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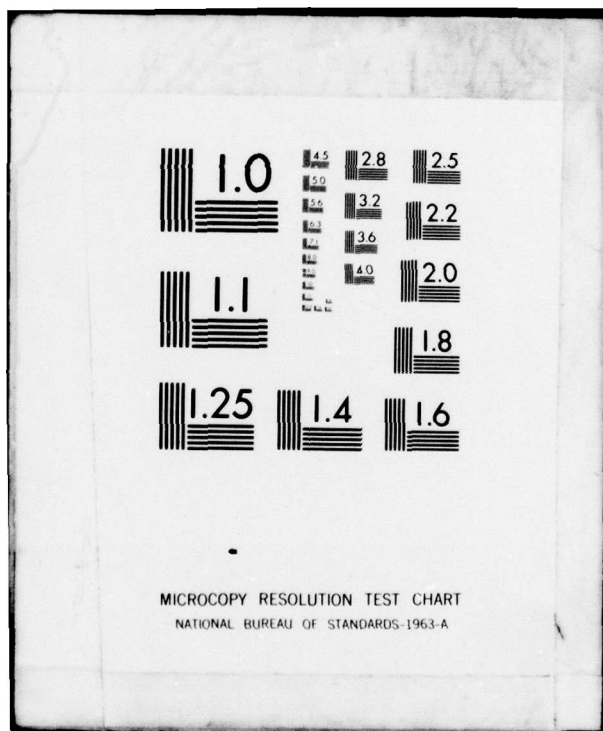
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SINTERING OF BETA SILICON NITRIDE
SOLID SOLUTIONS CONTAINING METAL OXIDE

T. Y. Tien

Technical Report No. 014536-78-1

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Reaction sintering of β-Si_3N_4 solid solutions has been studied, using powder mixtures of SiO_2 and AlN; Si_3N_4, AlN and Al_2O_3; and Si_3N_4, SiO_2 and AlN. Although the different starting mixtures resulted in the same final composition, substantial differences in sintering kinetics take place depending on the influence of chemical reactions, vaporization, and densification by transient liquid phase sintering. This behavior can be explained qualitatively on the basis of the solid-liquid equilibria in the Si,Al/N,O system.		

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Reaction sintered β - Si_3N_4 solid solutions with the highest densities were prepared from mixtures of Si_3N_4 , AlN and Al_2O_3 powders without application of external pressure or additional densification aids. In contrast, mixtures containing SiO_2 showed less densification even with liquid present because of vaporization during sintering.

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III. Sintering of Si₃N₄-AlN-Al₂O₃ Mixtures," accepted for publication
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PAPERS PRESENTED AT TECHNICAL MEETINGS

1. "1550°C Isothermal Plane in the System Si_3N_4 -AlN-Al₂O₃-Y₃Al₅O₁₂,"
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2. "Reaction Sintering of β - Si_3N_4 Solid Solutions in the System Si,Al/N,O,"
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Notre Dame.

Solid-Liquid Equilibria in the System $\text{Si}_3\text{N}_4\text{-AlN-SiO}_2\text{-Al}_2\text{O}_3$

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Solid-liquid equilibria at 1750°C and subsolidus phase relations in the system $\text{Si}_3\text{N}_4\text{-AlN-SiO}_2\text{-Al}_2\text{O}_3$ were determined for the composition region bounded by the $\beta\text{-Si}_3\text{N}_4$ solid solution line and silica-alumina join. X-ray diffraction and optical microscopy were used to determine the phases present in specimens cooled rapidly after equilibration. The extent of a single liquid-phase region and the tie lines for the β -solid solution + liquid field at 1750°C were established from quantitative X-ray diffractometry and lattice parameter measurements of β -solid solutions in equilibrium with liquid. The results were corroborated by optical microscopy and melting behavior observations. A new composition, $\text{Si}_{1.2}\text{Al}_{1.8}\text{O}_{3.8}\text{N}_{0.8}$, is suggested for the x_1 phase. The lowest melting temperature in the system is $\approx 1480^\circ\text{C}$ and the corresponding composition is 10 eq% Al-90 eq% O.

I. Introduction

CERAMIC materials based on the system Si,Al/N,O are currently being considered as one of the promising candidates for structural application in an energy-efficient gas turbine. Boskovic *et al.*¹ showed that Si_3N_4 -based ceramics can be made by pressureless sintering. Since Si_3N_4 -based materials have significant covalent character in their bond scheme, sintering to high density via solid state diffusion is not possible. Therefore, the alternative possibility of sintering in the presence of a liquid must be considered. For a liquid-phase sintering process, it is necessary to understand the solid-liquid equilibria in this system. Since such information is scarce in the literature, a study of these equilibria was undertaken.

The early work on phase relations in the system Si,Al/N,O concerned the formation and nature of the $\beta\text{-Si}_3\text{N}_4$ -based solid solution ($\beta\text{-ss}$) and other solid phases in the system.²⁻⁴ The first detailed study of subsolidus equilibria was reported by Gauckler *et al.*⁵ who found that, at 1760°C, adjacent the SiO_2 -rich side of the $\beta\text{-ss}$ phase, a 2-phase region (liquid + $\beta\text{-ss}$) existed. However, the solid-liquid equilibria were not studied in detail. Land *et al.*⁶ reported that liquid in this system was confined to the region close to the SiO_2 corner and that there was no region where $\beta\text{-ss}$ and liquid coexisted at 1800°C in their product or quasi-equilibrium diagram. They also reported that the x_1 phase does not melt at $< 1800^\circ\text{C}$. Layden⁷ proposed a tentative liquid-phase field using differential thermal analysis (DTA) and microstructure observations. The liquid field extends from the SiO_2 corner and includes the x_1 composition at 1750°C. The x_1 phase reportedly melts at $\approx 1720^\circ\text{C}$. A large $\beta\text{-ss}$ - liquid field is also indicated at 1750°C. Layden had difficulty in getting reasonable signal strengths during melting due to foaming of the liquid at the high temperatures involved. Therefore, an alternative method of quantitative phase analysis by X-ray powder diffractometry on a series of well-selected specimens should prove to be a more reliable method of studying solid-liquid equilibria in this system.

II. Experimental Procedure and Observations

The starting materials used were aluminum nitride,[†] silicon nitride,[‡] alumina,[§] and silica.[¶] The oxygen contents of the nitrides were considered in making up the compositions. Mixtures of different overall compositions in the region between the $\beta\text{-ss}$ line and silica-alumina join were made using aluminum nitride-silica-

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† HCST 2633 (combined oxygen = 2.9 wt%), H. C. Starck, Goslar, Federal Republic of Germany.

‡ Controlled phase 85, $\alpha\text{-Si}_3\text{N}_4$ = 85 wt%; $\beta\text{-Si}_3\text{N}_4$ = 12 wt%; combined oxygen = 1.8 wt%, Kawecki-Berylo Industries, Inc., Reading, Pa.

§ Linde A or calcined alumina A-16, > 99.5 wt% Al_2O_3 , Aluminum Co. of America, Pittsburgh, Pa.

¶ Flint 25, > 99.5 wt% SiO_2 , Rovin Ceramics, Dearborn Heights, Mich.

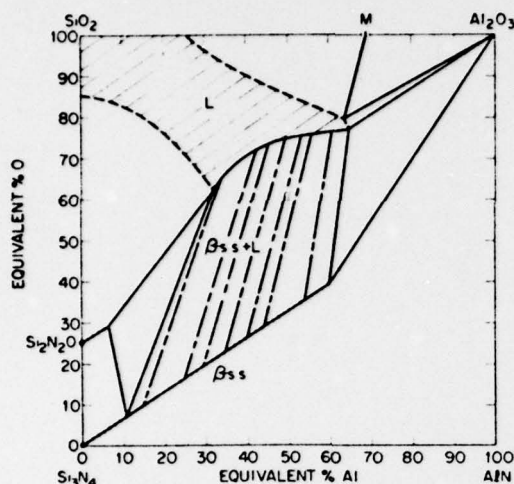


Fig. 1. Part of isothermal section of the system $\text{Si}_3\text{N}_4\text{-AlN-SiO}_2\text{-Al}_2\text{O}_3$ at 1750°C showing solid-liquid equilibria; $\beta\text{-ss}$ = $\beta\text{-Si}_3\text{N}_4$ -based solid solution, M = mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), L = liquid.

alumina, silicon nitride-silica-aluminum nitride, and silicon nitride-aluminum nitride-alumina as starting materials. The first group was the most commonly used since aluminum nitride-containing mixtures equilibrated more readily than silicon nitride-containing mixtures.

The selected compositions were made by milling the requisite amounts of starting materials in a tungsten carbide jar with tungsten carbide balls and high purity methanol (<0.2% water) for 30 to 60 min. It was found that the nitrides (AlN and/or Si_3N_4) are hydrolyzed, and thus pick up oxygen, if a significant amount of water is present in the grinding medium. Therefore, contact with water must be avoided during milling to preserve the overall composition of the as-weighted mixture. Tungsten carbide impurity introduced during milling was <1.5 wt%. The milled mixture was dried in shallow glass disks over a laboratory heater and cold-pressed into a pellet (1.3 cm in diam. by 1.3 cm thick) at 110 MPa. The pellet was put in a boron nitride crucible and, in most cases, packed in powder of the same composition to minimize weight loss in the pellet during firing.

Firing was done in a nitrogen atmosphere in an induction furnace using a graphite susceptor. A small nitrogen flow was maintained during firing. The heating rate was $350^\circ\text{C}/\text{min}$ and various holding times were used at different firing temperatures. Temperature was measured with an optical pyrometer. The specimens were furnace-cooled at a rate of $\approx 250^\circ\text{C}/\text{min}$ to 1000°C . Further cooling to room temperature was somewhat slower.

The specimens selected for quantitative measurements were those that showed minimum weight loss when fired and that gave equilibrium phase assemblages. Equilibrium was assumed to have been attained when the number, type, and amounts of phases, as determined by XRD, did not vary with time at a fixed temperature. Equilibrium was also confirmed in some selected specimens by obtaining the same type and amounts of phases from different starting materials for a given composition. Whenever a substantial amount of liquid (> about 10%) occurred at the firing temperature, equilibrium was readily achieved, typically within 15 min.

The use of packing powder, rapid heating, and short holding time at the firing temperature kept the weight loss in the pellet at <1.5% in most cases. However, compositions containing >40 eq% O and <40 eq% Al underwent large weight losses (5 to 15%) when fired at 1750°C . Excessive weight loss did not occur at $\leq 1650^\circ\text{C}$. About 50 compositions, lying in the area above the $\beta\text{-ss}$ line in Fig. 1, were fired at 1750°C to establish the isothermal section representing solid-liquid equilibria. Some selected compositions were fired at $\leq 1650^\circ\text{C}$ to determine subsolidus phase equilibria and the tempera-

ture and composition of the lowest melting point. The fired specimens were examined mainly by XRD, and in some cases metallography, to determine the number and type of phases present. An automatic recording diffractometer with $\text{CuK}\alpha$ radiation at 40 kV and 15 mA was used. The samples were scanned between 10° and $80^\circ 2\theta$ at a rate of $2^\circ/\text{min}$. Firing conditions and phases present in various specimens after firing are given in Table I.*

Standard quantitative X-ray powder diffractometry* was used to determine the amount of $\beta\text{-ss}$ in the selected specimens in the $\beta\text{-ss}$ + liquid field to establish the tie lines in this 2-phase field at 1750°C . The specimens were ground into powder for this purpose. Calibration standards were made using 10 wt% alumina as an internal standard with different amounts of single-phase $\beta\text{-ss}$ powder and silicon powder as a filler. Alumina could be used as an internal standard because the specimens in the $\beta\text{-ss}$ + liquid field contained no alumina themselves. Initial trials using integrated intensities of the diffraction peaks scanned at $0.2^\circ/\text{min}$ showed that no substantial improvement in the analysis was achieved by using the integrated intensities instead of the peak heights scanned at $2^\circ/\text{min}$. Therefore, the peak heights in the diffraction patterns scanned at $2^\circ/\text{min}$ were taken as a measure of the concentration of a given phase in a powder mixture.

A calibration curve of the peak-height ratio vs wt% $\beta\text{-ss}$ was made from the diffractometer traces of the standards. The peak-height ratio here refers to the ratio of the peak height of (301) or (321) reflection of $\beta\text{-ss}$ to the peak height of (012) or (113) reflection of the internal standard $\alpha\text{-Al}_2\text{O}_3$. The experimental error in determining the amount of $\beta\text{-ss}$ by this method is estimated to be ± 4 wt%. The composition of $\beta\text{-ss}$ in these selected specimens was determined from the change in the $\beta\text{-ss}$ lattice parameters. For this purpose, a calibration curve was made⁹ for lattice parameters vs eq% Al in different hot-pressed single-phase $\beta\text{-ss}$ standards. The scanning rate on the diffractometer used for the lattice parameter change measurements was $0.5^\circ/\text{min}$. The basis for determining tie lines in the $\beta\text{-ss}$ + liquid field from the amount and composition of $\beta\text{-ss}$ in the fired specimens of this field is discussed in the next section.

