pressed silicon nitride, one with 1% MgO addition and other with 5% MgO content. By three-point bending test, the mean room-temperature strength of 5% MgO content sample (3.17 g/cm$^3$ density) was measured as $83 \times 10^3$ psi, and this value decreased only slightly up to approximately 1000°C. Above this temperature a sharp drop in strength occurred, falling to $28 \times 10^3$ psi at 1400°C. Similar tests for 1% MgO content sample (3.08 g/cm$^3$ density) showed the mean room-temperature strength was $78 \times 10^3$ psi, this value falling slightly with increase in temperature but retaining a strength of $70 \times 10^3$ psi at 1400°C. No explanation was given by the author; however, as stated earlier, Wild et al. hypothesized the role of magnesia in hot-pressed silicon nitride and explained Lloyd's results. They applied their hypothesis to Lloyd's results and suggested that the presence of a vitreous phase in the hot-pressed material has a serious effect on its high temperature strength:

"If the glassy phase provides the bond between silicon nitride particles, a decrease in strength at high temperature might be expected because of the softening of the glass. As the temperature approaches the liquidus the strength should become very low. If the modulus of rupture versus temperature curve is extrapolated to zero, it intercepts the temperature axis in a region where a liquidus occurs in the MgO - SiO$_2$
Ashcroft\textsuperscript{38} also studied the change in rupture modulus with temperature for hot-pressed silicon nitride (98\% purity starting powder with 1 to 1.5\% magnesia additions and density of 3.17 g/cm\textsuperscript{3}) and flame-sprayed silicon nitride (density of 2.65 g/cm\textsuperscript{3} and 8\% free-silicon). The strength of flame-sprayed material was much lower (25 x 10\textsuperscript{3} psi) than the hot-pressed material (90 x 10\textsuperscript{3} psi) at low temperatures, but as the former was less temperature-dependent, it was only slightly lower at 1450\degree C. He also detected a white surface deposit on the hot-pressed specimens after exposure at or above 1200\degree C forming a pronounced crust at 1400\degree C. At 1400\degree C and 1450\degree C, where the surface attack was progressively more severe on hot-pressed silicon nitride, the rate of strength-loss with temperature was slightly lower than at lower temperatures. From this observation he suggested that oxidation is not the primary cause of strength reduction at high temperature, as rate of strength reduction and rate of oxidation do not correlate. However, he suggested the oxidized layer probably would have more effect if the temperature were cycled. A hot-pressed specimen heated to 1480\degree C in air subsequently tested at room temperature exhibited only about 60\% of its usual room-temperature strength. He also observed two regions on the fracture faces of hot-pressed silicon nitride, after rupture at 1450\degree C. The region adjacent to the tension face of the specimen was
very irregular, and appeared grooved at high magnification, whereas the area further from the tension face was flat and similar to low temperature fracture faces. From these observations he suggested that fracture commenced in a ductile manner before propagating as a brittle crack. This effect is less pronounced at 1400°C and not evident at 1300°C for hot-pressed silicon nitride. Richerson studied specimens of silicon nitride with controlled impurity levels which were prepared by hot-pressing and were tested for flexure strength at 1375°C. To investigate his hypothesis that the high temperature strength is controlled to a large degree by the effects of impurities on the glassy bond phase, he set up a model assuming that the major impurities are present in the bond phase modifying its composition and properties. Using spectrographic data plus oxygen analysis data, he approximated the composition of interstitial phase. Major impurities in his five different specimens were Fe, Al, Ca, Mg, Mn, Ti and/or their oxides. When he plotted the flexure strength at 1375°C versus impurities (Fe, Al, Ca, Mg, Mn) content, he found that strength was $65 \times 10^3$ psi at 1% impurity and decreased somewhat linearly to $15 \times 10^3$ psi at 2.5% impurity level. He suggested that any of the impurities could be present in the glassy bond phase modifying its viscosity, liquidus and other properties. He also studied two different grades of hot-pressed silicon nitride, one a high impurity material (HS-110) and a more pure material.
(HS-130). The strength versus temperature curves for these materials which were measured by Richerson with three-point loading is reproduced in Figure 3. It was reported that each point on the curves represents an average of four tests. The HS-130 retains 100,000 psi strength at 1200°C, but only 45,000 psi at 1400°C. The rapid strength decrease begins at ≈ 1250°C. The strength decrease for the HS-110 specimen is more gradual and begins at a lower temperature and the strength at 1400°C is about 24,000 psi. He also studied load versus deflection of both materials at 1000°C through 1400°C with 100°C intervals. At 1100°C, the morphology of the curve is identical for both materials, typical of a brittle material. At 1200°C there is a noticeable "yielding" in the HS-110 curve. At 1300°C the region of the HS-110 curve deviating from linearity has become the dominant feature. The HS-130 curve is just beginning to change morphology, broadening slightly. At 1400°C both curves exhibit non linear characteristics. These results correlate well with his hypothesis that the high temperature properties are controlled by the effect of impurities on the complex bond phase. At 1200°C the interstitial glassy bond in HS-110 has begun to soften and permit deformation, probably by grain boundary sliding. The same mechanism is occurring in HS-130, but at a higher temperature, again demonstrating that the lower level of impurities has produced a more refractory bond. Similar results were reported by Kossowsky.
Figure 3. Comparison of flexure strength of HS-110 and HS-130 Si$_3$N$_4$ as a function of temperature. From reference 39.
who studied cyclic fatigue of same materials used by Richerson. He concluded that at 1000°C and 1200°C, microstructural observations indicated that plastic deformation did not occur during cyclic fatigue testing but at 1300°C boundary sliding occurs during cyclic fatigue testing. He also concluded from the study of energy-dispersive x-ray analysis of corroded outside sample surfaces during exposure to air at high temperature that the corrosion process apparently involves the diffusion of Ca and Mg to the exposed surface. It follows therefore that, in the absence of a controlling plastic mechanism, the life time of a fatigue specimen depends on a slow crack growth which occurs as a result of glass formation at the crack tip, through a corrosion mechanism in air. Then for given conditions of stress and temperature, the rate of corrosion attack will determine the rate of growth of the subcritical flaw, which in turn controls the lifetime of the specimen. Lange concluded similarly that a preexisting crack with the largest stress intensity factor will more than likely be the location of accelerated creep (i.e. plasticity) and, therefore, subcritical growth. From the study of fracture-surface topography at higher temperatures he found two regions, a rough crack-shaped area and a smooth area. His observation is similar to that of Ashcroft previously mentioned. Lange explained that the rough appearance area was due to the crack front following weaker areas as it grows, while
smoother areas without radiating fracture steps indicate that no crack branching occurred. In order to show evidence of subcritical crack growth he lapped the surface to remove the external oxide surface layer and linear feature was observed to be a narrow groove which extended \( \approx \frac{1}{2} \) the width of the tensile surface and \( \approx \frac{2}{3} \) the distance down the side surface of the specimen. Since he did not detect this crack prior to stressing, he concluded that extensive subcritical crack growth occurred during stressing. He also concluded the susceptibility of the material to subcritical crack growth phenomenon increases with increasing impurity content (i.e. Ca content) and increasing temperature.