III. Results and Discussion

Solid-liquid equilibria at 1750°C determined in this study are shown in Fig. 1 in equivalent percent representation.⁸ At this temperature, x_1 phase is molten; evidence for this is presented later. Tie lines for the $\beta\text{-ss}$ + liquid field and the corresponding part of the liquidus curve were established from the compositions and amounts of $\beta\text{-ss}$ in selected specimens which had overall compositions in this 2-phase field. This derivation was possible because, during cooling from 1750°C , no significant amount of $\beta\text{-ss}$ crystallized from the liquid phase as shown by the fact that compositions lying just above the liquidus curve (solid line) in the all-liquid field showed only x_1 as the crystalline phase. No $\beta\text{-ss}$ was detected in these specimens by XRD. The minimum concentration of $\beta\text{-ss}$ that could be detected in synthetic mixtures was 3 wt%, which means that those compositions which are totally liquid at 1750°C partially crystallized into x_1 and the rest remained as a glass and that <3 wt% $\beta\text{-ss}$ precipitated during cooling.

Another feature indicating that no significant amount of $\beta\text{-ss}$ crystallized during cooling in the 2-phase $\beta\text{-ss}$ + liquid field is the fact that two compositions lying on the same tie line but containing significantly different amounts of liquid at 1750°C did not give different lengths of the tie line. These composition pairs are identified by the numbers 5,6; 7,16; and 8,30 (Table I). The part of the liquidus determined from the X-ray results is represented by the solid line in Fig. 1. It matches well with the melting behavior and microstructural observations. A similar determination of tie lines for the $\text{Si}_3\text{N}_4\text{-O-ss}$ + liquid field and the corresponding liquidus could not be done since liquids in this field crystallized $\text{Si}_3\text{N}_4\text{-O-ss}$ on cooling and the specimens in this field showed large weight losses by vaporization when fired at 1750°C . Therefore, the liquidus here was determined from the melting behavior and microstructural

*For Table I, order ACSD-143 from Data Depository Service, The American Ceramic Society, 65 Ceramic Drive, Columbus, Ohio 43214.

Table II. Lattice Parameter Changes in $\text{Si}_2\text{N}_2\text{O}$ Solid Solution

Comp		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
Al (eq%)	O (eq%)			
0	25.5	8.890	5.488	4.857
2.5	26.3	8.895	5.507	4.857
6.3	30.0	8.906	5.529	4.859

observations alone; it is drawn as a dashed line, indicating a somewhat larger margin of error.

Some of the specimens (Nos. 10, 41, 43, and 44 in Table I) that experienced large weight losses in firing were dissolved in a borate glass made of equal weight proportions of $\text{Na}_2\text{B}_4\text{O}_7$ and LiBO_2 . The glass samples were then analyzed for Si and Al by the electron microprobe analyzer and for N₂ content by wet chemical analysis.¹⁰ In this analysis, NH_3 was liberated from the specimens by dissolving them in lithium hydroxide. The NH_3 liberated was determined volumetrically using standard H_2SO_4 . The analyses showed that Si, N₂, and O₂ were lost by vaporization but that the Al content of the specimens increased. As a result, the overall composition shifted toward the AlN corner.

The segments of the liquidus for the mullite + liquid and the

alumina + liquid fields were deduced from the phases present in the fired specimens as determined by XRD and are also shown as dashed lines. The extent of the liquid field found here is in reasonable agreement with that tentatively proposed by Layden⁷ from DTA and microstructural studies. However, the shape of the liquidus is quite different, particularly for the β -ss + liquid field. This field is larger than Layden's and its liquidus curves more strongly toward the N₂-rich compositions. The solid solubility of Al in $\text{Si}_2\text{N}_2\text{O}$ was determined from lattice parameter changes of the single-phase specimens and the appearance of secondary x_1 and β -ss phases in the neighboring compositions. The lattice parameters of $\text{Si}_2\text{N}_2\text{O}$ -ss are given in Table II.

The composition $\text{Si}_{1.2}\text{Al}_{1.8}\text{O}_{3.0}\text{N}_8$ (i.e. $2\text{Si}_3\text{N}_4 \cdot 9\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) gave the highest peak intensities for the x_1 diffraction pattern and showed no other crystalline phases after firing at 1750°C. Microstructural observations showed that this composition contained less glass than any other compositions having x_1 as the only crystalline phase. Furthermore, when fired at 1650°C this composition gave x_1 phase only, whereas neighboring compositions contained secondary mullite or β -ss. Therefore, it is suggested that the stoichiometric composition of x_1 is $\text{Si}_{1.2}\text{Al}_{1.8}\text{O}_{3.0}\text{N}_8$. When heated to 1750°C, this composition spread freely in the crucible (like a melt). An optical micrograph (Fig. 2) of a polished section of this composition shows large, elongated x_1 grains, with some glass present along the grain



Fig. 2. Optical micrograph of polished section of 53 eq% Al-76 eq% O specimen fired at 1750°C for 10 min; HF etched.

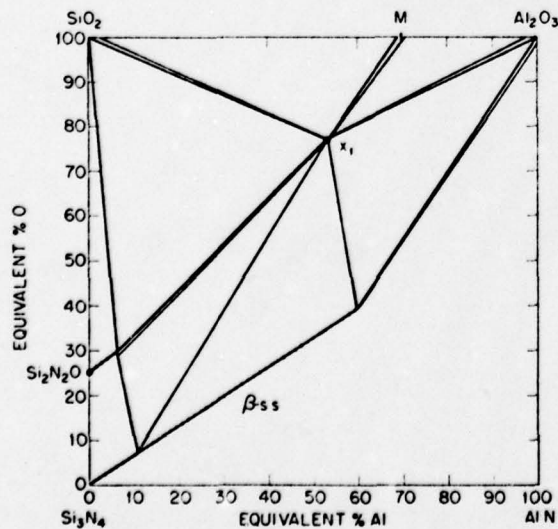


Fig. 3. Subsolidus phase equilibria; $x_1 = \text{Si}_{1.2}\text{Al}_{1.8}\text{O}_{3.0}\text{N}_8$.

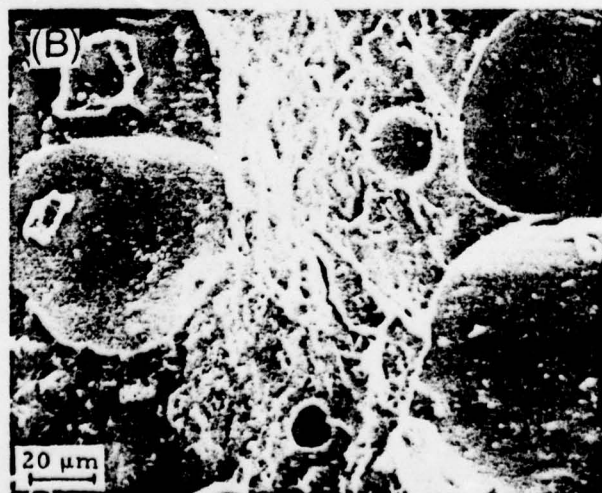
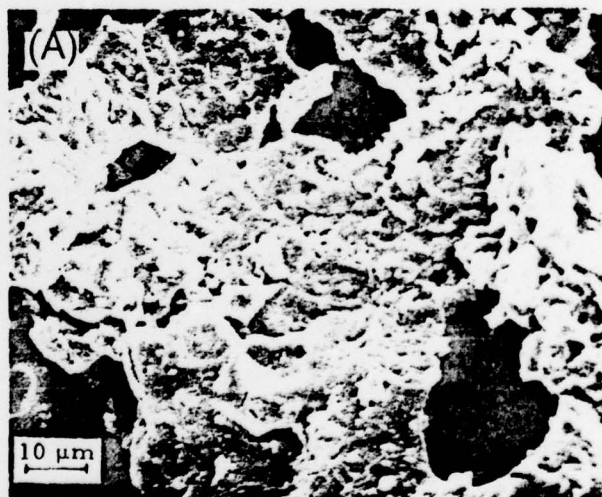


Fig. 4. Scanning electron micrographs of fracture surfaces of 10 eq% Al-90 eq% O specimen fired at (A) 1450°C for 2 h and (B) 1500°C for 2 h.

boundaries. A few light-colored β -ss grains (estimated as <2 vol%) which apparently precipitated from the x_1 phase during cooling are also visible. Thus, if this is the single-phase x_1 composition, the specimen must be completely molten at 1750°C since the specimen fired at this temperature showed no other crystalline phases in the XRD pattern. The melting temperature of the x_1 phase is estimated as 1720°C. This composition lies on the line joining Si_3N_4 and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) compositions.

Subsolidus phase equilibria in part of the system are shown in Fig. 3. The lowest-melting composition is ≈ 10 eq% Al-90 eq% O which melts at 1480°C ($\pm 20^\circ\text{C}$). The evidence for melting in this composition is seen in the scanning electron micrographs of the fractured surfaces (Fig. 4). The specimen fired at 1450°C shows no rounded pores, whereas the specimen fired at 1500°C shows such pores which occur when densification takes place in the presence of a liquid. The appearance of the specimens and the extent of densification also indicated a large amount of liquid in the 1500°C-fired specimen and little in that fired at 1450°C.

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- ¹⁰ G. Glaeser, private communication.

Reaction Sintering Forming β - Si_3N_4 Solid Solutions in the System $\text{Si}_3\text{Al/N}_2\text{O}$

I. Sintering of SiO_2 -AlN Mixtures

S. BOSKOVIC*, L. J. GAUCKLER**, G. PETZOW** and T. Y. TIEN***

Abstract

Reaction sintering of β - Si_3N_4 solid solution containing 60 equivalent percent of aluminum in the system $\text{Si}_3\text{Al/N}_2\text{O}$ was investigated. The starting materials used for this study were quartz form of SiO_2 and AlN. The results can be discussed on the basis of "chemical reaction", "vaporization" and "densification". At low temperatures (1400-1600°C) chemical reaction took place and resulted in porosity increase. At intermediate temperature interval

(1600-1800°C) liquid phase formed. High vapor pressure of the liquid in the specimen caused heavy weight loss and hence reduction in apparent density. At higher temperatures (above 1800°C), large quantity of liquid sealed open pores and prevented material loss. This liquid facilitated densification and chemical reaction. No or little densification was observed when single phase β - Si_3N_4 solid solution was sintered.

Herstellung von β - Si_3N_4 Mischkristallen durch Reaktionssintern

Es wurde das Reaktionssintern von β - Si_3N_4 Mischkristallen mit 60 Äquivalentprozent Aluminium im System $\text{Si}_3\text{Al/N}_2\text{O}$ untersucht. Die Ausgangsmaterialien für diese Arbeit waren SiO_2 in Quarzform und AlN. Die Ergebnisse können auf der Basis „Chemische Reaktion“, „Verdampfung“ und „Verdichtung“ diskutiert werden. Bei tiefen Temperaturen (1400-1600°C) findet chemische Reaktion statt, die zu einer Porositätszunahme führt. In einem mittleren Temperaturbereich (1600-1800°C) bildete sich Schmelzphase.

deren hoher Dampfdruck zu einem starken Gewichtsverlust und damit zu einer starken Abnahme der scheinbaren Dichte führt. Bei höheren Temperaturen (über 1800°C) versiegelt eine große Menge flüssiger Phase die offenen Poren und verhindert so den Materialverlust. Die Schmelze erleichtert außerdem die Verdichtung und die chemische Reaktion. Keine oder geringe Verdichtung wird beobachtet, wenn einphasige β - Si_3N_4 Mischkristalle gesintert werden.

Production de solutions solides de β - Si_3N_4 par frittage avec réaction

Le rapport s'agit de frittage par réaction des solutions de β - Si_3N_4 contenant 60 pour cent équivalent d'aluminium dans le système $\text{Si}_3\text{Al/N}_2\text{O}$. Les résultats sont discutés en termes de "réaction chimique", "évaporation" et "retracissement". Aux basses températures (1400-1600°C) la réaction chimique se produit, résultant dans une augmentation de la porosité. Aux moyennes températures (1600-1800°C) la phase liquide se forme dont la

haute tension de vapeur produit une forte perte de poids ainsi qu'une diminution de la densité. Aux hautes températures (au dessus de 1800°C) la grande quantité de liquide qui se produit, ferme les pores ouvertes empêchant l'évaporation. La phase liquide accélère aussi le retracissement des pores et la réaction chimique. On observe un retracissement très faible quand seulement la solution β - Si_3N_4 est frittée.

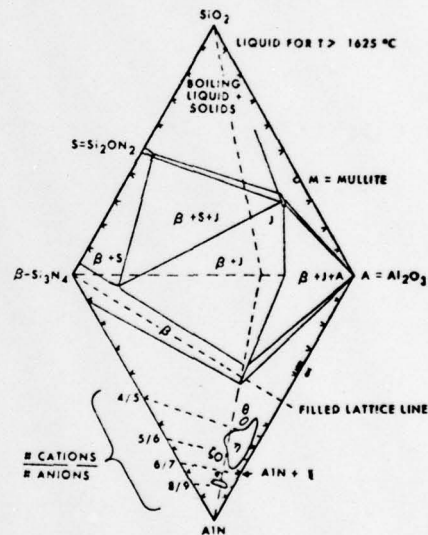
Introduction

Solid solutions formation of β - Si_3N_4 containing metal oxide has been reported in the system Si_3N_4 - Al_2O_3 independently by Oyama and Kamigaito¹ and Jack². Both reported extensive solid solubility of Al_2O_3 in β - Si_3N_4 . In later publications, these authors reported the extent of solid solutions in ternary systems. Jack³ studied the system Si_3N_4 - SiO_2 - Al_2O_3 and Oyama⁴ studied the system Si_3N_4 - Al_2O_3 -AlN. Both of their phase diagrams showed wide ternary solid solution regions.

The solid solution formation of Al_2O_3 in Si_3N_4 requires either non-metal interstitials or metal site vacancies in the β - Si_3N_4 lattice. Oyama⁴ suggested silicon vacancies to explain his results. It was suggested that these lattice defects facilitated ionic diffusion, hence the sintering of these solid solutions became possible.

Gauckler, Lukas and Petzow⁵ re-examined the system Si_3N_4 - Al_2O_3 at 1760°C. They considered that at high temperatures, the reaction $\text{Si}_3\text{N}_4 + 2\text{Al}_2\text{O}_3 \rightarrow 3\text{SiO}_2 + 4\text{AlN}$ may occur. Therefore, the system Si_3N_4 - Al_2O_3 was treated as a quasi-ternary reciprocal salt system Si_3N_4 - SiO_2 -AlN- Al_2O_3 . A representation of multi-component Si_3N_4 -based systems containing metal oxides was given elsewhere⁶.

Gauckler et al.⁵ were not able to repeat the results of Oyama⁴ and Jack³. According to these authors, single phase β - Si_3N_4 solid solution occurs between Si_3N_4 and Al_2O_3 . Instead, single phase solutions were found to be restricted to a very narrow region along the line Si_3N_4 -(AlN: Al_2O_3). The phase diagram is given in Fig. 1. These solid solutions have a fixed metal to non-metal ratio of



A Mole Percent (n/o) Product or Quasi-Equilibrium Phase Diagram of the System

Fig. 2 The system Si_3N_4 - SiO_2 -AlN- Al_2O_3 in mole percent after Land et al.⁸

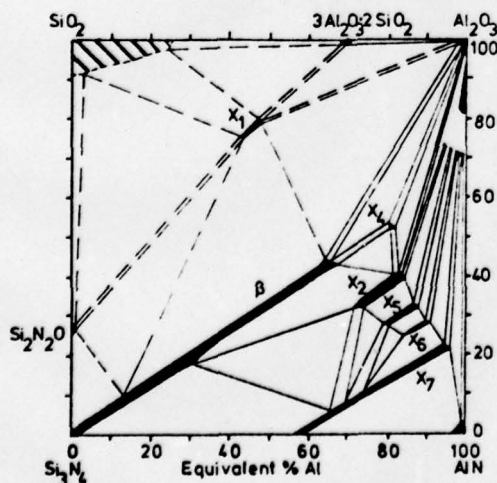


Fig. 1 Isothermal section at 1760°C of the system Si_3N_4 - SiO_2 -AlN- Al_2O_3 in equivalent percent after Gauckler et al.⁵

3:4 and hence do not require the existence of lattice defects. Five new phases were found on the AlN rich side of the system Si_3N_4 - SiO_2 -AlN- Al_2O_3 . All of these solid solutions have fixed metal to non-metal ratios. Between the β - Si_3N_4 solid solution and the SiO_2 corner, at 1760°C, β -phase and a liquid phase are in equilibrium. As the temperature decreases, χ_1 crystallizes.

In a recent review, Jack⁷ revised the phase diagram for the system Si_3N_4 - Al_2O_3 . The diagram was presented as a reciprocal salt system. In general, the diagram agrees with that of Gauckler's as shown in Fig. 1 except that the locations of the AlN rich "polytype phases" are slightly different.

Similar "polytype phases" were also reported by Land et al.⁸ in the system $\text{Si}_3\text{Al/N}_2\text{O}$ (Fig. 2). However, the compositions of these phases are again different from both of those reported by Gauckler et al.⁵ and by Jack⁷.

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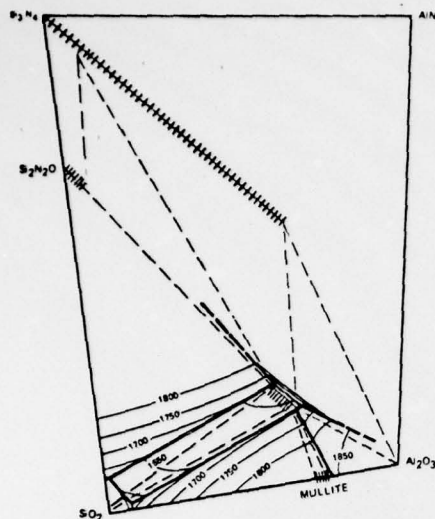


Fig. 3 The system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-AlN-Al}_2\text{O}_3$ in mole percent after Layden⁹.

Liquidus temperatures in part of the system Si,Al/N,O were determined by Layden⁹ using DTA. He found that low melting compositions were located in the SiO_2 corner of the diagram (Fig. 3).

Melting of some compositions in the system Si,Al/N,O has been reported earlier^{9,10}. It was proposed that the presence of liquid phase at high temperatures facilitated densification. Layden⁹ introduced the term "transient liquid phase sintering". It was proposed that initially, a liquid was present which accelerates densification and at the later stage, crystallizes to form single phase dense $\beta\text{-Si}_3\text{N}_4$ ceramics.

The formation of $\beta\text{-Si}_3\text{N}_4$ solid solutions in the system Si,Al/N,O from the starting materials (e.g., $\text{Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3$, etc.) should lower the total free energy by (1) completion of the chemical reaction (2) reduction of the total surface area of the particles. This may result in densification as well. However, a density decrease (or porosity increase) could also be expected depending on the relative density of the reaction product in comparison with the starting materials in the compact.

Because the phase equilibria in the system Si,Al/N,O have been established⁹, one of the $\beta\text{-Si}_3\text{N}_4$ solid solutions was chosen for this study. Compositions $\text{Si}_{6-x}\text{Al}_x\text{O}_4\text{N}_{8-x}$ can be formulated by mixing either Si_3N_4 , AlN and Al_2O_3 powders or Si_3N_4 , AlN and SiO_2 powders. For one particular composition, where $x = 4$, the starting materials can be SiO_2 and AlN only. Different reactions mechanisms would be expected for different sets of starting materials, hence different sintering kinetics. This paper reports the results of reaction

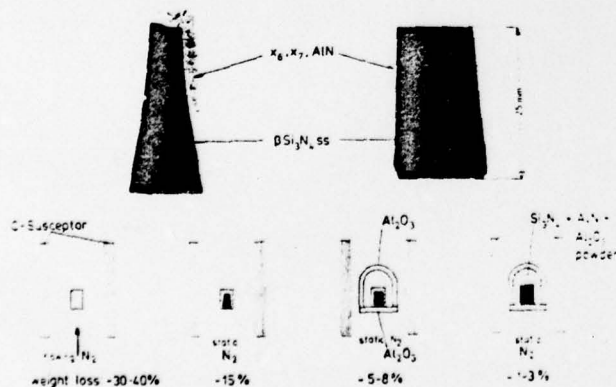


Fig. 4 Experimental arrangement and the sintering results of $\beta\text{-Si}_3\text{N}_4$ solid solution from mixtures of Si_3N_4 , AlN and Al_2O_3 at 1800°C for one hour¹⁰.

Top Left: Sintered in nitrogen atmosphere. The center black core was single phase $\beta\text{-Si}_3\text{N}_4$ solid solution and the skin was identified as a mixture of Si_3N_4 , Al_2O_3 and AlN (see phase diagram in Fig. 1). This result indicates that SiO_2 was lost during firing.

Top Right: The specimen was packed in loose powder of the same composition during firing. Bottom figures show various experimental arrangements. The extreme left was in flowing nitrogen. The second left was fired in static nitrogen and the third was fired in a covered alumina crucible. The extreme right shows the specimen packed in loose powder of the same composition. Weight losses after one hour of heating at 1800°C decreases from left to right.

and densification during sintering of $\beta\text{-Si}_3\text{N}_4$ solid solution using SiO_2 and AlN as starting materials. The sintering behavior using other sets of starting materials will be reported separately. Single phase $\beta\text{-Si}_3\text{N}_4$ solid solution powders were also sintered and the results are reported in this paper.

Experimental

One mole of quartz form of SiO_2 and 2 moles of AlN powders (where $x = 4$ in the formula $\text{Si}_{6-x}\text{Al}_x\text{O}_4\text{N}_{8-x}$, 60 eq. % Al) were mixed in a hard metal mill under fluid. The mixtures were dried and then compacted under an isostatic pressure of 650 MN/m² and were then fired at temperatures from 1400-1950°C for different lengths of time (0-180 minutes). The heating rate of the furnace was about 400°C/minute. The furnace was cooled from 1900°C to 600°C in about 3 minutes.

In the early stage of this investigation, the compacts were heated in a carbon resistance furnace under flowing nitrogen. Later, an induction furnace with graphite susceptor was used. During firing, the samples lost weight and the compacts became porous skeletons of AlN and "AlN-polytype phases". It was found later that heavy weight loss could be prevented by packing the compacts in loose powder of the same composition. The experimental arrangement used for this study are shown in Fig. 4.

Sample weights were measured before and after heating. Apparent porosities of the sintered samples were measured using liquid absorption method. Relative bulk densities were computed from these data. Phases present after heating were detected using x-ray diffraction.

Results and Discussion

Sintering of $\text{SiO}_2\text{-AlN}$ Mixture: Nitrogen concentration of the powder mixture (1 mole of SiO_2 and 2 moles of AlN) after milling was analyzed¹² and was found to be 18.6 wt. %. This figure corresponds to a concentration of 60 eq. % of Al and 48.5 eq. % of oxygen which is slightly above the single phase $\beta\text{-Si}_3\text{N}_4$ solid solution with 60 eq. % of Al in the phase diagram. The correct oxygen content should be 40 eq. %.

For each sintering experiment, a new powder compact was used. The density as a function of time between 1400 and 1950°C is shown in Fig. 5. Density decrease was observed for all specimens in the range from 1400 to 1800°C. Large shrinkage occurred between 1850 and 1950°C.

Weight losses after sintering are shown in Fig. 6. Very low weight loss was observed for those specimens heated at 1400, 1500 and 1600°C. 1700 and 1800°C sintered samples showed higher weight losses. A reduction in weight loss was observed for specimens heated at 1850 and 1900°C. From the weight loss and sintered density results, one can conclude that liquid formation occurred during sintering. Above 1600°C, higher vapor pressure of the liquid re-

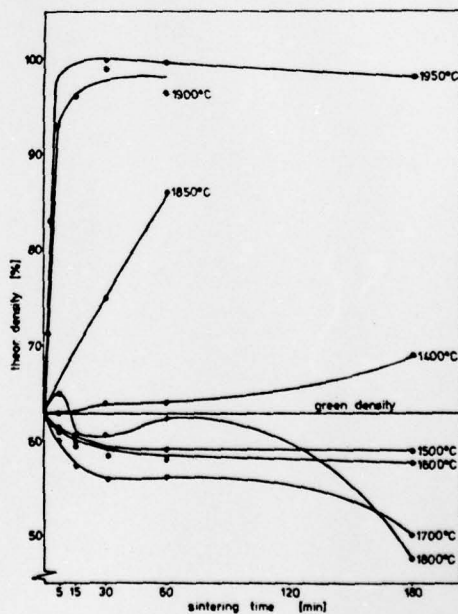


Fig. 5 Isothermal density changes of $\text{SiO}_2\text{-AlN}$ powder compacts after sintering.

sulted in higher weight loss. Above 1600°C, the amount of liquid formed was more in quantity and was enough to seal the pores in the specimen, therefore, reduction in weight loss.

The above results can be substantiated by the microstructures as shown in Fig. 7. Fine grain materials are shown in the samples fired at 1400°C. Open channel structure is present in the 1700°C samples and closed pores only existed in the 1900°C samples. The open channels are responsible for the heavy weight loss in the intermediate temperatures.

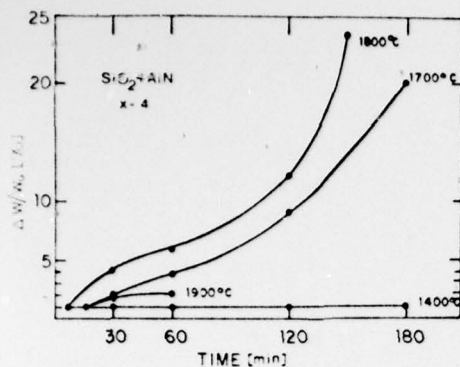


Fig. 6 Isothermal weight losses of $\text{SiO}_2\text{-AlN}$ powder compacts after sintering.

After sintering, part of the specimens were pulverized and the amount of phases present were measured by comparing the intensities of their x-ray diffraction lines with those of a hot pressed single phase material prepared earlier¹¹. Peak heights were used to compare the quantities of phases in the specimens. The results are given in Fig. 8.