E. EFFECTS OF ADDITIVES

As suggested by Richerson\textsuperscript{39} the use of higher purity \( \text{Si}_3\text{N}_4 \) powder improves the high temperature properties by increasing the refractoriness of the grain boundary phase. However, the cost of producing higher purity \( \text{Si}_3\text{N}_4 \) powder is high and the high temperature properties although improved, may be limited by the properties of the reaction products produced by the particular additive being used to enhance densification. Thus, many studies have concentrated on the effects of additives which would increase the refractoriness of the boundary phase by producing a more refractory reaction product. Gazza\textsuperscript{42} has studied the additions of from 1.0 to 3.3 wt\% \( \text{Y}_2\text{O}_3 \) to a high alpha phase \( \text{Si}_3\text{N}_4 \) powder. After hot-pressing 1750\( ^\circ \text{C} \) to 1800\( ^\circ \text{C} \) with a 2 hours hold time
and 6000 to 7000 psi uniaxial pressure the density of the specimens varied from 3.22 to 3.26 g/cm³ increasing with the amount of additive used (from 1.0 to 3.3 wt%). He did not then quantitatively identify the formed grain boundary phase but he suggested that it was yttrium silicate. He also measured the modulus of rupture values at room temperature and 1315°C. Average four-point bending room temperature value was 118,000 psi and 1315°C value in an argon atmosphere ranged from 58,000 to 69,000 psi. Rae et al. described the effectiveness of yttria as an additive to silicon nitride as due to the formation of a refractory yttrium-silicon oxy-nitride. They also suggested that this phase can accommodate calcium and other impurity cations which lower the softening temperature of the glassy bond. Tsuge et al. have studied the reactions in the Si₃N₄ - Y₂O₃ systems. They mixed commercial grade alpha Si₃N₄ powder, which has a particle size range of ≈ 0.1 to 1.0 μm, with 0 to 100 mol% high purity Y₂O₃ (99.9%) with particle size of ≈ 2 μm at intervals of 10 mol%. They hot pressed these mixtures about 4300 psi at 1750°C, 1780° and 1800°C for 1 hour. From the powder x-ray diffraction examination they detected two phases; phase I contained ≈ 50 mol% Y₂O₃ and phase II ≈ 70 mol% Y₂O₃. They assigned phase I as Si₃N₄ · Y₂O₃ and phase II as Si₃N₄ · 2 Y₂O₃. From these results they also drew a hypothetical phase diagram which is analogous to SiO₂ - Y₂O₃ systems. Will also performed a similar experiment to Tsuge et al.
and found $\text{Si}_3\text{N}_4 \cdot 3 \text{Y}_2\text{O}_3$ phase along with $\text{Si}_3\text{N}_4 \cdot \text{Y}_2\text{O}_3$ phase. While preparing $\text{Si}_3\text{N}_4 \cdot 3 \text{Y}_2\text{O}_3$ by hot-pressing at 1730°C for 1 hour, he observed considerable extrusion from the die, indicating that the material had melted. Thus he concluded that the probable explanation of the role of the $\text{Y}_2\text{O}_3$ additive in the hot-pressing of $\text{Si}_3\text{N}_4$ is that the $\text{Y}_2\text{O}_3$ initially reacts at the grain boundaries to form the lower-melting $\text{Si}_3\text{N}_4 \cdot 3 \text{Y}_2\text{O}_3$, which then acts as a densification aid. Further reaction transforms the grain boundary phase to the more refractory $\text{Si}_3\text{N}_4 \cdot \text{Y}_2\text{O}_3$, which is responsible for the improved high-temperature properties of the resulting $\text{Si}_3\text{N}_4$. Gazza also studied the effect of yttria additions to various grades of $\text{Si}_3\text{N}_4$ powder up to 20 wt% $\text{Y}_2\text{O}_3$. He studied the modulus of rupture test at room temperature for hot-pressed materials fabricated by starting with high alpha phase powders and the values fell generally between 98,000-138,000 psi. Hot-pressed specimens produced with high beta phase starting powder, however, yielded only 70,000-80,000 psi. He also discussed high temperature modulus of rupture values of the specimens which were hot-pressed 1750°-1800°C for 2 hours with 10 wt% $\text{Y}_2\text{O}_3$ addition. The MOR values for specimens with Ca impurity levels below \( \approx 6000 \) ppm showed no direct correlation of strength with Ca impurity level. The MOR values of these specimens at 1315°C were ranging 87,000-110,000 psi and the specimen prepared from very high purity powder showed excellent strength retention of \( \approx 80,000 \)
psi MOR at 1485°C. He also tested specimens fabricated with commercially pure powder by the same method, and MOR values at 1315°C = 70,000 psi were only slightly lower than obtained with high purity material. He concluded that a minimum amount of $Y_2O_3$, generally 5-10 wt%, appears to be required to complete formation of the yttrium-silicon oxy-nitride boundary phase and produce significant improvement in high temperature properties. More recently Tsuge et al. reported the elimination of the glass phase by crystallizing a liquid at high temperatures, with resultant formation of refractory-hard material as a secondary grain-boundary phase. They intimately mixed commercial silicon nitride which contained 88% alpha with 5 wt% $Y_2O_3$ and presintered the compact at 1600°C to 1700°C under atmospheric pressure in either AlN or Si$_3$N$_4$ powder. The presintered compact then was hot-pressed by a powder-vehicle method, using BN as the vehicle, with the pressure of $\approx$ 7000 psi at 1750°C for 90 minutes. After fabrication they compared three-point flexural strengths of the compact presintered in AlN, Si$_3$N$_4$ and no presintering treatment as a function of temperature. At all temperatures, materials presintered in AlN were significantly stronger ( $\approx$ 130,000 psi room temperature, 115,000 psi at 1000°C, 75,000 psi at 1300°C) than materials presintered in Si$_3$N$_4$ and no presintered. The strength of the materials presintered in Si$_3$N$_4$ is rapidly degraded at $\approx$ 800°C (105,000 psi at room temperature, 75,000 psi at
800°C, 55,000 psi at 1300°C); the strength of material without presintering treatment also degraded (115,000 psi at room temperature, 90,000 psi at 1000°C, 35,000 psi at 1300°C) with increasing temperature. From the x-ray powder diffraction they only found beta silicon nitride for both materials presintered in \( \text{Si}_3\text{N}_4 \) and no presintering treatment, but found an additional crystalline phase \( \text{Si}_3\text{N}_4 \cdot \text{Y}_2\text{O}_3 \), in material presintered in AlN. One other approach to alleviate the high temperature degradation in strength for MgO added silicon nitride was proposed by Mazdiyasni and Cooke.\(^{48}\) They added rare-earth compounds (\( \text{Ce}_2\text{O}_3, \text{CeO}_2, \text{CeH}_3, \text{CeN}, \text{La}_2\text{O}_3 \)) to 97 to 98.5% purity commercially available silicon nitride powder and hot-pressed to 1650°C for 30 minutes with 5 to 6 \( x \times 10^3 \) psi, and for some samples the hot-pressing temperatures was increased stepwise to 1700°C and 1750°C and held for an additional 15 to 30 minutes. They determined the room-temperature flexural strength of silicon nitride samples doped with 2.5 at% \( \text{Ce}_2\text{O}_3 \) with four-point bending, and reported the average value of 150,000 psi. They also measured the creep rate of \( \text{Ce}_2\text{O}_3 \)-doped silicon nitride and compared the value with those of HS-130 of Richerson\(^{39}\) and found that their sample had an order of magnitude smaller rate than HS-130. They believed this improvement of the creep properties may be associated with the absence of low-temperature glasses around grain boundaries as well as with the mullite-like elongated grain
morphology indicated by the microstructure they presented. Rice and McDonough also suggested Zr-based compounds could be used as hot-pressing additives for silicon nitride. They achieved near theoretical density with 3 wt% addition of ZrO₂, ZrN, ZrC or ZrSiO₄ which ranged in room-temperature modulus of rupture value from 75 to 136 x 10³ psi. From the various densities achieved from different grades of silicon nitride used, they speculated either limited impurity effects or the observed milling behavior would appear to correlate with densification. In any event, they concluded that Zr-based additions to some silicon nitride powder have produced densification and promising properties.

F. MICROSTRUCTURE

The microstructure of the final product of reaction-sintered silicon nitride is determined by the purity of the silicon powder, the particle size, the green density, and the nitriding atmosphere, time and temperature. The volume change of a silicon compact during nitriding is < 0.1%, so the increase in volume of each silicon particle of some 20% must be accommodated in the voids between particles. Dalgleish and Pratt studied the microstructure of partially and fully nitrided materials. The nitriding conditions influenced the microstructure of the fully nitrided materials. They presented optical micrographs of materials prepared by nitriding primarily above and
below the melting-point of silicon. From x-ray analysis they showed that the former consists of 40% alpha phase and ≈ 60% beta silicon nitride (density 2.34 g/cm³), whereas the latter consists of 60% alpha phase and ≈ 40% beta silicon nitride (density 2.5 g/cm³). Both these materials contain substantial porosity and discrete bright regions of unreacted silicon. Most of the pores are <2 µm in diameter, and the largest pores (≈ 20 µm) occur in the predominantly beta material. The microstructure of both these materials consists of discrete beta silicon nitride grains surrounded by a dense matte of alpha silicon nitride.

As stated earlier in this section, the details of the microstructure of reaction-sintered silicon nitrides are governed by various factors (alpha/beta phase ratio, nitriding time and temperature, starting silicon particle size, etc.); the final microstructures differs depending on their course of fabrication. The general features of reaction-sintered silicon nitride, however, are similar to the work of Dalgleish and Pratt.²⁶

The microstructure of hot-pressed silicon nitride differs generally with the nature of starting powder. Commercially available high alpha silicon nitride powder (85 to 95% alpha) has a wide distribution of particle size and occasional elongated particles, while high beta silicon nitride powder (65 to 90% beta) is slightly more uniform in size distribution with none of the elongated particles.
Lange et al. have studied microstructures of two different starting powders (AME; 90% alpha, 10% beta, AC; 10% alpha, 90% beta). The microstructure resulting from hot-pressing AME powder with 5 wt% MgO addition showed an elongated grain morphology while 5 wt% MgO in the AC starting powder resulted in an equiaxed morphology. The sample fabricated from AME powder appeared to be a bimodal size distribution, i.e. large elongated grains and smaller grains which were equiaxed. They also measured grain sizes using electron micrographs of polished, etched, and replicated surfaces of the materials made from the AME and AC powders and determined respective average values of 1.2 and 1.7 μm assuming a uniform spherical grain morphology. Their assumption did not take into account the apparent bimodal grain-size distribution and the elongated grains of the specimens hot-pressed from the AME powder. For this material, the average length of the elongated grains would be larger than the calculated average grain size. Similar observation was reported by Kossowsky who studied Norton company designation HS-110 and HS-130. He measured a bimodal distribution of grain sizes in which about 80% of the grains are equiaxed, and vary in size between 0.5 and 3 μm, with an average size of 1.3 μm. The other 20% of the grains have an elongated appearance, with the short axis between 1 and 2 μm and the long axis between 2 and 5 μm. He also reported that about 1% of the elongated grains are larger.
(up to 20 \text{um} long) and were identified as the alpha phase of silicon nitride. Mazdiyasni and Cooke\textsuperscript{13} also studied microstructures of hot-pressed silicon nitride, which were prepared by ammonolysis of SiCl\textsubscript{4}, with addition of 1 to 4 \text{wt\%} of -400 mesh Mg\textsubscript{3}N\textsubscript{2} powder. The microstructure of this material was composed of interlocking elongated and/or acicular grains. It also appeared as bimodal size distribution and elongated grain sizes were \( \approx 0.5 \text{ um} \) wide and 2 to 5 \text{um} long for hot-pressing soak time of 1 hour at 1650\textdegree C. The same material with 2 hours soak time exhibited similar microstructure to 1 hour soaked material; however, the grains show chunkier habits and increase in the proportion of more equiaxed grains. Lange\textsuperscript{50} and Kossowsky\textsuperscript{51} also suggested the existence of preferred orientation of elongated grains in the hot-pressed silicon nitride. Lange\textsuperscript{50} studied x-ray diffraction of hot-pressed silicon nitride for surfaces parallel and perpendicular to hot-pressing direction and found that all crystallographic planes that include the c-axis, i.e. (hkl) planes, had an equal or greater intensity on the surface parallel to the hot-pressing direction; all planes not including the c-axis, i.e. (hk0) planes, had a greater intensity on surfaces perpendicular to the hot-pressing direction. Thus he concluded that the c-axis is oriented preferentially perpendicular to the hot-pressing direction. Since beta silicon nitride has a hexagonal structure, in which its crystal growth
pattern should be symmetrical with respect to the c-axis, he assumed this c-axis coincided with the long direction of the grains. He also supported his assumption by both strength and fracture energy difference (by \( \Xi 20\% \)) for crack planes perpendicular and parallel to the hot-pressing direction (fracture energy values were \( 68.6 \times 10^3 \pm 14\% \) erg/cm\(^2\) for crack plane induced perpendicular to hot-pressing direction, \( 81.5 \times 10^3 \pm 19\% \) erg/cm\(^2\) for crack plane induced parallel to hot-pressing direction; flexural strength, \( 98,000 \pm 6\% \) psi for the perpendicular set, and \( 73,000 \pm 14\% \) psi for the parallel set). Since the grain morphology greatly affects the strength of the material, Lange\(^50\) and Kossowsky\(^51\) also studied this relationship for hot-pressed silicon nitride with the aid of fracture surface topographs. Fracture surface topographs of the material prepared from the AME powder (high alpha) were extremely rough, containing deep holes and many jagged fractured grains, while the material fabricated from the AC powder (high beta) was relatively smooth. Lange compared his fracture energy value and fracture surface topograph, and explained that the intergranular fracture of a material containing elongated grains can lead to a much rougher surface with a higher specific surface area than that of an equiaxed microstructure, estimated as less than 2 times of planar surface. Thus the more irregular fracture surface topography of the material containing the elongated grains
may be one reason for its higher fracture energy. He also suggested from the observation of the strong resemblance of the fracture surface of the silicon nitride composed of elongated grains to that of a fibrous composite (i.e. deep holes and protruding fiberlike grains), energy dissipation by frictional sliding may also be responsible for the large fracture energy of strong silicon nitride. He also discussed the resemblance of the properties and microstructure of silicon nitride fabricated from the beta-phase starting powder to those of many other ceramics, and concluded that by changing its grain structure from equiaxed to elongated, the fracture energy of silicon nitride was increased by a factor of \( \approx 4 \) and its strength by a factor of \( \approx 2 \). Coppola et al.\(^{52} \) also studied the fracture surface energies of four hot-pressed and two reaction-sintered silicon nitrides from \(-196^\circ C\) to \(1400^\circ C\) by the work of fracture technique. These materials exhibited a general variation of a decrease in fracture energy with increasing temperature and then, at higher temperature, a rapid increase along with substantial flow at the advancing crack tip. By examining the fracture surface topographs both room temperature and \(1200^\circ C\), they concluded that for hot-pressed structures the elevated temperature flow is a combination of both dislocation plastic flow mechanisms and the viscous flow of the additive glassy phase, but only the dislocation plastic flow mechanism is responsible in the reaction-sintered bodies. Tsuge
et al. also found evidence of a significant degree of preferred orientation in the $Y_2O_3$-added hot-pressed silicon nitride as well as the bimodal size distribution. Gazza showed microstructure of 2 wt% $Y_2O_3$-added hot-pressed silicon nitride and measured the duplex nature of the structure with finer grains 0.5 to 1.5 um in diameter and large grains which occasionally were up to 10 um in their longest direction. The microstructure of the samples of Mazdiyaani and Cooke which were hot-pressed silicon nitride with the addition of 2.5 wt% of $La_2O_3$ also showed elongated and bimodal size distribution.

G. GLASS-CERAMICS

The development of a new area of glass technology, the production of glass-cristalline materials, became possible because of the discovery of the catalytic crystallization method. The essence of this technique is that the growth of crystals starts simultaneously from a large number of nuclei which are uniformly distributed in the preshaped glass article.

If the formation of nuclei of the new phase of the material proceeds within a different phase of the same material in the absence of or without the help of foreign particles, then it is generally called 'homogeneous' crystallization, to distinguish it from 'heterogeneous' crystallization- also called catalyzed crystallization- which
occurs when the nuclei of the new phase are formed on surface having a different chemical composition than this new phase.

The production of glass-ceramics consists of the following fundamental technological stages, according to Stookey:

1. Melting of the batch containing the necessary amounts of catalysts at a temperature 100°C higher than the melting point of its most refractory component; 1600°C is a typical temperature. The crystallization catalyst dissolves in the fused glass.

2. Shaping of the glass products and cooling them to a temperature at which the submicroscopic particles of the catalyst will precipitate, a temperature which is usually 50°C higher than the annealing temperature of glass, and may reach 800°C. The products are held at this temperature for 1 hour so as to precipitate the maximum number of particles of the catalyst.

3. Heating at a rate of several degrees per minute to the temperature of the formation and growth of crystal, and holding at that temperature for 4 hours so as to complete at least 80% of the crystallization process.

4. Cooling of the crystallized product to room temperature."

For a large number of glasses of the MgO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} system, as well as for certain other glasses, the complete
temperature cycle of heat-treatment for the preparation of
glass-ceramics may be more complex than is represented in
the above paragraph, and may include several intermediate
stages of cooling and of gradual heating.

The chief advantage of glass-ceramics over traditional
ceramics seems to lie in the possibility of conferring on
the ceramic end product any desired shape that can be ob­
tained by the working of glass (draw of tubes, pressing,
blowing, deformation in automatic glass machines, etc.).
Changes in volume on tempering and crystallization of the
processed glass are less than 1%. One significant property
of some glass-ceramics is the high-temperature softening
behavior, 1250°C and 1350°C for 9608 and 9606 of the Corning
Glassworks respectively. On the other hand, their coeffi­
cients of expansion are exceptionally low, 4 to 11 x 10^{-7}
and 56 x 10^{-7}°C^{-1} respectively.55
III. METHODS OF INVESTIGATION

A. MATERIALS

The silicon nitride powder used in this investigation was obtained from The Advanced Materials Engineering Company, Ltd. of England. The chemical composition of this AME powder was not reported by the supplier but described as 95% alpha phase. The chemical analysis of similar AME powder which was done by Lange and Terwilliger is reproduced in Table 1 for reference.

Pennsylvania Glass Sand Corporation's five micron Min-u-sil having the chemical composition given in Table 2 was used in compositions requiring silicon dioxide. This material was chosen on the basis of fineness, purity, and closely controlled particle size distributions. Due to the fact that approximately 98% of the Min-u-sil was less than five microns, it was highly reactive upon firing and melting.

Alcoa A-1 low soda, low iron alumina was used in all glass composition requiring aluminum oxide. This material was chosen because of its low soda content and small average particle size of 2 to 5 microns. Specifications for X-14 alumina are given in Table 3.