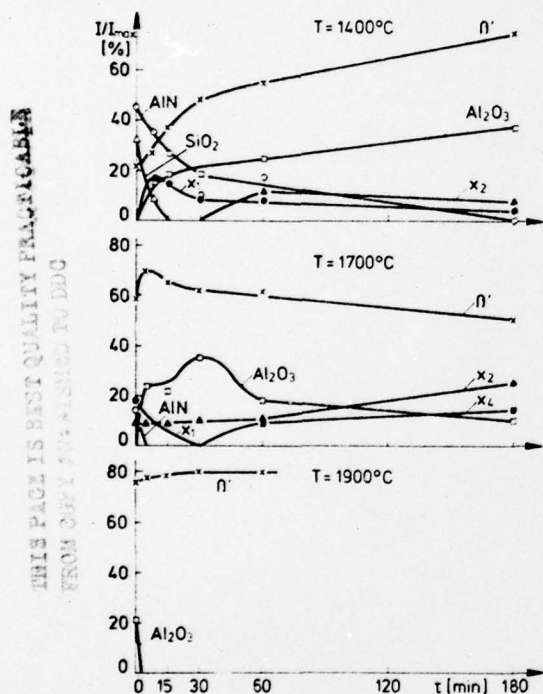


Fig. 8 Phases present after sintering.

The results showed that the reaction $\text{SiO}_2 + 4\text{AlN} \rightleftharpoons \text{Si}_3\text{N}_4 + 2\text{Al}_2\text{O}_3$ took place at the beginning of the process. At 1400°C, the amount of crystalline SiO_2 decreased rapidly and $\beta\text{-Si}_3\text{N}_4$ and Al_2O_3 formed already during heating. Intermediate phases appeared during the reaction. X_1 was observed first and decreased in quantity. X_2 was also observed and persisted until the longest time used in this experiment. In the intermediate temperature range, the 1700°C curve is representative. At shorter times, the reaction was observed to be similar to that at 1400°C. However, after prolonged heating, material loss resulted. The decrease of β -phase and increase of X_2 indicated some oxygen containing components were vaporized. At 1900°C, after 2 minutes of heating only $\beta\text{-Si}_3\text{N}_4$ was observed.

All phases in the system $\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3$ should have been observed during the reaction between SiO_2 and AlN . Probably, because of kinetic reasons, some of the phases were not observed. Low melting liquid ($<1500^\circ\text{C}$) has been observed to exist in the system at about 80 eq. % Si and 80 eq. % O^{12} . Therefore, it is reasonable to assume that all the chemical reactions took place in the liquid state.

Lattice parameters of the $\beta\text{-Si}_3\text{N}_4$ solid solution were measured for samples sintered at different temperatures for different times. The lattice parameters were determined by x-ray diffraction using high angle lines. The results are plotted in Fig. 9 versus time at constant temperatures. The 1500°C curve represents low temperature behavior and the 1900°C curve represents high

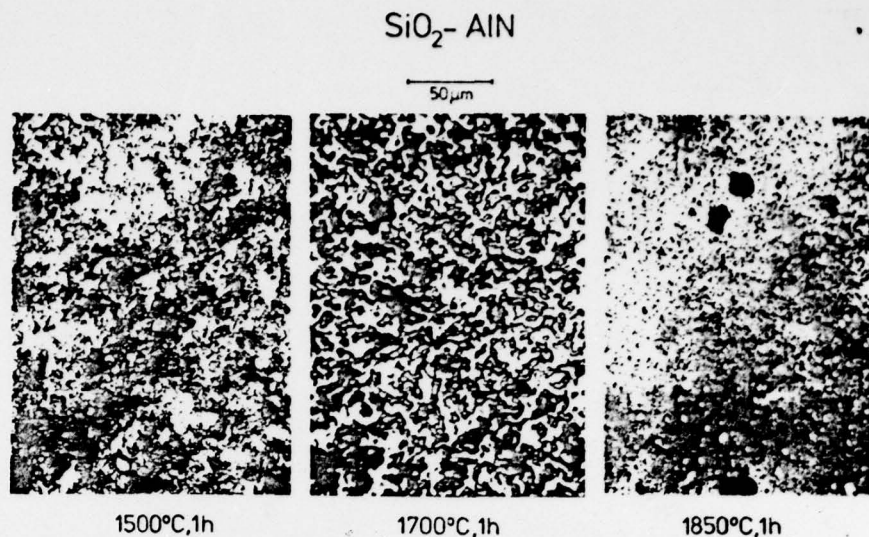


Fig. 7 Microstructure of sintered compacts.

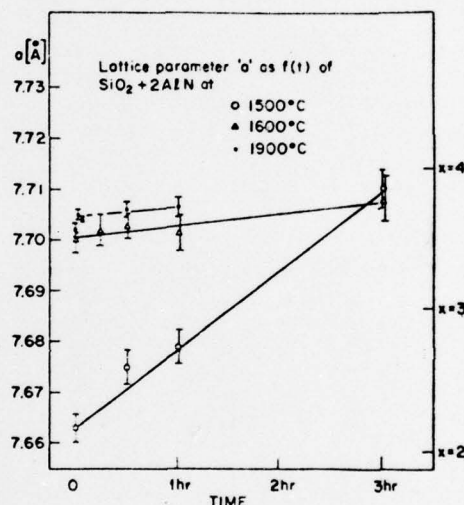


Fig. 9 Change of lattice parameter as a function of sintering time at constant temperature.

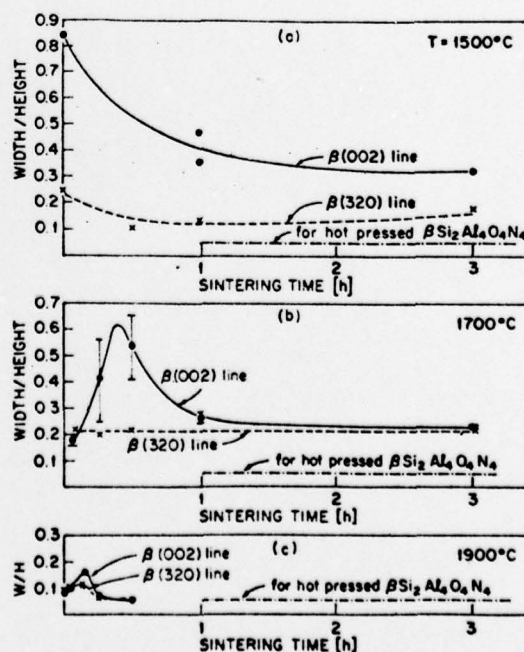


Fig. 10 X-ray diffraction line broadening of the $\beta\text{-Si}_3\text{N}_4$ phase sintered at different temperatures as a function of sintering time. (a) at 1500°C, (b) at 1700°C, (c) at 1900°C

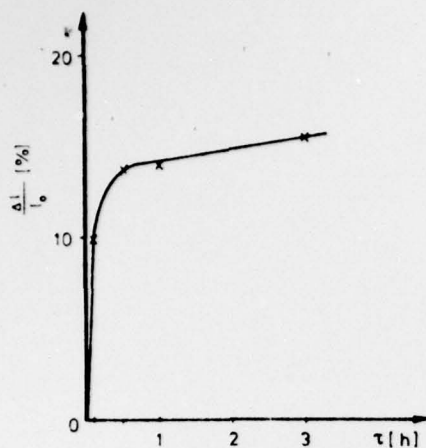


Fig. 11
Firing shrinkage of β -60
compacts sintered at 1950°C
for different length of time.

temperature behaviour. The results showed that the β - Si_3N_4 solid solution formed at the beginning of the reaction contained low aluminium concentration. Higher aluminium concentration solid solutions formed at the later state of the reaction. X values in the formula $\text{Si}_{6-x}\text{Al}_x\text{N}_{8-x}\text{O}_x$ are also plotted.

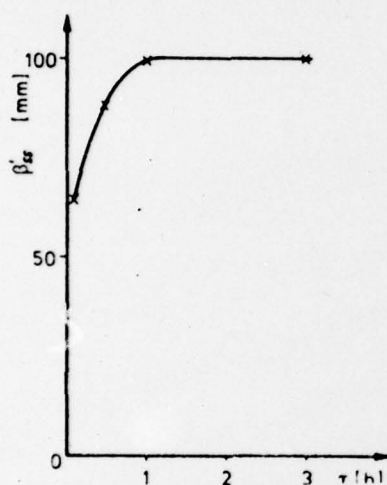


Fig. 12
Relative intensities of β -phase
x-ray peaks for specimens
sintered at 1950°C for differ-
ent length of time.

X-ray diffraction line broadening of β -phase was observed for some of the sintered samples. The line widths and heights were measured for (002) and (320) diffraction lines. The results are plotted in Fig. 10 as width to height ratios vs. sintering time at different temperatures. In general, sharper peaks were observed for the shorter sintering time and broadened for longer time. After pro-

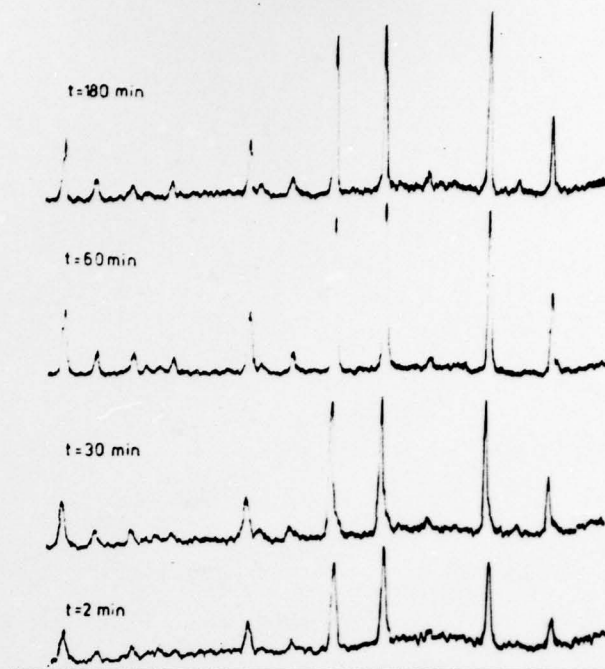
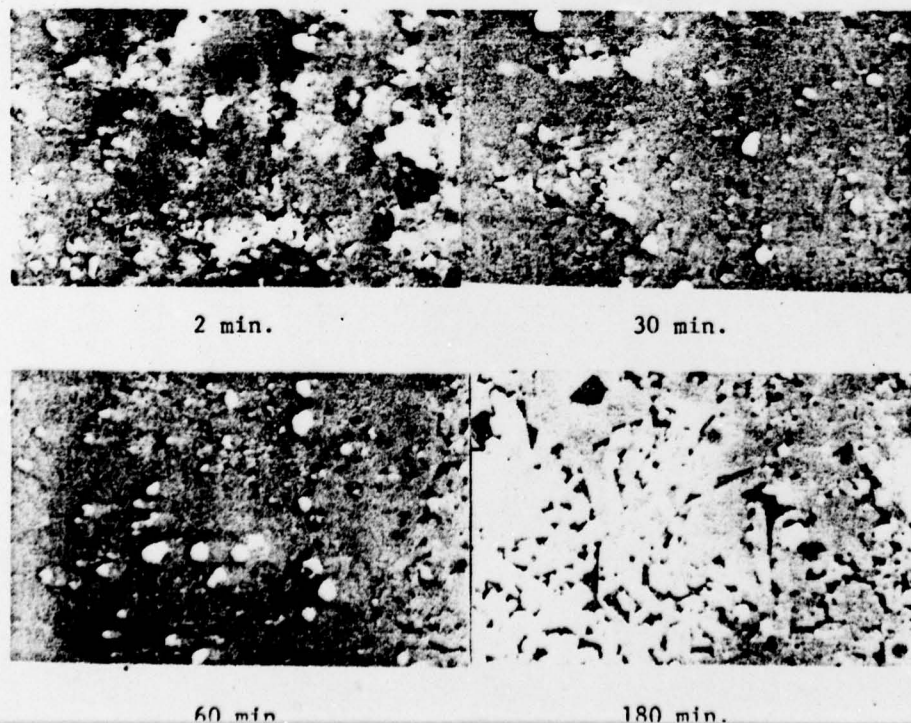


Fig. 13 X-ray diffraction patterns of β -60 composition fired at 1950°C for different length of time.

longed heating, the x-ray diffraction lines became sharp again. The initial broad peaks for the 1500°C sintered samples can be explained as small particle size of β -phase during sintering.

The results shown in Fig. 9 (lattice parameter) and Fig. 10 (line broadening) can be interpreted as homogenization of the β - Si_3N_4 solid solution. In the beginning of the reaction, very fine particles of β - Si_3N_4 containing low aluminium concentration formed. This gives lower lattice parameter value and sharper diffraction lines. Solid solution of different aluminium concentration formed later during the reaction and deposited on the already formed β - Si_3N_4 surface. This will give a broader diffraction and peak at a lower diffraction angle. Sample heated for 3 hours showed lower diffraction angle and sharper diffraction lines. This indicates homogenization of the solid solution grains.

The homogenization within each grain should be the result of diffusion in the solid state through the β - Si_3N_4 solid solution lattice. However, in diffusion couple experiments¹³ no measurable homogenization could be observed when different aluminium containing β - Si_3N_4 solid solution slabs were fused together and heated for one hour at 1800°C. These results seem to be in conflict with the sintering results.