Baker analyzed reagent grade titanium dioxide from J.T. Baker Chemical Company was used in two compositions. The
Table 1. Chemical analysis of AME silicon nitride. 
From reference 31.

<table>
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<tr>
<th>Element</th>
<th>Si</th>
<th>N</th>
<th>Fe</th>
<th>Al</th>
<th>Ni</th>
<th>Ca</th>
<th>Total</th>
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</thead>
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<td>Quantity (wt%)</td>
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<td>37.15</td>
<td>0.78</td>
<td>0.55</td>
<td>0.15</td>
<td>0.11</td>
<td>97.55</td>
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Table 2. Chemical analysis of Min-U-Sil

<table>
<thead>
<tr>
<th>SiO₂</th>
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</thead>
<tbody>
<tr>
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<tr>
<td>Al₂O₃</td>
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<tr>
<td>TiO₂</td>
<td>0.009</td>
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<tr>
<td>CaO</td>
<td>trace</td>
</tr>
<tr>
<td>MgO</td>
<td>trace</td>
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</table>

Table 3. Chemical analysis of Alcoa A-14 alumina

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>99.6%</td>
</tr>
<tr>
<td>( \text{Na}_2\text{O} )</td>
<td>0.04%</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>0.04%</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>0.06%</td>
</tr>
<tr>
<td>Ignition Loss at 1100°C</td>
<td>0.15%</td>
</tr>
<tr>
<td>Water Adsorbed at 50% Humidity</td>
<td>0.10%</td>
</tr>
</tbody>
</table>

Supplier: Aluminum Company of America

Table 4. Chemical analysis of Baker Reagent Grade Titanium Dioxide and Zinc Oxide

<table>
<thead>
<tr>
<th></th>
<th>Titanium Dioxide</th>
<th>Zinc Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water soluble salt</td>
<td>0.05%</td>
<td></td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>0.0001%</td>
<td>0.0001%</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.003%</td>
<td>0.0005%</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.002%</td>
<td>0.005%</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>0.007%</td>
<td></td>
</tr>
<tr>
<td>Chloride (Cl)</td>
<td></td>
<td>0.0005%</td>
</tr>
<tr>
<td>Nitrate (NO\textsubscript{3})</td>
<td>0.003%</td>
<td></td>
</tr>
<tr>
<td>Sulfur Compound (as ( \text{SO}_4 ))</td>
<td>0.005%</td>
<td></td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td></td>
<td>0.0005%</td>
</tr>
<tr>
<td>Insoluble in ( \text{H}_2\text{SO}_4 )</td>
<td></td>
<td>0.010%</td>
</tr>
<tr>
<td>Substance not Precipitated by (NH\textsubscript{4})\textsubscript{2}(as ( \text{SO}_4 ))</td>
<td></td>
<td>0.10%</td>
</tr>
</tbody>
</table>
analysis of this material is given in Table 4 along with Baker analyzed reagent grade zinc oxide.

Morton Chemical Company's magnesium carbonate was used in two glass compositions requiring magnesium oxide. Magnesium carbonate was chosen instead of magnesium oxide on the basis of fineness and decarbonation action which promote homogeneity of glass melts. The analysis of the material is given in Table 5.

Foote Mineral Company's petalite was used in a glass composition requiring lithium oxide. This material was chosen to promote more homogeneous melting. The chemical analysis of this material is given in Table 6.

B. GLASS FRIT COMPOSITIONS

Since the object of this investigation was to study the recrystallization phenomenon of glass bonding phases, several factors were considered when choosing the glass frit composition. The glass frit should recrystallize easily with proper heat treatment, and the thermal expansion coefficient of the recrystallized phase should be low or at least close to the value of silicon nitride. Three different kinds of glass composition were studied and are listed in Table 7. Also included are details of the preparation processes and heat-treatment processes along with the final crystallized phases of each glass frits.
Table 5. Chemical analysis of Magnesium Carbonate

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>40.0 - 43.5 %</td>
</tr>
<tr>
<td>CaO</td>
<td>0.6 % maximum</td>
</tr>
<tr>
<td>Fe</td>
<td>0.02 % maximum</td>
</tr>
<tr>
<td>Pb</td>
<td>0.003 % maximum</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>0.0005 % maximum</td>
</tr>
<tr>
<td>Water soluble salts</td>
<td>1.0 % maximum</td>
</tr>
<tr>
<td>Acid insoluble substances</td>
<td>0.05 % maximum</td>
</tr>
</tbody>
</table>

Supplier: Morton Chemical Company.

Table 6. Chemical analysis of Petalite

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O</td>
<td>4.3 %</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.39 %</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.16 %</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.06 %</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.8 %</td>
</tr>
<tr>
<td>SiO₂</td>
<td>77.0 %</td>
</tr>
<tr>
<td>Ignition Loss</td>
<td>0.80 %</td>
</tr>
</tbody>
</table>

Supplier: Foote Mineral Company.
### Table 7. Glass-Ceramics Frit Composition

<table>
<thead>
<tr>
<th></th>
<th>Glass-Ceramics 1</th>
<th>Glass-Ceramics 2</th>
<th>Glass-Ceramics 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiO}_2$</td>
<td>70.7 wt%</td>
<td>45.5 wt%</td>
<td>42.5 wt%</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>18.1</td>
<td>30.5</td>
<td>28.33</td>
</tr>
<tr>
<td>$\text{Li}_2\text{O}$</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>2.8</td>
<td>12.5</td>
<td>29.17</td>
</tr>
<tr>
<td>$\text{ZnO}$</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>4.8</td>
<td>11.5</td>
<td>-</td>
</tr>
</tbody>
</table>

**Melting in platinum crucible**
- 1650°C for 2 hrs.
- 1650°C for 1 hr.
- 1650°C for 1 hr.

**Color**
- clear
- light grey
- clear

**Grinding after through 100 mesh in plastic bottle with alumina balls**
- 48 hrs. in distilled water
- 24 hrs. in distilled water
- 20½ hrs. in T-Butanol

**Heat-Treating**
- 1 hour at 800°C $\equiv 5$ C/min
- 3 hours at 1175°C $\equiv 5$ C/min
- 1½ hour at 820°C $\equiv 3$ C/min
- 2 hours at 1350°C $\equiv 3$ C/min
- 1 hour at 800°C $\equiv 5$ C/min
- 2½ hours at 1250°C $\equiv 2$ C/min

**Crystalline phases**
- beta-Spodumene
- Cordierite
- Cordierite
- Spinel
C. GLASS MELTING

Three glass compositions listed in Table 7 were weighed and separately mixed in V-type blender. After mixing, glass compositions were melted in a platinum crucible (3" diameter and 1 1/2" deep) in a gas furnace. Glass composition 1 was melted at 1650°C for 2 hours and glass compositions 2 and 3 were melted at the same temperature for 1 hour. Glass compositions 1 and 3 were clear and glass composition 2 was light grey after melting. All the melts were quenched in flowing cold water.

D. POWDER PREPARATION AND MIXING

Three glass melts were crushed and sieved through 100 mesh. Each glass frit powder was then placed in a pint plastic bottle with 1/2" diameter and 1/2" long alumina cylinders (about five times of the weight of the frit) and tertiary butyl alcohol or distilled water and milled at 288 rpm. Glass 1 was milled 48 hours, glass 2 for 24 hours, and 20 1/2 hours for glass composition 3. After milling, the powders were dried in an oven at 80°C for glass 2 and 3, and at 150°C for glass 1. The typical mixing procedure of silicon nitride and glass frit was as follows: weigh proper amounts of both powders depending on the glass frit content and place with alumina balls and T-butanol in plastic bottle and mill at about 80 rpm for about 20 hours. Milling time was varied from sample to sample slightly. After milling,
the powder was dried in an oven at 80°C overnight and mixed with a mortar and pestle to break up large agglomerates formed during drying.

E. **HOT-PRESSING EQUIPMENT AND SCHEDULE**

Figure 4 is a schematic diagram of the hot-pressing equipment used in this investigation. The induction power supply was a 15 KW, 10,000 Hz. motor generator feeding an eight-tap autotransformer in a portable work station. The induction coil was 7 inches in diameter, 2 1/4 inches long, and contained 5 evenly spaced turns of 3/8 inch diameter copper tubing. The hot-pressing die was enclosed by a 6 inches I.D. and 6 1/2 inches O.D. 10 inches long Amersil fused silica and a 4 1/8 inches I.D. and 4 1/2 inches O.D. and 6 inches long Mcdanel MV 30 High Temperature Mullite. Double insulation was designed between fused silica tube and mullite tube. The outer 1/4 inch was wrapped with Fiberfrax paper and the inside gap between tubes was filled with bubbled alumina. Fiberfrax paper insulation was placed between Babcock and Wilcox ALLMUL mullite block and steel base plate which has a 3/8 inch deep, 6 3/4 inches O.D. and 6 1/4 inches I.D. groove. Steel base and fused silica were sealed with General Electric RTV 106 silicone rubber and cooled with two turns of 3/8 inch copper tubing which was soldered on the steel plate. Two pieces of graphite susceptor were placed on the mullite block. One was 3 7/8 inches
Figure 4. Schematic diagram of the hot-pressing die unit.
0. D., 2 inches I.D. and 2 1/2 inches high and the other was 3 7/8 inches O.D., 1 1/2 inches I.D. and 3 inches high. The bottom one has a 1/8 inch hole in the middle punch which served for thermocouple and nitrogen flow. Graphite cloth spacer was placed between two graphite susceptor punches. The top one had dual purpose as susceptor and die. Molybdenum foil of 5 mil thickness was lined inside the die and between graphite punch and sample powder to avoid contamination by carbon. The top of the fused silica was insulated with 3000° alumina insulating brick and alumina block was placed between graphite punch and hydraulic press ram. Pressing was performed by an ENERPAC JH-12G hydraulic hand jack and the load was monitored by an ENERPAC Model No. GF-812 gauge. Temperature was measured by 22 gauge Iridium/Iridium-40% Rhodium thermocouple which was placed at the bottom of the die through the lower susceptor and a Platinum/Platinum-10% Rhodium thermocouple which was placed at the middle of the die wall. Nitrogen was flowed from the bottom through the hole which served as a thermocouple insulator tube and from top parts through alumina insulating brick and fused silica tube which enclosed the graphite punch and alumina block.

A typical hot-pressing schedule was as follows. About 40 gms of silicon nitride and glass frit mixture was loosely charged into the Molybdenum lined die and the motor-generator set and field were energized. At the same time the flow of
nitrogen both from top and bottom was adjusted to the rate of 5 liters/min and 4 liters/min respectively. The field strength was increased with some time interval depending on the run. Usually it took about 3 hours to reach 1600°C. Pressure was raised to 2000 psi when temperature reached 1600°C and both temperature and pressure were held for 2 hours. After hot-pressing the field strength was reduced gradually to avoid thermal stress to the whole unit. The general view of the hot-pressing assembly is shown in Figure 5.

F. DENSITY MEASUREMENT

Density was measured using an Archimedes technique. Calculated densities of the hot-pressed sample were based on the weight fraction of the starting silicon nitride, glass frit powder and their respective densities. Weights were read to the fourth decimal place with Stanton Instrument’s Unimatic CL 41 electric balance.

G. X-RAY DIFFRACTION

X-ray diffraction analyses were made on a Norelco wide range goniometer x-ray unit utilizing Cu Kα radiation through a Ni filter. The tube voltage was 35 kilovolts and the current was 15 milliamperes. The angular aperture and receiving slit were 1° and 0.006 inch respectively. The detector was a sealed proportional counter and the pulse height analyzer was set at 100 percent. The specimens
Figure 5. The general view of the hot-pressing assembly.
were scanned at 1° 20/min from 5° to 65° and the chart
speed was 0.5 inch/min. The scale factor was 32, the multi-
plier was 1 and the time constant was 1.

H. ELECTRON MICROSCOPY

1) Preparation of Polished Specimens for Electron
Microscopic Examination

Three sets of samples were examined with a scanning
electron microscope. Two sets of hot-pressed samples
which contained 10% and 20% glass composition 3 were ex-
amined both parallel and perpendicular to the hot-pressing
direction and before and after being heat treated. In pre-
paring a specimen for electron microscopic examination a
section was taken from the specimen by using a water-cooled
metal-bonded diamond cut-off wheel. Sectioned specimens
were mounted with Fulton Metallurgical Products Corpora-
tion's 'Quickmount' and ground. The mounts were successive-
ly wet lapped on 240, 320, 400, and 600 grit silicon carbide
paper. This was followed by Syntron Vibratory lapping-
polishing machine with 15-micron levigated alumina on
Buehler AB Selvyt for 15 minutes, 5-micron levigated alpha
alumina on Buehler AB Selvyt for 30 minutes, 0.3-micron
alpha polishing alumina on Buehler AB Microcloth for 45
minutes, 0.05-micron gamma polishing alumina on Buehler
AB Microcloth for 90 minutes. Between polishing stages
the specimens were cleaned by immersion in distilled water
in an ultrasonic cleaner. The polished silicon nitride specimens were removed from their mounts by heating the mount to about 150°C.

2). Etching of Polished Sections

Polished specimens were etched in reagent assay 49.00 ± 0.25% Hydrofluoric acid of Fisher Scientific Company. The specimens containing 10% glass-ceramics 3 frit were etched 3 hours at room temperature and 20% glass-ceramics 3 frit specimens were etched 2 hours at room temperature. 50% content specimens were etched 5 minutes. After etching the specimens were rinsed in distilled water and ultrasonically cleaned for 15 minutes in acetone. The specimens were then mounted on the sample stage with silver conductive paint. Polished surface were then coated with about 300 Å of Au/Pd in a DC sputtering Mini-coater of Commonwealth Scientific Corporation.

3). Examination of Polished Sections and Preparation of Electron Micrographs

Polished, etched and Au/Pd coated specimens were examined by Model SMSM "Super-Mini-SEM-II" of International Scientific Instruments Inc. This electron microscope had a capability of 30 to 160,000 magnifications. A polaroid camera, type #545 attachment permitted the rapid taking of micrograph pictures of the polished sections. AME silicon nitride powder, ball milled glass-ceramics composition...
frit and mixtures of them were suspended in 4% collodion solution in amyl acetate and coated with about 500 Å Au/Pd. These powders were then examined and photographed by the same procedures as above.
IV. RESULTS AND DISCUSSION

Table 7 shows three different kinds of glass compositions studied through this investigation. Glass composition 1 was adopted from Corning Glass Works patent and it was reported that final glass-ceramics properties are: \( \alpha = 6.9 \times 10^{-7}/^\circ\text{C} \), specific gravity = 2.5073 and fracture strength \( \approx 30,000 \) psi. Glass composition 2 also was adopted from the patents of Stokey and Corning Glass Works, with final glass-ceramics properties reported as: \( \alpha = 14.1 \times 10^{-7}/^\circ\text{C} \), specific gravity = 2.62 and fracture strength \( \approx 37,000 \) psi. The primary crystallized phase of glass composition 1 is reported as beta spodumene along with cordierite and rutile, and that of glass composition 2 is reported as cordierite with rutile as a minor phase.

Glass composition 3 was made without the TiO\(_2\) nucleating agent and has about 21 wt% excess MgO based on the theoretical cordierite composition. X-ray powder diffraction patterns of the above three glass compositions after being heat-treated, as described in Table 7, are shown in Figure 6 along with AME silicon nitride powder. For the case of glass-ceramics composition 1, beta spodumene is the major crystalline phase and cordierite is also crystallized. For the case of glass-ceramics composition 2, only cordierite
Figure 6. X-ray diffraction patterns of three glass-ceramics compositions after heat-treatment and AME silicon nitride powder.
is formed and for glass-ceramics composition 3, cordierite is the major phase formed and forsterite and spinel as minor phases. AME silicon nitride powder is reported by supplier to be 95% alpha and the balance is mainly beta with a trace of Si$_2$N$_2$O. Glass-ceramics composition 3 was also heat treated in flowing nitrogen and there was no difference whether heat-treated in air or nitrogen.

To test the thermal stability, a piece of glass composition 1 frit was gradually heated in a platinum boat to 1200°C at a 4°C/min heating rate and was mostly crystallized. Similar experiments to 1300°C resulted in very fluid clear melts. The same clear melt also resulted when already heat-treated and crystallized glass-ceramics 1 were heated to 1300°C. Therefore it could be concluded that glass-ceramics 1 melts between 1200°C and 1300°C, so no further attempt was made to utilize this composition since this melting point was far below that expected. Crude measurement of the "softening temperature" of glass-ceramics composition 2 frit was made by gradually heating rectangular shaped (1/2 cm x 1/2 cm x 1 1/2 cm) piece on the platinum foil boat. The temperature was measured by Pt/Pt 10% Rh thermocouples. The change of the shape was viewed through the mica window of the peep hole of the furnace. At 1385°C the corners of the piece changed to a round shape which suggests the softening of the frit. By 1410°C the piece seems 'melted'. The platinum dish was taken out at 1410°C.
and quenched in cold water. The bottom of the melt, which as a minor amount, looked clear but the majority of the top part was opaque and light milky color. Thus it could be speculated that the crystallization process took place while heating and retained its crystallinity up to 1410°C.