Glass Formation in the System $\text{Si}_3\text{Al/N}_2\text{O}$: The SiO_2 - AlN mixture was heated at 1950°C in the graphite furnace with a heating rate of 200 K/min for various lengths of time. The linear shrinkage versus heating time are plotted in Fig. 11. Relative intensities of the x-ray diffraction lines of the β -phase are plotted in Fig. 12. No other crystalline phase present in the specimens was observed after cooling. The relative amount of β -phase estimated from the x-ray intensity data were about 65, 75, 85 and 95 percent for 2, 30, 60 and 180 minute fired samples, respectively.

The x-ray diffraction traces of these specimens are given in Fig. 13. Note the higher background of the base line at low diffraction angles. The high background indicated the presence of glass in the sample. Microstructures of these specimens are shown in Fig. 14. Quantitative metallographic analysis confirmed the amount of crystalline material present as obtained by x-ray diffraction analysis. From this data, one can estimate the composition of the glass. For instance, the 2 minute heat treated sample has a lattice parameter corresponding to $x = 2.18$. Using the lever rule, the composition of the liquid will be close to that of X_4 on the phase diagram.

Fig. 14 Photomicrograph of specimens sintered
at 1950°C for different lengths of time.

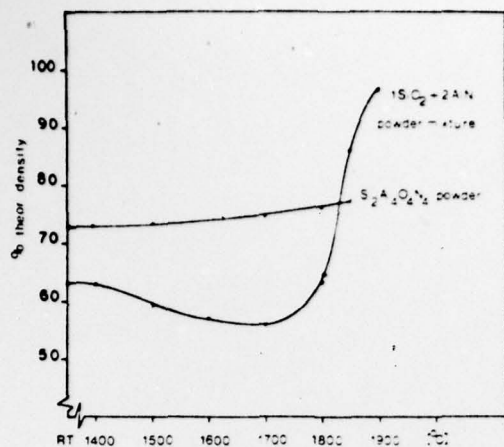


Fig. 15 Bulk densities of various powder mixtures after 1 hour sintering at different temperatures.

Grain growth was observed in these samples as shown in Fig. 14. The crystals in these mixtures are β - Si_3N_4 solid solution, therefore, one can conclude that nitrogen species diffuse through the liquid, hence the glass should be a nitrogen containing glass.

The slope change in the time dependence of the shrinkage curve (Fig. 11) can be interpreted as "melting" and "crystallization" for the two distinctively separated regions. In the initial stage, the sharp volume changes are due to melting and pore removal. The slight increase in shrinkage in the later stage is the result of crystallization of β -phase from the liquid, since the density of the crystalline phase usually has a higher density than the liquid of the same composition.

Sintering of Single Phase β - Si_3N_4 Solid Solution Powder: Hot pressed β - Si_3N_4 solid solution having the same composition as the SiO_2 -AlN mixture ($x = 4$) was pulverized and compacted. The x-ray diffraction pattern showed the hot pressed material is a well crystallized single phase β - Si_3N_4 solid solution. The compacts were heat treated for one hour at different temperatures. The fired densities are plotted in Fig. 15. There is a slight density increase when the specimen was heated at high temperatures. Density changes of pure Si_3N_4 compacts are also shown in the same figure for comparison. The pure Si_3N_4 compact did not densify at all. However, it is not conclusive whether the densification of the single phase solid solution is the result of solid diffusion. The possibility of the presence of liquid at that temperature cannot be ruled out. The densification curve for the SiO_2 -AlN mixture is replotted in the same figure for specimens heated for one hour at different temperatures.

Conclusion

The sintering behaviour of SiO_2 -AlN mixture can be discussed on the basis of "chemical reaction", "vaporization" and "densification". The moderate density decrease at low temperatures (1400–1600°C) is due to "chemical reaction". Because there was no sample shrinkage and the reaction products have higher densities than the starting materials, the apparent density decreased. At intermediate temperatures (1600–1800°C), small amounts of liquid formed and located at the open channels in the specimen. The vapor pressure at these temperatures becomes high and heavy weight loss resulted, hence low sintered densities. At high temperatures (>1800°C), large amounts of liquid formed, sealing open pores. This reduction of the total liquid surface area results in lower weight loss and higher sintered density. At the same time, large amounts of liquid enhanced densification and facilitated chemical reaction. At high temperatures (1800°C and above), crystalline β -phase and liquid only existed and the amount and composition of β increased with time. It is reasonable to conclude that the composition of liquid changed with time too. These results supported the concept "transient liquid phase sintering" proposed by Layden⁹. This is very reasonable because for this composition liquid should be one of the intermediate phases during reaction.

Acknowledgment

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Reaction Sintering Forming β - Si_3N_4 Solid Solutions in the System Si, Al/N, O

II. Sintering of Si_3N_4 - SiO_2 - AlN Mixtures

S. BOSKOVIC*, L. J. GAUCKLER**, G. PETZOW*** and T. Y. TIEN**

Abstract

Reaction sintering of β - Si_3N_4 solid solution containing 30, 50 and 60 equivalent percent of aluminium in the system Si, Al/N, O was investigated. The starting materials for this study were α - Si_3N_4 , AlN and quartz form of SiO_2 . Specimens of compositions could be densified

Herstellung von β - Si_3N_4 Mischkristallen durch Reaktionssintern

Es wurde das Reaktionssintern von β - Si_3N_4 Mischkristallen mit 30, 50 und 60 Äquivalentprozent Aluminium im System Si, Al/N, O untersucht. Die Ausgangsmaterialien für diese Arbeit waren α - Si_3N_4 , AlN und SiO_2 in Quarzform. Proben aller drei Zusammensetzungen

Production de solutions solides de β - Si_3N_4 par frittage avec réaction.

Le présent rapport décrit le frittage par réaction des solutions de β - Si_3N_4 contenant 30, 50 et 60% d'aluminium dans le système Si, Al/N, O. Les mélanges de poudre utilisés pour ce travail consistaient de α - Si_3N_4 , AlN et de SiO_2 sous forme de quartz. Les spécimens des

via transient liquid phase sintering to densities greater than 96% of theoretical density. Increasing amounts of α - Si_3N_4 in the starting materials reduced weight losses to less than 2 wt.-% for one hour sintering time.

konnten durch Reaktionssintern mit temporär auftretender Schmelzphase auf über 96% der theoretischen Dichte verdichtet werden. Werkstücke mit hohem α - Si_3N_4 -Gehalt im Ausgangspulver zeigten nur noch geringe Gewichtsverluste (< 2 Gew.-%) nach einer Stunde Sinterzeit.

trois compositions ont pu être densifiées à plus de 96% de la densité théorique par frittage avec réaction en phase liquide. Les poudres contenant beaucoup de Si_3N_4 ne montraient que peu de perte de poids (< 2%) après une heure de frittage.

Introduction

In a previous paper¹, we have reported that high density β - Si_3N_4 solid solution ceramics (having a formula β - $\text{Si}_{6-x}\text{Al}_x\text{O}_4\text{N}_{8-x}$, where $x = 4$) could be obtained by reaction sintering without applied pressure. The starting materials used for that experiment were one mole of SiO_2 and two moles of AlN. The results indicated that densification and chemical reaction took place in the presence of liquid. The liquid was formed in the beginning of the reaction and the composition of this liquid was rich in SiO_2 . The β - Si_3N_4 solid solution grains were formed by double exchange reaction between the SiO_2 rich liquid and AlN crystals. In the meantime, the powder compact densified when the amount of the liquid was sufficient. At the end of the reaction the liquid was consumed. It has been shown by Gauckler et al.³ that the mechanical properties of the β - $\text{Si}_{6-x}\text{Al}_x\text{O}_4\text{N}_{8-x}$ ceramics with lower x values are superior to those of the higher x values. This investigation was designed to test if additional Si_3N_4 can be dissolved in a SiO_2 -AlN mixture forming β - Si_3N_4 solid solution ceramics with lower x values.

The compositions studied were $\beta 30$ and $\beta 50$ ($x = 2.18$ and $x = 3.14$ respectively when $x = 4$, i. e., $\beta 60$). These compositions can be regarded as $\beta 60$ plus various amounts of Si_3N_4 .

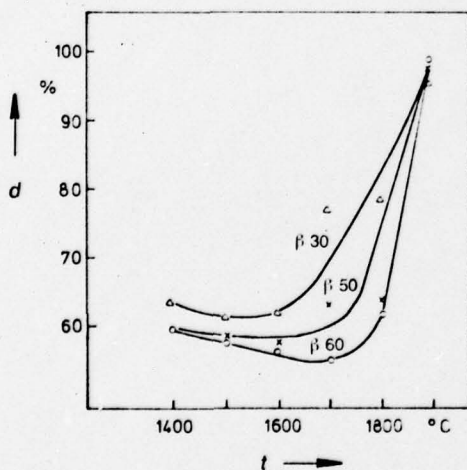


Fig. 1 Relative apparent density d of specimen sintered for 1 h at different temperatures t

$$d = \frac{\rho_R}{\sum f_i \rho_i}$$

- d $\triangleq$ apparent density related to theoretical density TD
 ρ_R $\triangleq$ bulk density of specimen
 f_i $\triangleq$ the amount of each phase
 ρ_i $\triangleq$ the true density of each phase

Experimental

Appropriate amounts of Si_3N_4 , SiO_2 and AlN powders were blended in a hard metal mill under alcohol for one hour. The characteristics of the chemicals are given in Table 1. The mixtures were dried and compacted under an isostatic pressure of 650 MN/m². The pressed compacts were packed in powders of the

same composition in BN lined graphite crucibles and were sintered in a carbon resistance furnace for one hour at temperatures from 1400 to 1900°C. Sintered densities, weight losses and phases present were determined after each heat treatment.

Table 1 Starting Materials

Chemicals	Surface area (BET)	Particle size	Oxygen	Nitrogen
SiO_2^*	—	5.2 μm	—	—
AlN	2.0 m ² /g	2.5 μm	1.4 wt%	32.1 wt%
Si_3N_4	9.0 m ² /g	—	2.5 wt%	27.0 wt%

* SiO_2 is in quartz form, before using, it was ground for 4 h in an agate planetary ball mill.

Results and Discussion

Relative apparent densities after sintering at different temperatures are given in Fig. 1. For comparison, the results for $\beta 60$ from the previous paper¹ are also plotted in this figure. These results showed that high density β - Si_3N_4 solid solution ceramics containing 30 and 50 equivalent percent of aluminium ($\beta 30$ and $\beta 50$ respectively) could be obtained by reaction sintering without applied pressure. As shown in Fig. 1, the sintered density of $\beta 30$ ceramics is higher than that of $\beta 50$, and $\beta 50$ is higher than that of $\beta 60$ for the same heat treatment. At the highest temperature used in this experiment, 100% dense ceramics were obtained for all compositions studied.

Weight losses after sintering are given in Fig. 2. From these data, one can conclude that the densification of these mixtures is closely related to their weight losses. One can consider there are two competing processes during sintering: Vaporization and liquid phase sintering. The reaction steps should have been as follows: 1) SiO_2 and AlN react to form SiO_2 rich liquid, 2) liquid reacts with AlN and Si_3N_4 and 3) β - Si_3N_4 solid solutions precipitate. Densification can only be accomplished when vaporization is low and the amount of liquid is sufficient. This is clearly demonstrated when Fig. 1 and 2 are compared.

The phases present after sintering are given in Fig. 3. The phase x_1 , appeared in some of the specimens after sintering. As shown by Naik et al.², the pre-

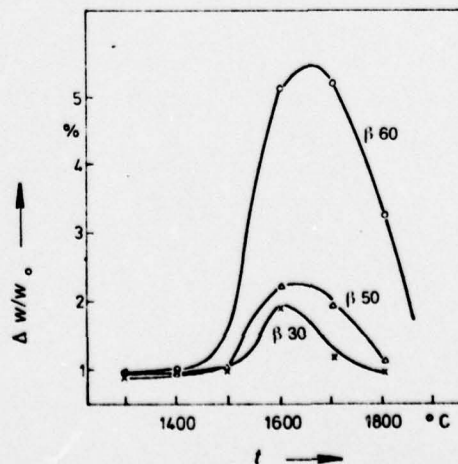


Fig. 2 Weight losses of specimens $\Delta w/w_0$ sintered for one hour at different temperatures t

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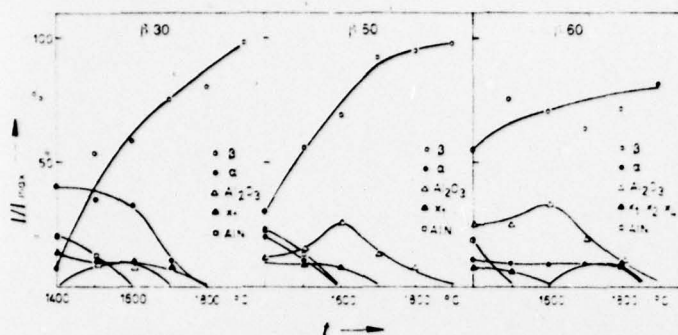


Fig. 3 Quantities of phases $wt\%$, as determined by x-ray diffraction. Specimens were sintered for one hour at different temperatures t

sence of x_1 indicates that the β - Si_3N_4 solid solution was not in equilibrium with the SiO_2 rich liquid at temperatures below $1700^\circ C$. The SiO_2 rich liquid should have been the first phase appearing during reaction. Naik et al.² also showed that the SiO_2 rich liquids were less stable than those of the Al_2O_3 rich liquids. At

higher temperatures, more aluminium oxide and nitride dissolved in the liquid and became more stable. This may explain the high weight losses and low densities for specimens sintered at temperatures of 1600 and $1700^\circ C$.