For the preliminary experimental purpose 10 wt% of glass-ceramics composition 1 powder, which had been through 100 mesh screen and alumina wet ball milled 48 hours, plus 90 wt% AME silicon nitride powder were alumina ball milled again for 68 hours in T-butanol. The mixed dry powder was then cold pressed in a steel die at 45,000 psi. These discs were then fired at 1450°C and 1500°C in a SiC tube furnace in flowing nitrogen. Upon reaching the temperature, the furnace was shut off immediately. The heat-treatment schedule was 800°C for 1 hour and 1175°C for 4 hours. X-ray powder diffraction patterns showed alpha Si₃N₄ as a major phase and beta spodumene was also detected along with Si₂N₂O.

Glass-ceramics composition 2 frit which had been melted at 1650°C for 1 hour was crushed and passed through a 100 mesh screen. The powder was then ball milled for 24 hours. Three different glass-ceramics composition 2 contents (5%, 10%, 20%) were made by mixing proper amount of frit and AME powder in a plastic bottle with alumina balls and T-butanol milling fluid for about 20 hours milling. These powders were then cold pressed at 40,000 psi in a steel die without
binder. The discs were then fired at 1405°C in a SiC tube furnace with flowing nitrogen. When the temperature reached 1405°C the furnace was shut off. The heat-treatment schedule was 820°C for a hour and 1350°C for 1 1/2 hours. X-ray powder diffraction showed alpha Si₃N₄ diffraction and a small unidentified peak around 25°20 angle which increased with the proportion of glass-ceramics frit contents. Another x-ray diffraction chart was made for the sample with 20 wt% of glass-ceramics frit 2 and fired at 1450°C for 1 1/2 hours and heat-treated 820°C 1 1/2 hours, 1350°C for 5 hours. There was rather distinct diffraction (about 27 relative intensity) around 25°20 angle along with alpha Si₃N₄ major phase and Si₂N₂O. Cordierite diffractions were not seen in the above samples containing glass-ceramics frit 2.

During the initial portion of hot-pressing work, 10 wt% glass-ceramics composition 2 frit content silicon nitride powder was charged in molybdenum foil lined 1/2 inch diameter graphite die. When hot-pressed at 1420°C the relative density of final disc was about 50%. Increased hot-pressing temperature to 1600°C improved densification significantly. Figure 7 shows the densification curve of the isobaric data at temperature of 1600°C. It took 2 to 2 1/2 hours to reach 1600°C for the induction furnace which is described in the previous section. Pressures of 6000 psi were applied when the furnace reached about 1500°C.
Figure 7. Isothermal and Isobaric Densification Curve.
Density was measured using an Archimedes technique. Calculated densities of the powder prior to hot-pressing were based on the volume fractions of silicon nitride and glass-ceramics frit and their respective densities. Insufficient data was obtained to support the reproducibility of the above results. X-ray diffraction patterns of polished surfaces of samples hot-pressed for 1 hour and 2 hours revealed that intensities of beta phase diffraction were greater in the 2 hours case than for the 1 hour sample. Alpha phase diffraction was, however, still the major portion and Si$_2$N$_2$O was also formed. Again cordierite was not detected but a trace of unidentifiable phase was observed in the heat-treated sample.

Another hot-pressing was performed on the powder with 20 wt% glass-ceramics composition 2 frit. After being hot-pressed for 2 hours at 1600°C with 6000 psi, the sample was bulged out and the graphite die was broken. Just before shutting off the induction furnace there was an unusually high current shown on the gauge and this explains the graphite die breakage. The final density of the 1 1/2 inches diameter hot-pressed sample was 3.08 g/cm$^3$ which is 99.6% calculated theoretical density. X-ray diffraction of the polished surface showed that beta phase was a major phase and Si$_2$N$_2$O was also observed. No attempt was made to determine the alpha/beta ratio. After heat-treatment of this disc (1 1/2 hours at 810°C and 2 1/2 hours at 1300°C),
the unidentifiable phase was also detected weakly but distinctly.

At this point another glass-ceramics composition 3 was made. This composition contains about 21% excess MgO based on the theoretical cordierite composition \((2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)\). The batch was melted in a platinum crucible at 1650°C for 1 hour in a gas furnace, then quenched and crushed. The frit powder was made by ball milling the <100 mesh powder 20 1/2 hours. About 40 gms of powder (36 gm alpha \(\text{Si}_3\text{N}_4\) and 4 gm glass-ceramics composition 3 frit powder ball milled for 17 hours) was charged in molybdenum lined 1 1/2 inches graphite die and hot-pressed at 2000 psi for 2 hours at 1600°C. Bulk density was measured after hot-pressing and a value of 3.0414 g/cm\(^3\) was calculated and about 0.258% apparent porosity. A piece of the disc was cut by diamond saw and heat-treated at 820°C for 2 1/2 hours and 1310°C for 14 hours. Another hot-pressed sample was made containing 20 wt% glass-ceramics composition 3 frit. About 40 gms of this powder was loosely charged in molybdenum foil lined 1 1/2 inches graphite die as before and hot-pressed 2000 psi for 1 1/2 hours at 1650°C. The bulk density was 3.094 gm/cm\(^3\) and apparent porosity was 0%. Diamond sawed pieces were heat-treated 2 hours at 820°C and 14 hours at 1310°C. Figure 8 shows an x-ray diffraction chart of rough polished surface of 10 wt% and 20 wt% glass-ceramics composition 3 hot-pressed samples before and after
Figure 8. X-ray diffraction patterns of 10 wt% and 20 wt% glass-ceramics hot-pressed silicon nitride samples before and after heat-treatment.
heat-treatment. As can be seen in as-hot-pressed charts only silicon nitride was detected. For the sample of 20 wt% glass-ceramics 3 frit content very strong beta phase was detected as would be expected with the higher hot-pressing temperature. In the case of hot-pressed and heat-treated samples, alpha and beta phase diffraction appears at similar relative intensities to as-hot-pressed samples, but other diffractions occurred near 25°20 angle. Since these only showed after heat-treatment, it appeared that some sort of crystallization of glass took place in the sample.

On the basis of these results, it was decided to characterize more details of this phase. Five sets of different glass-ceramics composition 3 frit content sample mixtures were prepared by ball milling AME silicon nitride powder with proper amounts of frit. Weighed powders were placed in a pint plastic bottle with 35 alumina cylinders (½ inch diameter x ½ inch height) and 100 cc T-butanol as milling fluid. Five plastic bottles which contain five different frit contents (5%, 10%, 20%, 30%, 50%) were placed in large jar and milled with 80 rpm for 20 hours. The reason for T-butanol as milling fluid is the finding by Lange and Terwilliger that they detected strong ammonia odor after milling in water and they assumed the silicon nitride was being hydrolyzed to Si(OH)4. There was contamination with alumina while milling, but no
An attempt has been made to measure the degree of contamination nor the amount of surface silica on alpha silicon nitride powder. (Colquhoun et al. reported about 2 wt% contamination would be added when milling with alumina balls for 18 hours and about 2 wt% of alpha silicon nitride powder would be developed as a silica form at the surfaces).

Figure 9 shows the SEM micrograph of the AME silicon nitride powder morphology which was used in this investigation. It illustrates the wide distribution of the particle size and the elongated nature of many of the particles. An average particle size of about 1 μm was determined for the starting powder. Figure 10 shows the glass-ceramics composition 3 frit which had been ball milled. It shows that the powder has various irregular shapes and sizes from 1 μm to about 40 μm size. Figures 11 and 12 show the typical morphology of 50/50 and 20/80 (silicon nitride) mixture after ball milling. Each powder was suspended in collodion solution and examined directly under SEM. These illustrate that glass-ceramics frit still remains as large particles but smaller than the average original starting particle size. After drying, each powder was cold pressed at 40,000 psi in 3/4 inch steel die. Each set of different glass-ceramics composition 3 frit content discs was then fired in SiC tube furnace in high temperature alumina tube with nitrogen flow at a rate of about 1.5 liters/min. The sample discs were placed
Figure 9. SEM micrograph of the AME silicon nitride (6600X)

Figure 10. SEM micrograph of the glass-ceramics composition 3 frit. (600X)
Figure 11. SEM micrograph of 50/50 mixture. (1600X)