The higher the SiO_2 content in the starting mixture (in the SiO_2 , Si_3N_4 , AlN series), the larger the quantities of SiO_2 rich liquid which will be formed upon heating. Therefore, higher weight losses will be observed. This explains the higher weight losses observed for the $\beta 60$ versus $\beta 50$ and $\beta 50$ versus $\beta 30$. Work is in progress at the present time to measure the vapor pressure at different temperatures for different powder mixtures giving the same final composition. After this, it is possible that a better understanding can be obtained.

Acknowledgement

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Reaction Sintering Forming β - Si_3N_4 Solid Solutions
in the System Si,Al/N,O

III. Sintering of Si_3N_4 , AlN , Al_2O_3 Mixtures

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2

During the course of reaction sintering studies of the $\beta\text{-Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$ solid solutions (1,2,3), we have observed drastic differences in densification behaviors when different chemicals were used as starting materials. However, detailed mechanisms for the chemical reaction and densification are still not understood. It is felt that further studies are warranted. In this paper, we deal with only one composition-- $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$. The reaction sintering of the same composition has been reported previously (2). In the previous paper (2), the starting materials used were a mixture of SiO_2 and AlN . The same composition can also be prepared by using a mixture of Si_3N_4 , AlN and Al_2O_3 .

The results obtained from the reaction sintering of SiO_2 and AlN mixture indicated that densification and chemical reaction took place in the presence of liquid. The liquid was formed in the beginning of the reaction and the composition of this liquid is rich in SiO_2 (4). $\beta\text{-Si}_3\text{N}_4$ solid solutions were formed by double exchange reaction between the liquid and AlN crystals. In the meantime, the powder compacts densified.

It has been shown by Naik et al. (4) that the lowest melting liquid in the system Si,Al/N,O is located at the SiO_2 corner containing 10 eq.% of aluminum and 10 eq.% of nitrogen. This composition lies on the line connecting the SiO_2 and AlN corners in the phase diagram (5). During the reaction of SiO_2 with AlN , this low melting liquid must have been the first phase formed. As shown by Naik et al. (4), this composition melts at a temperature about 1400°C . This liquid region is being separated from

the β phase below 1700°C by the tie line $\text{Si}_2\text{N}_2\text{O} - \text{X}_1$. Two isothermal planes of the Si,Al/N,O diagram are shown in Figure 1.

At temperatures above 1700°C, X_1 melted and the liquid dissolved more AlN and became aluminum rich and the join $\text{X}_1 - \text{Si}_2\text{N}_2\text{O}$ disappeared. These aluminum rich liquids are then at equilibrium with the β phase.

Naik et al. (4) have shown that the weight loss for SiO_2 rich liquids was much higher than that of the aluminum rich liquids at all temperatures. The formation of the SiO_2 rich liquids must have been the cause of the heavy weight losses and low sintered densities of some of the SiO_2 , AlN mixtures.

The composition, $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ blended by mixing Si_3N_4 , AlN and Al_2O_3 should not form the low melting liquid upon heating, until the temperature reaches slightly below 1700°C. Therefore, one would expect that the reaction sintering behavior of the mixture Si_3N_4 , AlN and Al_2O_3 would be different from that of the mixture SiO_2 and AlN. The weight loss for the Si_3N_4 , AlN, Al_2O_3 mixture should be lower than that of SiO_2 and AlN mixture because the SiO_2 rich liquid is not in the triangle formed by these three chemicals. This experiment was designed to test this postulation.

Appropriate amounts of Si_3N_4 , AlN and Al_2O_3 powders giving composition $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ were blended in a hard metal mill under alcohol for one hour. The characteristics of these chemicals

are given in the footnote. The mixture was dried and compacted under an isostatic pressure of 650 MN/m^2 . The pressed compacts were packed in powders of the same composition in alumina crucibles and were sintered in a graphite resistance furnace at 1400 to 1900°C for various lengths of time. Sintered densities, weight losses and phases present were determined after each heat treatment. The detailed experimental procedures can be found in reference 2.

Relative apparent densities of specimens sintered at different temperatures for different lengths of time are given in Figure 2. The specimens sintered at 1400 to 1600°C showed very little or no densification. Densification began at 1700°C and rapid reaction and densification were observed for specimens heated at 1900°C.

Phases present at different stages of sintering were analyzed and the results are given in Figure 3. These curves show that very little or no reaction occurred at 1500°C, and reaction began at 1600°C. These results should be compared with that of the reaction sintering of the mixture $\text{SiO}_2\text{-AlN}$. For the $\text{SiO}_2\text{-AlN}$ mixture, the reaction already began at 1400°C.

<u>Sample</u>	<u>Specific Surface Area (m^2g^{-1})</u>	<u>Mean Particle Size</u>	<u>Content (wt.%)</u>	
			<u>O₂</u>	<u>N₂</u>
AlN	2.0	2.5	1.4	32.1
$\alpha\text{-Si}_3\text{N}_4$	9.0	--	2.5	27.0
$\alpha\text{-Al}_2\text{O}_3$	7.8	0.5	--	--

Lattice parameters of the β -phase formed at different temperatures and time were measured. No noticeable lattice parameter change was observed for specimens sintered at temperatures above 1700°C. Specimens sintered at 1600°C showed that the β -phase contained lower concentrations of aluminum in the lattice.

The weight losses after sintering were measured and the results are given in Figure 4. The weight losses were very low compared with our previous results (2).

Bulk densities of specimens sintered for one hour at different temperatures for the same composition using different starting chemicals are striking. Pre-reacted $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ did not densify at all. Densification was observed above 1800°C for SiO_2 and AlN mixture. For the specimens using Si_3N_4 , AlN and Al_2O_3 as starting materials, noticeable densification was observed at 1700°C.

The lack of low melting SiO_2 rich liquid may have been the major cause of this difference in sintering behavior. The low melting SiO_2 rich liquid could only form from the surface oxygen on the Si_3N_4 particles. The low melting liquid could have vaporized before the chemical reaction proceeded further. The presence of X_2 and the absence of X_1 confirmed the vaporization of the high SiO_2 containing liquid. This may have been beneficial because the liquid formed at higher temperatures at the later stage should contain more alumina which is more stable.

Specimens sintered at 1600°C showed that the chemical reaction had already begun, even though no densification was

observed. The decreasing amount of individual starting chemicals should be discussed separately. AlN crystals were consumed to react with the surface SiO_2 layer on the Si_3N_4 crystals to form liquid. At the same time, $\alpha\text{-Si}_3\text{N}_4$ converted to $\beta\text{-Si}_3\text{N}_4$ in the presence of the low melting liquid. $\text{Si}_2\text{N}_2\text{O}$ was never formed (as shown by the x-ray data because of the kinetic reaction, therefore, the tie line between X_1 and $\text{Si}_2\text{N}_2\text{O}$ did not exist. The formation of X_2 could be interpreted as an intermediate phase formed between AlN and the liquid.

At 1700°C and above, Si_3N_4 and Al_2O_3 contact points start to melt giving aluminum rich liquid and β solid solution. Further reaction between the liquid and AlN would have resulted in the β formation. This could explain the rapid densification at temperatures as low as 1700°C . Since the liquid formed contains more aluminum, the weight loss was low and the liquid formed helped the densification.

Acknowledgement

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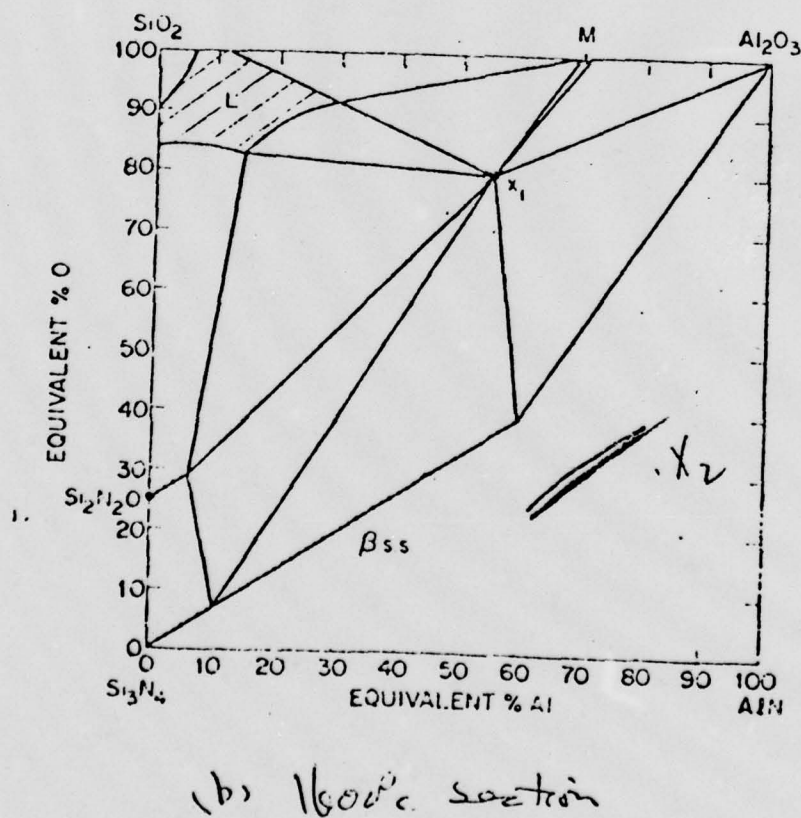
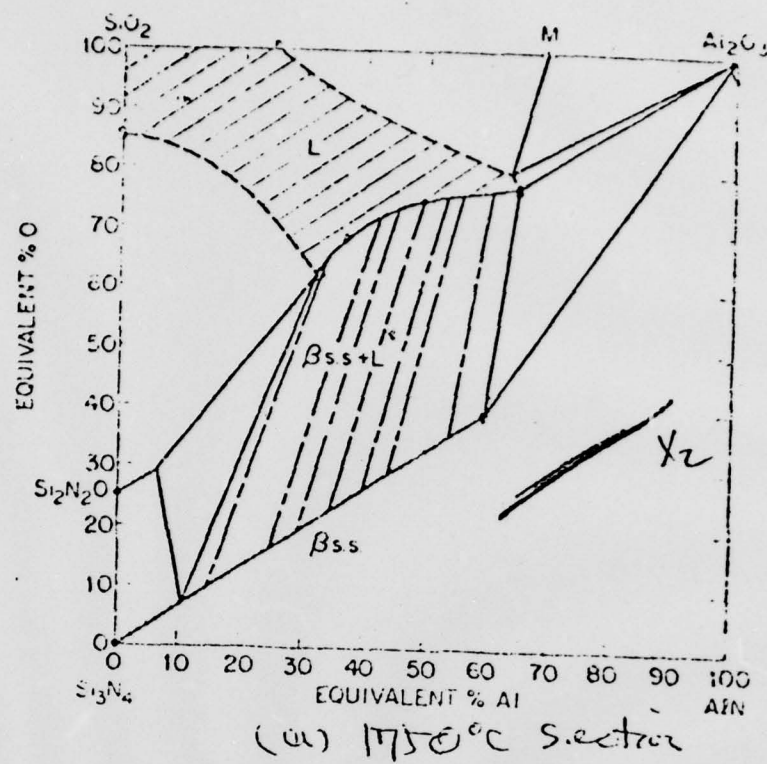


Fig. 1. Isothermal Sections of the System $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-AlN-Al}_2\text{O}_3$.
After Naik et. al. (4).

and the skin was identified as a mixture of X_1 , X_2 , and AlN (see phase diagram in Fig. 1). This result indicates that SiO_2 was lost during firing.

Top Right: The specimen was packed in loose powder of the same composition during firing.

Bottom figures show various experimental arrangements. The extreme left was in flowing nitrogen. The second left was fired in static nitrogen and the third was fired in a covered alumina crucible. The extreme right shows the specimen packed in loose powder of the same composition. Weight losses after one hour of heating at $1800^\circ C$ decreases from left to right.

reduction in weight loss.

The above results can be substantiated by the microstructures as shown in Fig. 7. Fine grain materials are shown in the samples fired at $1400^\circ C$. Open channel structure is present in the $1700^\circ C$ samples and closed pores only existed in the $1900^\circ C$ samples. The open channels are responsible for the heavy weight loss in the intermediate temperatures.

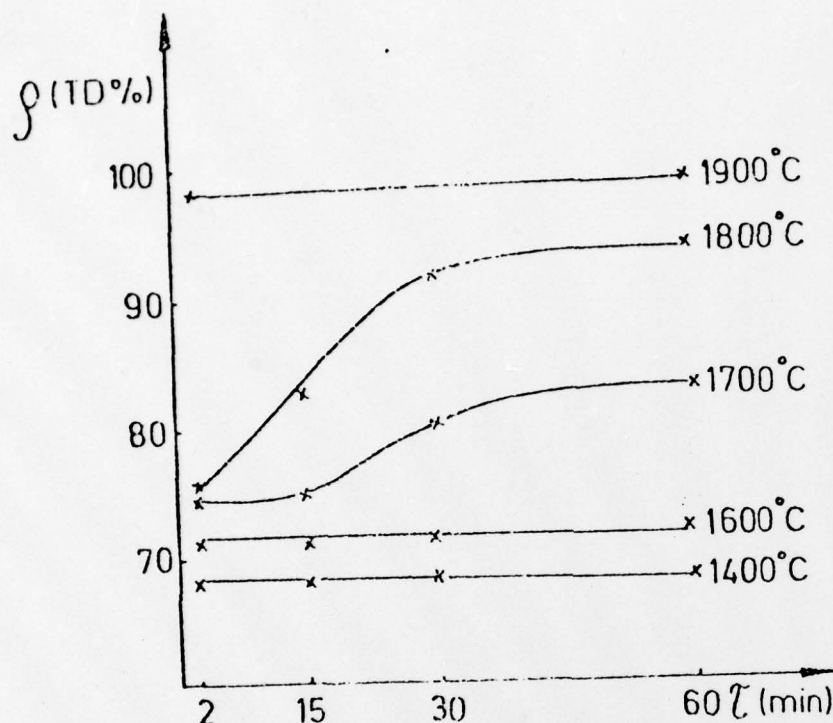


Figure 2. Relative Apparent Densities of Specimens Sintered for one hour at Different Temperatures.

$$\text{Relative Apparent Density} = \frac{\text{Bulk Density of Specimen}}{\sum (f_i) (\text{sp.gr.}_i)}$$

Where f_i is the amount of each phase, and
 'sp.gr._i is the true density of each phase.

The amounts of phases were determined by x-ray diffraction as shown in Fig. 3.

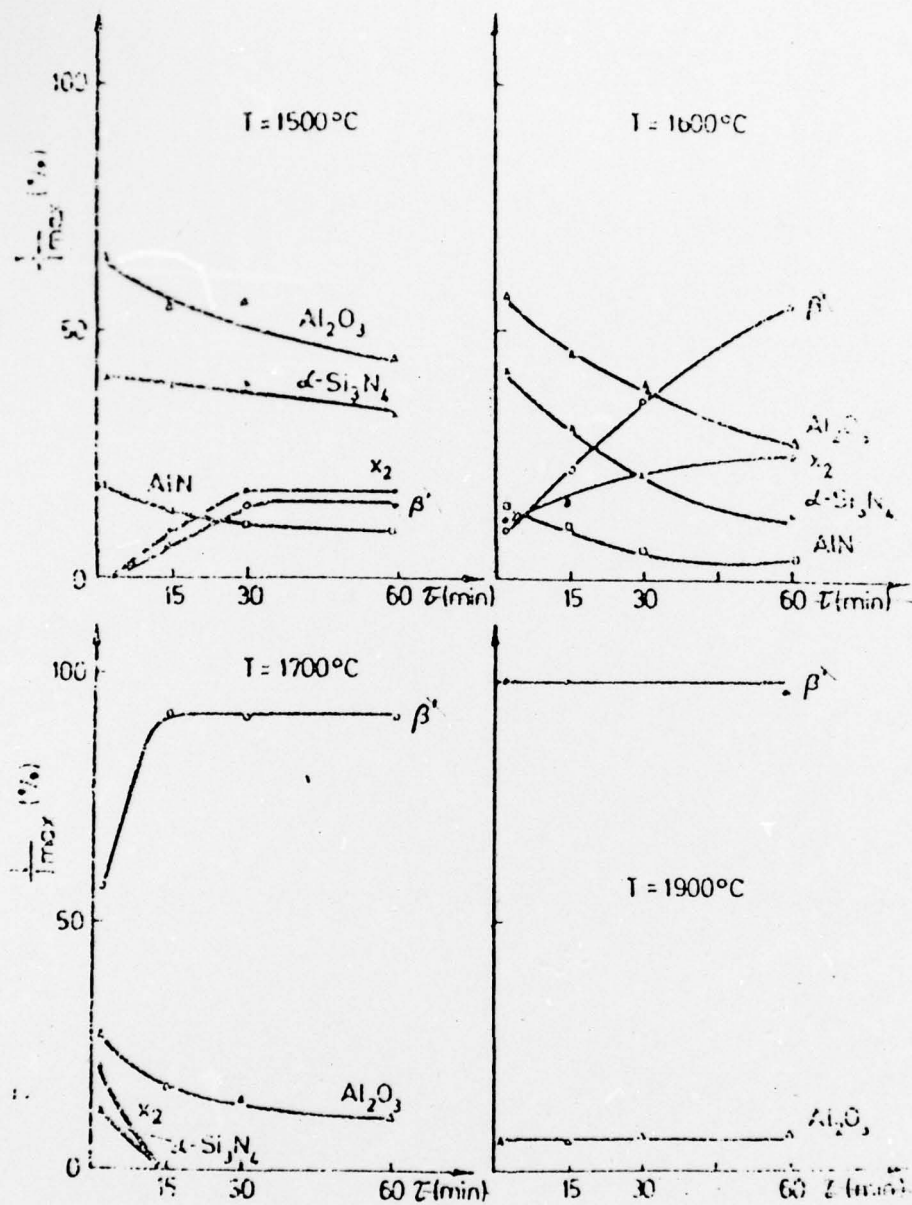


Fig. 2. Phases present in sintered specimens.

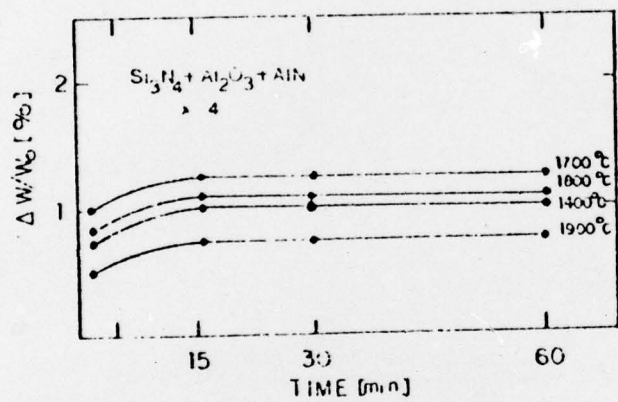


Fig. 4. Weight losses after sintering.

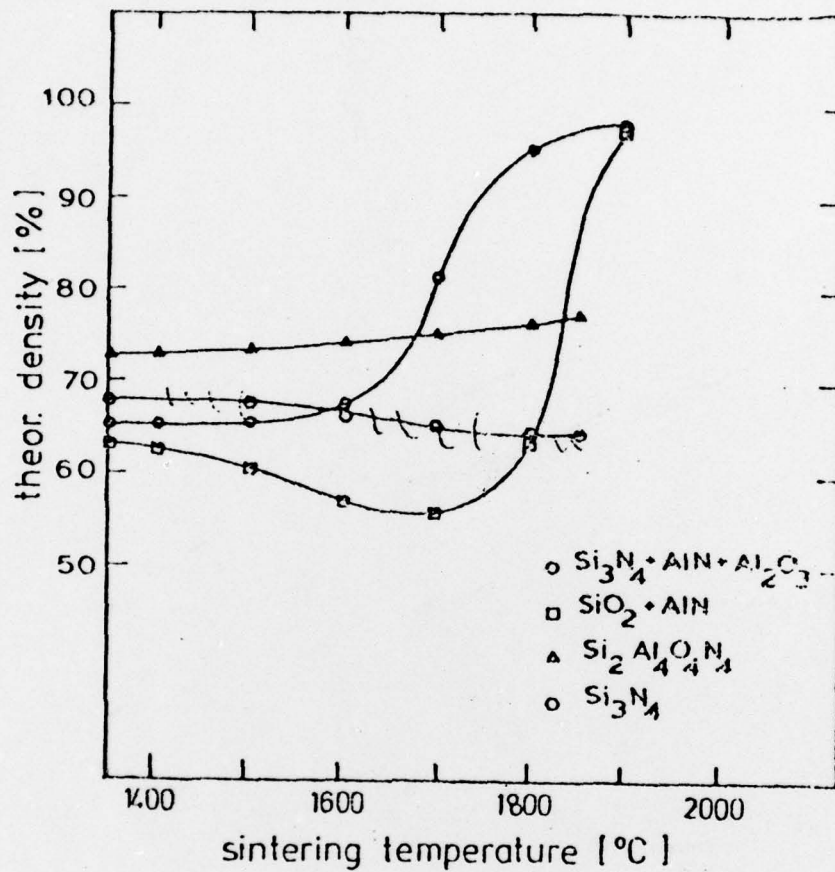


Fig. 5. Bulk densities of specimens after sintering for one hour at different temperatures. The specimens were prepared using different starting materials.

SUBSOLIDUS PHASE RELATIONSHIPS IN PART OF THE SYSTEM Si,Al,Y/N,O

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Various metal oxides such as Al_2O_3 , Y_2O_3 and MgO have been shown to be useful densifying aids in fabricating high-density ceramics from Si_3N_4 powder. It is necessary to know the phase equilibria in these Si_3N_4 -metal oxide systems to understand the densification process and to get structurally well-characterized nitrogen ceramics which would give predictable and reproducible properties. For treating phase equilibria, the reciprocal systems can be represented in terms of the constituent elements as $\text{Si}, \text{M}/\text{N}, \text{O}$ where M is a metal such as Al, Y and Mg.

Subsolidus phase equilibria in the $\text{Si}, \text{Al}/\text{N}, \text{O}$ and $\text{Si}, \text{Y}/\text{N}, \text{O}$ systems have been studied in detail (1-4). Solid-liquid equilibria at 1750°C in the $\text{Si}, \text{Al}/\text{N}, \text{O}$ system have also been reported (5). The combination of these two systems gives a quasi-quaternary system $\text{Si}, \text{Al}, \text{Y}/\text{N}, \text{O}$. The study of phase equilibria in the $\text{Si}, \text{Al}, \text{Y}/\text{N}, \text{O}$ system is necessary to understand the effects of Al_2O_3 and Y_2O_3 used together as the densifying aids.

The starting powders used were aluminum nitride,[†] silicon nitride,[‡] alumina,[§] silica^{††} and yttria^{‡‡}. The oxygen contents of the nitrides were taken into account in making up the compositions. The compositions investigated were restricted to the region bounded by the points Si_3N_4 , AlN , Al_2O_3 , SiO_2 and Y_2O_3 in Fig. 1, because it was difficult to obtain and maintain yttrium nitride in a chemically well-characterized condition.

[†] HCST No. 2633, combined oxygen = 2.9%, H. C. Starck, Berlin, W. Germany.

[‡] Controlled phase 85; $\alpha\text{-Si}_3\text{N}_4$ = 85%; $\beta\text{-Si}_3\text{N}_4$ = 12%; combined oxygen = 1.8%; Kawecki-Beryleo Industries, Reading, Pennsylvania.

[§] Linde A or calcined alumina A-16; >99.5% Al_2O_3 ; Aluminum Company of America, Pittsburgh, Pennsylvania.

^{††} Flint #25; >99.5% SiO_2 ; Rovin Ceramics, Dearborn Heights, Michigan.

^{‡‡} Molycorp No. 5600 yttrium oxide, 99.9% pure.

The selected compositions were made by mixing the requisite amounts of the starting powders in polyethylene bottles using tungsten carbide balls and high purity methanol as the mixing media. The mixtures were dried in shallow glass discs over a laboratory heater and then cold-pressed into 3.3 cm diameter x 1.3 cm thickness pellets at 110 MPa. The pellets were placed in screw-top graphite crucibles which were lined with boron nitride to avoid direct contact between the pellets and the graphite crucibles. The graphite crucibles were placed in a large resistance-heated furnace that used a graphite heating element. Firing of the specimens at 1550°C was carried out in nitrogen at atmospheric pressure. The heating rate was 200°C/min and the holding time at 1550°C was 1 hr. The specimens were cooled in the furnace at a rate of about 200°C/min to 800°C. Further cooling to room temperature was somewhat slower. Samples with less than 2% weight loss upon firing were considered for deriving the phase relationships.

Selected specimens, some of which showed continued presence of $\alpha\text{-Si}_3\text{N}_4$ after first firing, were ground and refired to obtain equilibrium phase assemblages. Equilibrium was assumed to have been attained when the number and type of phases did not change with increased firing time or upon grinding and refiring. This procedure indicated that when the amount of silicon nitride in the overall composition was less than 60 wt.%, equilibrium was readily obtained in the first firing. This was also the case when some liquid (> about 10%) was formed in the samples at the firing temperature.