Figure 12. SEM micrograph of 20/80 mixture. (580X)
in the furnace center on an alumina boat which was lined with molybdenum foil. The temperature gradient from center to end of the alumina boat was negligible. Figure 13 shows a schematic drawing of the typical firing schedule. The heating rate was approximately 1.2°C/min and cooling rate was about 2.5°C/min. It was held at the desired temperature for 2 hours. The firing temperatures were 1450°C, 1500°C, 1550°C, and 1600°C. Since the SiC tube furnace could not be used above 1550°C, 1600°C samples were fired in the induction furnace by a stacking configuration with graphite cloth and molybdenum foil spacers. After firing, each disc was cut in half and heat treated in the manner shown in Figure 14. After heat treatment each disc was crushed and ground to <325 mesh and studied by the x-ray powder diffraction technique. Figure 15, specimens fired at 1600°C, shows no other crystalline phase except alpha silicon nitride and a small amount of beta phase. The conversion from alpha to beta silicon nitride was very low and hardly noticeable in the diffraction chart, probably due to the low temperature and the high oxygen potential or partial pressure because of the high content of glass. Figure 16 shows the diffraction patterns taken after heat-treatment of the same samples, which contain diffraction peaks around 25° and 30.8°, 36.4°, 37.05°... etc. for 2θ angle. The top chart which is 50% glass 3 frit content was taken from a polished surface. The following
Figure 13. Schematic drawing of the typical firing schedule.
Figure 14. Schematic drawing of the typical heat-treatment schedule.
Figure 15. X-ray diffraction patterns of the specimens fired at 1600°C showing alpha silicon nitride.
Figure 16. X-ray diffraction patterns of the specimens fired at 1600°C and heat-treated, showing alpha silicon nitride and unidentified phase X.
figures from 17 to 20 show the as-fired and heat-treated samples of 1550°C and 1500°C. As can be seen in the figures, the new phase intensity increases with increasing amounts of glass frit additions. Figures 21 and 22 are the x-ray diffraction charts of the samples fired to 1450°C. For this case the new phase can be clearly seen in both as-fired and heat-treated samples at about the same intensity. Table 8 shows the relative intensities of the most intense peak of this new phase which appears at 25.25° 2θ angle with varying firing temperatures and glass-ceramics composition 3 frit content. Relative intensity calculations were based on 20.65° 2θ angle alpha silicon nitride diffraction as 100. The peak intensities increase with increasing amount of glass-ceramics composition 3 frit additions. Since 1450°C samples showed the new phase either heat-treated or not, the heat-treating temperature effect was studied in more detail. A set of discs which contained 30 wt% glass-ceramics 3 frit were fired as the same manner as before at 1500°C for 2 hours. After firing, the discs were heat-treated at different temperatures. Figure 23 shows the diffraction charts of these results. As can be seen in Table 9, there is no difference in intensity for all different heat-treatment temperatures. From the above results and findings from the 1450°C firing, it could be speculated that this new phase can be crystallized over a wide range of temperature, as high as 1450°C,
Figure 17. X-ray diffraction patterns of the specimens fired at 1550°C showing alpha silicon nitride.
Figure 18. X-ray diffraction patterns of the specimens fired at 1550°C and heat-treated, showing alpha silicon nitride and unidentified phase X.
Figure 19. X-ray diffraction patterns of the specimens fired at 1500°C showing alpha silicon nitride.
Figure 20. X-ray diffraction patterns of the specimens fired at 1500°C and heat-treated, showing alpha silicon nitride and unidentified phase X.
Figure 21. X-ray diffraction patterns of the specimens fired at 1450°C showing alpha silicon nitride and unidentified phase X.
Figure 22. X-ray diffraction patterns of the specimens fired at 1450°C and heat-treated, showing alpha silicon nitride and unidentified phase X.
Table 8. RELATIVE INTENSITIES OF THE 25.25° 2θ ANGLE OF THE HEAT-TREATED SAMPLES (based on the 20.65° 2θ angle of the alpha silicon nitride diffraction as 100).

<table>
<thead>
<tr>
<th>TEMPERATURE</th>
<th>5%</th>
<th>10%</th>
<th>20%</th>
<th>30%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1450°C</td>
<td>H.N.</td>
<td>14</td>
<td>39</td>
<td>52</td>
<td>144</td>
</tr>
<tr>
<td>1500°C</td>
<td>H.N.</td>
<td>9</td>
<td>24</td>
<td>44</td>
<td>84</td>
</tr>
<tr>
<td>1550°C</td>
<td>H.N.</td>
<td>9</td>
<td>21</td>
<td>46</td>
<td>86</td>
</tr>
<tr>
<td>1600°C</td>
<td>H.N.</td>
<td>12</td>
<td>21</td>
<td>45</td>
<td>200*</td>
</tr>
</tbody>
</table>

H.N.: Hardly Noticeable

*: Diffraction of Polished Surface
Figure 23. X-ray diffraction patterns of the specimens fired at 1500°C and heat-treated at different temperatures.
Table 9. RELATIVE INTENSITIES OF THE 25.25° 2θ ANGLE OF THE SAMPLES AT DIFFERENT HEAT-TREATMENT TEMPERATURES (fired at 1500°C with 30% glass-ceramics composition 3 frit addition for 2 hours, based on the 20.65° 2θ angle of the alpha silicon nitride diffraction as 100).

<table>
<thead>
<tr>
<th>TEMPERATURE</th>
<th>RELATIVE INTENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250°C*</td>
<td>44</td>
</tr>
<tr>
<td>1300°C</td>
<td>48</td>
</tr>
<tr>
<td>1350°C</td>
<td>36</td>
</tr>
<tr>
<td>1400°C</td>
<td>48</td>
</tr>
<tr>
<td>1450°C**</td>
<td>52</td>
</tr>
</tbody>
</table>

*: Heat-treated 10 hours

**: Fired at 1450°C, no heat-treatment
and the melting point of this phase is between 1450°C and 1500°C which is higher than the previously formed cordierite base glass-ceramics. Table 10 shows the d spacing and relative intensities of this new phase(s). Also shown are the tentative indices of diffraction which may be of hexagonal structure.\textsuperscript{57,58} It is speculated that this new phase(s) is a compound of Si\textsubscript{3}N\textsubscript{4} - SiO\textsubscript{2} - Al\textsubscript{2}O\textsubscript{3} - MgO, and TiO\textsubscript{2} is not involved in this compound. Glass-ceramics composition 2 lies in the Mullite primary field in the MgO - Al\textsubscript{2}O\textsubscript{3} - SiO\textsubscript{2} systems and composition 3 lies in the Spinel primary field. Considering the SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} contamination, composition 2 and composition 3 still lies in Mullite and Spinel primary phase region respectively. For the case of composition 3 the final crystallized phases are Cordierite, Spinel, and Forsterite whether it is contaminated or not with SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. The crystallized phase of frit composition 3 alone satisfied the MgO - Al\textsubscript{2}O\textsubscript{3} - SiO\textsubscript{2} phase diagram but the involvement of Si\textsubscript{3}N\textsubscript{4} supressed the crystallization of these phases. It is therefore speculated that the solubility of Si\textsubscript{3}N\textsubscript{4} to frit composition 3 or vise versa is quite large at certain temperature.

Considerable difficulty was experienced in chemically etching the silicon nitride for microstructural analysis. Lange and Terwilliger\textsuperscript{31} described a method of chemically etching silicon nitride as etching in molten salt (95.4 gm K\textsubscript{2}CO\textsubscript{3} + 12 gm NaF) for 30 minutes. Mazdiyasni and Cooke\textsuperscript{13}
Table 10. d SPACINGS AND RELATIVE INTENSITIES OF NEW PHASE(S)

<table>
<thead>
<tr>
<th>2θ</th>
<th>d</th>
<th>I/I₀</th>
<th>hkl  (tentative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.85</td>
<td>3.587</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>24.95</td>
<td>3.565</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>25.25</td>
<td>3.523</td>
<td>100</td>
<td>(100)</td>
</tr>
<tr>
<td>30.8</td>
<td>2.9005</td>
<td>45</td>
<td>(101)</td>
</tr>
<tr>
<td>36.45</td>
<td>2.463</td>
<td>45</td>
<td>(002)</td>
</tr>
<tr>
<td>37.15</td>
<td>2.418</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>39.3</td>
<td>2.290</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>44.55</td>
<td>2.032</td>
<td>21</td>
<td>(110)</td>
</tr>
<tr>
<td>48.0</td>
<td>1.8937</td>
<td>16</td>
<td>(111)</td>
</tr>
<tr>
<td>52.9</td>
<td>1.7293</td>
<td>10</td>
<td>(200)</td>
</tr>
<tr>
<td>61.0</td>
<td>1.5173</td>
<td>9</td>
<td>(103)</td>
</tr>
<tr>
<td>61.8</td>
<td>1.4999</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>62.0</td>
<td>1.4955</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>
found the results were best when specimens were etched with 7:2:2 concentrated $\text{H}_2\text{SO}_4$ : HF : $\text{NH}_4\text{F}$ solution in teflon or platinum container at 300°C for 30 to 45 minutes. Later they also described boiling phosphoric/sulfuric acid (3/1) for 8 hours as a good etching method for rare-earth doped silicon nitride. The hot-pressed silicon nitride specimens, which contain glass-ceramics composition 3 frit, were preliminarily etched according to each of the above methods with considerably shorter time than they described. The results were badly over-etched specimens in each case. By varying the concentration and time, it was found that HF solution alone was also a good etchant to boundary phase and silicon nitride.

Figure 21 shows the 10 wt% frit 3 specimen taken perpendicular to the hot-pressing direction. With magnification of 500X or so, the polished and etched surface shows many pitted holes of size in the order of 10 um. This observation could possibly be explained by the mixture morphology which is seen in Figure 12. Some of the frit still remained in large size, and while hot-pressing, its melt reacted with silicon nitride and still remained localized. Figure 25 shows the same specimen with the view parallel to the hot-pressing direction. As can be seen in this and previous figures, it is difficult to tell whether the microstructure is a preferentially oriented one. Some indication of a bimodal size distribution may be seen.
Figure 24. SEM micrograph of polished surface of the as-hot-pressed 10 wt% frit 3 specimen taken perpendicular to the hot-pressing direction (top: 5000X, bottom: 10650X)
Figure 25. SEM micrograph of polished surface of the as-hot-pressed 10 wt% frit 3 specimen taken parallel to the hot-pressing direction (top: 5000X, bottom: 9650X)
Figures 26 and 27 show the perpendicular and parallel surface to hot-pressing direction of 10% frit 3 content samples which were hot-pressed and then heat-treated. No significant differences were observed whether the specimens were heat-treated or not, and whether the specimens were viewed perpendicular or parallel to the hot-pressing direction.

Figures 28 and 29 clearly show the more uniform and elongated nature of the structure when compared with 10% frit mixture. Again with low magnification, many pitted 1 to 2 um sized holes were observed. Figures 30 and 31 are the heat-treated samples of Figures 28 and 29 respectively. Here again a wide range of grain sizes was observed as well as the bimodal (elongated and equiaxed) grain distributions.

Figures 32 and 33 show the microstructure of 50/50 mixtures. Extensive and preferential etching was achieved even though etching was only 5 minutes. It is seen that some of the large silicon nitride grains have remained. When the 50/50 mixture was removed from the induction furnace after firing at 1600°C for 2 hours, the sample-disc was covered with whitish bubbles and also about 1/3 of the outer part of the disc contained many large pores (≈ 1 mm diameter). This observation may be explained by considering that at the firing temperature of 1600°C the glassy phase (whether it contained silicon nitride or not),
Figure 26. SEM micrograph of polished surface of the hot-pressed, heat-treated 10 wt% frit 3 specimen taken perpendicular to the hot-pressing direction (top: 4900X, bottom: 10500X).
Figure 27. SEM micrograph of polished surface of the hot-pressed, heat-treated 10 wt% frit 3 specimen taken parallel to the hot-pressing direction (top: 4760X, bottom: 10200X).
Figure 28. SEM micrograph of polished surface of the as-hot-pressed 20 wt% frit 3 specimen taken perpendicular to the hot-pressing direction (top: 5040X, bottom: 10800X)
Figure 29. SEM micrograph of polished surface of the as-hot-pressed 20 wt% frit 3 specimen taken parallel to the hot-pressing direction (top: 5240X, bottom: 10200X)
Figure 30. SEM micrograph of polished surface of the hot-pressed, heat-treated 20 wt% frit 3 specimen taken perpendicular to the hot-pressing direction (top: 5240X, bottom: 10200X).
Figure 31. SEM micrograph of polished surface of the hot-pressed, heat-treated 20 wt% frit 3 specimen taken parallel to the hot-pressing direction (top: 5040X, bottom: 9450X).
Figure 32. SEM micrograph of polished surface of the as-sintered 50/50 mixture (2000X)

Figure 33. SEM micrograph of polished surface of the sintered, heat-treated 50/50 mixture (1950X)
boils or evolves a gaseous substance and entraps this gas which remains as pores.

RECOMMENDATIONS FOR FURTHER STUDY

Based on the findings of this investigation, the following are recommended for further study:

A). Characterization of New Phase

Greater proportions of this new compound could possibly be achieved by adjusting MgO- $\text{Al}_2\text{O}_3-\text{SiO}_2$ frit compositions and add these frits to varying amounts of silicon nitride powder. Since the new phase melts above 1500°C, the final products of the above mixtures would be a homogeneous melt and subsequent heat-treatment would develop the single phase. The mixing procedures of the frits and silicon nitride powder should be carefully controlled to avoid contamination. Once the new phase is obtained in adequate amounts the chemical composition and structure should be studied, and the physical properties such as thermal properties and stability should be established.

B). Fabrication

After characterizing the new phase, optimization of the frit addition to silicon nitride powder should be studied to develop final silicon nitride bodies. It may be possible to achieve full density by hot-pressing as low as 1500°C. Here again the frit compositions should be adjusted to take into account the contamination while
mixing, and the surface silica in silicon nitride powder if any. The particle size of glass-frit and the mixing of glass-frit and silicon nitride powder both should be carefully controlled to avoid isolated regions of glass-frit. Crystallization behavior of this new phase when associated with the silicon nitride and also the percent of crystallinity after heat-treatment should be studied with respect to thermal history.

C). Properties

After fabricating the dense silicon nitride bodies which contain the crystallized bonding phase, the physical properties of this final product should be studied. The critical property measurements suggested are high temperature strength, creep tests at elevated temperature, thermal shock resistance and oxidation behaviors.
V. SUMMARY

Recrystallization processes of cordierite based glass-ceramics frit were studied by varying composition and heat-treatment schedules. Glass-ceramics frit 2, which is near theoretical cordierite composition with TiO$_2$ nucleating agent, was heat-treated with an appropriate schedule and only cordierite was crystallized. Glass-ceramics frit 3, which is a theoretical cordierite composition with about 21% excess MgO content, resulted in the crystallization of cordierite, forsterite and spinel phases after heat-treatment.

After firing above 1450°C followed by proper heat-treatment schedule, either of the mixtures of glass-ceramics frit 2 or 3 with silicon nitride did not show the crystallization of cordierite. Instead of cordierite crystallization, a new unidentifiable phase or phases were observed.

Hot-pressing behaviors of these glass-ceramics frits added to silicon nitride were investigated to produce near theoretical density of the mixtures. Proper heat-treatment schedules were studied in order to crystallize the glassy phase in the hot-pressed specimens.

After finding a new phase or phases which had been formed during heat-treatment schedule, its characterization
was attempted. This new phase(s) has a melting point range of 1450°C to 1500°C and is believed to be a compound of MgO- Al$_2$O$_3$- SiO$_2$- Si$_3$N$_4$. And also the attempt was made to assign the tentative indices of diffraction which may be of hexagonal structure.

Microstructure of hot-pressed samples, which were mixed with glass-ceramics frit added to silicon nitride before hot-pressing, were studied by scanning electron microscopy. The mixture of silicon nitride powder with glass-ceramics frit were also examined by SEM as well as the individual powders.

Recommendations are given for further study and characterization of this new phase and properties evaluation of the final hot-pressed product and the application of the technique of this investigation.
VI. CONCLUSIONS

Within the limits of this investigation, the following conclusions are indicated:

1) spodumene- and cordierite-based glass-ceramics frit 1 and 2 are easily crystallized by proper heat-treatment.

2) upon appropriate heat-treatment of glass-ceramics frit 3, which is a theoretical cordierite composition with about 21% excess MgO content, also can be easily crystallized.

3) final crystallized phases of the glass-ceramics frit 3 are cordierite, forsterite and spinel, and the crystallization behavior is not affected by heat-treatment atmosphere (air or nitrogen).

4) subsequent heat-treatment after firing above 1500°C does not crystallized cordierite in the mixture of glass-ceramics frit 2 and 3 with silicon nitride powder.

5) the mixture of 10 wt% and 20 wt% of the glass-ceramics frit 2 and 3 with silicon nitride powder is easily hot-pressed to reach almost theoretical densities.

6) proper heat-treatment of the above hot-pressed samples show recrystallization of the glassy bonding phase.

7) melting temperature range of the recrystallized bonding phase is 1450°C to 1500°C.
8) It is speculated that this new phase(s) is a compound of MgO - Al₂O₃ - SiO₂ - Si₃N₄, and has an hexagonal structure.

9) d spacing and relative intensities of this tentatively assigned hexagonal crystalline phase and so far unidentifiable phase are reproducibly obtained, and presented in Table 10.

10) Heat-treatment employed in this study does not affect the microstructure of hot-pressed silicon nitride specimens.

11) Microstructure of hot-pressed specimens show a wide range of grain sizes as well as the bimodal size distributions.
VII. REFERENCES CITED


58. Bell, J. C. and Austin, A. E., Battelle Indexin., Charts for Diffraction Patterns of Tetragonal, Hexagonal and Orthorhombic Crystals, Battelle Memorial Institute, Columbus 1, Ohio