About 50 compositions were fired at 1550°C to obtain the phase relationships. The compositions that contained substantial amounts of glass after firing were annealed at 1150 to 1250°C for extended time (about 24 hours) to

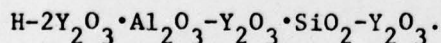
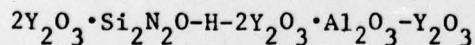
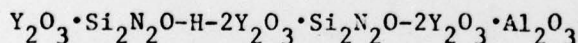
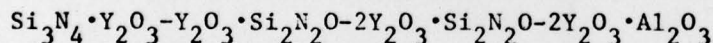
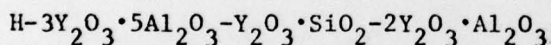
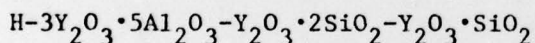
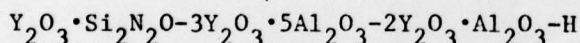
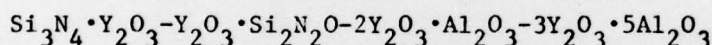
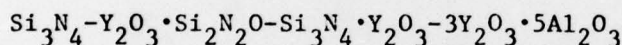
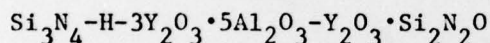
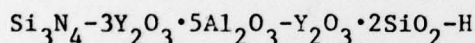
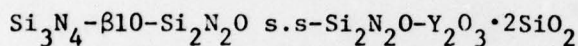
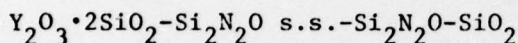
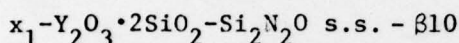
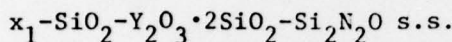
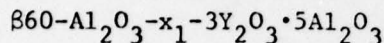
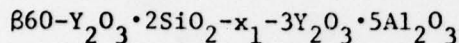
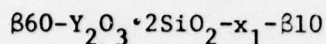
devitrify the glass. Subsolidus phase relationships in the region that is liquid at 1550°C were obtained by this devitrification treatment.

The fired specimens were examined by x-ray diffractometry and optical microscopy to determine the number and type of phases present. An automatic recording diffractometer with monochromated CuK_α radiation was used to scan the powdered samples between 10 and 80° 2 θ at a rate of 2°/minute. Standard optical microscopy was used for microstructure observation. The compositions made, heat treatment used and the phases observed are listed in Table 1*.

The quasi-quaternary system Si,Al,Y/N,O has three independent composition variables. Therefore, the subsolidus phase relationships in the system can be represented in a triangular prism shown in Fig. 1. The known compounds in the oxide ternary Y_2O_3 - Al_2O_3 - SiO_2 and the quasi-ternaries Si,Al/N,O and Si,Y/N,O are indicated in this figure. A four-phase field can be represented as a tetrahedron in this prism. The volume of the prism is filled by such tetrahedra. The faces of a tetrahedron are, generally, three-phase regions and the edges generally represent binary equilibrium. However, in case of extended homogeneity range in one of the phases, the face will be a two-phase region and the edge a single-phase line. The important compatibility regions found in this system are shown in Figs. 2 and 3. These are Si_3N_4 - $\beta 60$ - Y_2O_3 · 2SiO_2 - $3\text{Y}_2\text{O}_3$ · $5\text{Al}_2\text{O}_3$ tetrahedron in Fig. 2 and x_1 - $3\text{Al}_2\text{O}_3$ · 2SiO_2 - Al_2O_3 - Y_2O_3 · 2SiO_2 and x_1 - $3\text{Al}_2\text{O}_3$ · 2SiO_2 - Y_2O_3 · 2SiO_2 - SiO_2 tetrahedra in Fig. 3. Here $\beta 60$ is $\beta\text{Si}_{6-x}\text{Al}_x\text{O}_8\text{N}_{8-x}$ solid solution containing 60 eq.% Al, i.e., $x = 4.00$. $3\text{Y}_2\text{O}_3$ · $5\text{Al}_2\text{O}_3$ is the well-known cubic yttrium-aluminum garnet. The yttrium disilicate Y_2O_3 · 2SiO_2 has four polymorphic forms α , β , γ and δ and their identification was done based on the work of Ito and Johnson (6). Other

*Table I will be deposited in the Data Depository Service.

compatibility tetrahedra in the system are listed below.



No quinary, i.e., five-component, compounds were found in the part of the system investigated here. $2Y_2O_3 \cdot Si_2N_2O$ and $2Y_2O_3 \cdot Al_2O_3$ are isostructural having a monoclinic structure. They form a complete series of solid solutions involving interchange of Si-N and Al-O pairs (7). $Y_2O_3 \cdot Si_2N_2O$ probably has the same structure as the high temperature phase $Y_2O_3 \cdot Al_2O_3$.

However, $Y_2O_3 \cdot Al_2O_3$ was not observed in the specimens made at $1550^\circ C$. It is reported to be stable only above $1835^\circ C$ (8). H phase has the apatite structure and its formula is $Y_5(SiO_4)_3N$ which can also be represented as $(Y_2O_3 \cdot Si_2N_2O) \cdot 4(Y_2O_3 \cdot SiO_2)$. The homogeneity ranges of the phases $Y_2O_3 \cdot Si_2N_2O$, $Si_3N_4 \cdot Y_2O_3$ and $Y_5(SiO_4)_3$ are limited. This aspect of the phase diagram needs further investigation. There is no phase in the Si,Y/N,O plane corresponding to the garnet $3Y_2O_3 \cdot 5Al_2O_3$.

It is known that the high temperature mechanical properties of hot-pressed and sintered silicon nitride ceramics fabricated using MgO or Y_2O_3 as sintering aids are limited by the presence of a glassy phase at the grain boundaries. The compatibility relations found here will be useful in developing β - Si_3N_4 -based ceramics which have a more refractory crystalline second phase instead of the glassy grain boundary phase. This will significantly improve the high temperature mechanical properties of these ceramics.

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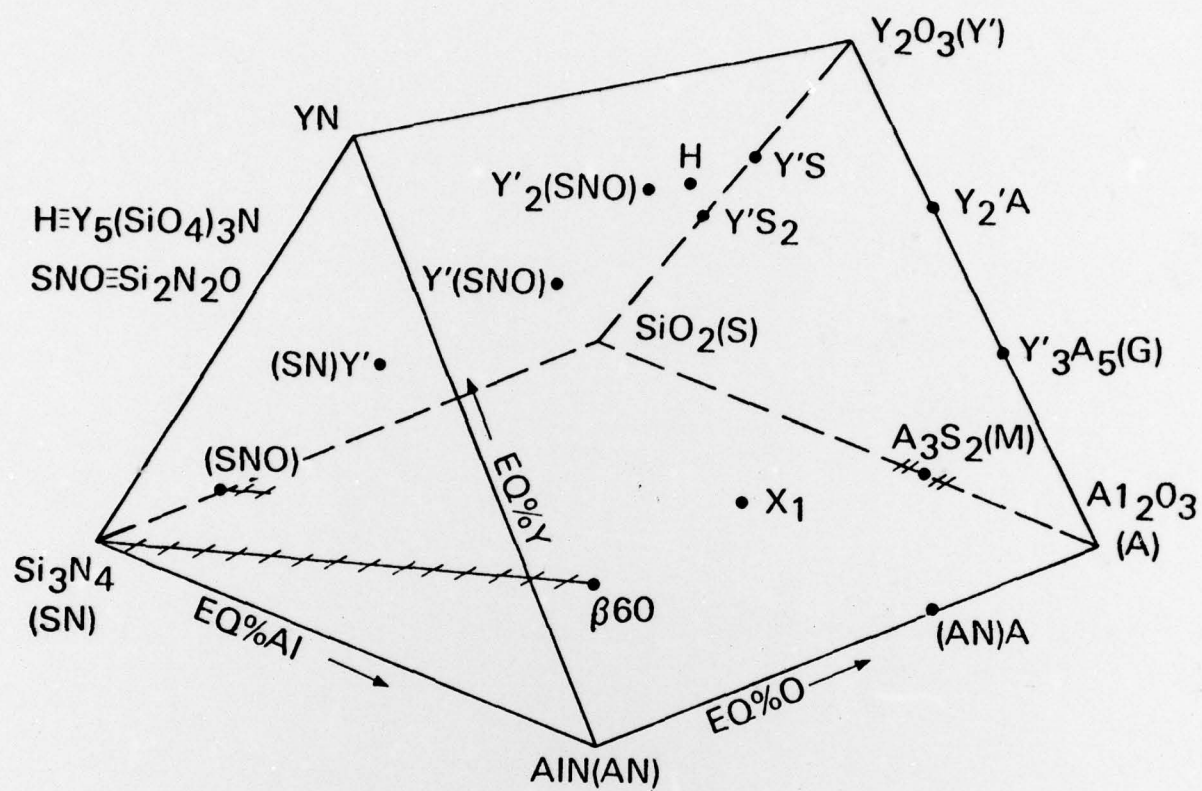


Fig. 1. Representation of the system Si,Al,Y/N,O.

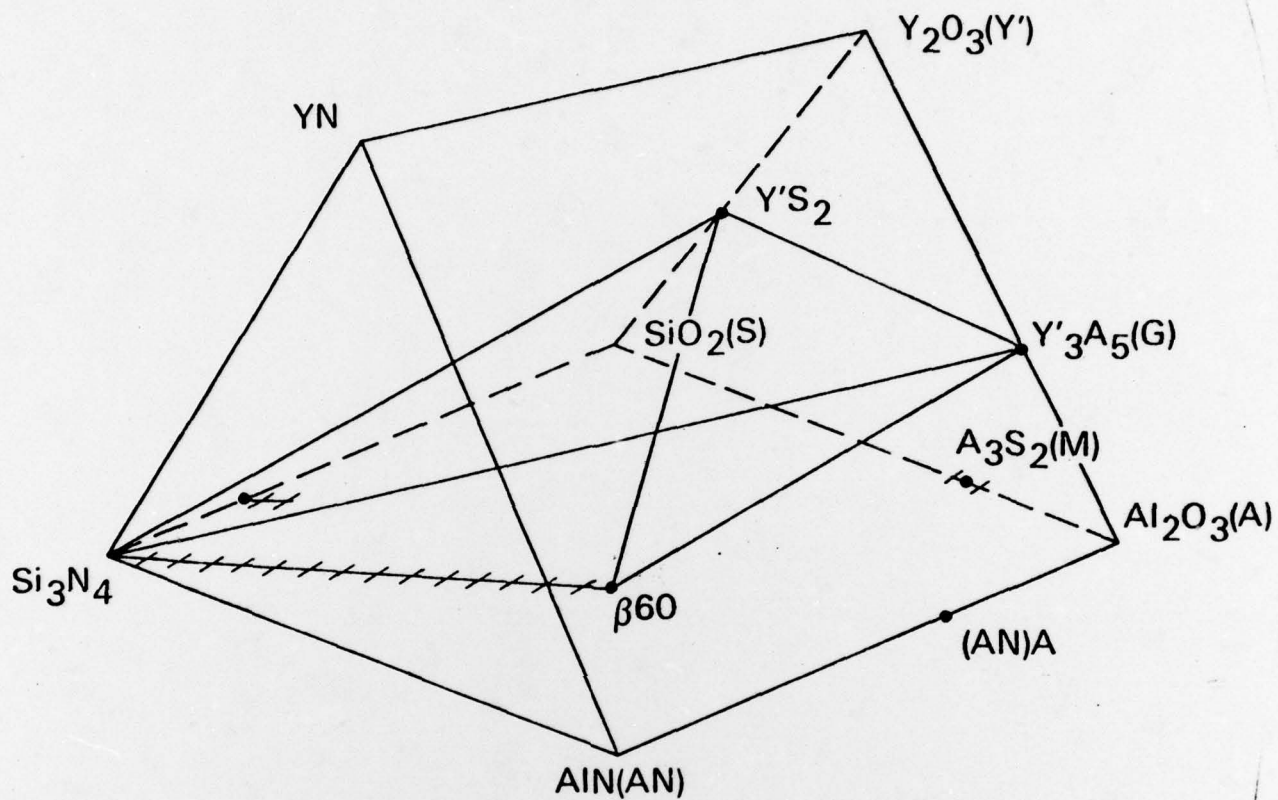


Fig. 2.

Compatibility tetrahedron Si_3N_4 - $\beta 60$ - $\text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2 (\text{Y}'\text{S}_2)$ - $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3 (\text{Y}'_3\text{A}_5)$.

TABLE I
Specimens and Experimental Data

Specimen No.	Composition			Heat Treatment	Phases Present	Remarks
	Eq. % Al	Eq. % Y	Eq. % O			
1 1'	15.5 15.5	0 0	10.4 10.4	1550°C, 1 hr Second firing 1550°C, 1 hr	β s.s., α -Si ₃ N ₄ , Al ₂ O ₃ β s.s.	No densification
2 2'	51.2 51.2	0 0	34.2 34.2	1550°C, 1 hr Second firing 1550°C, 1 hr	β s.s. β s.s.	No densification
3 3'	100 100	0 0	66.7 66.7	1550°C, 1 hr Second firing 1550°C, 1 hr	AlN, Al ₂ O ₃ AlN, Al ₂ O ₃	
4 4'	38.8 38.8	21.4 21.4	23.0 23.0	1550°C, 1 hr Second firing 1550°C, 1 hr	β s.s., δ 'S ₂ β s.s., δ 'S ₂	Densified; shrinkage = 15%
4"	38.8	21.4	23.0	Densification at 1250°C, 21 hrs	Y ₃ 'A ₅ & β -Si ₃ N ₄ crystallized	
5 5'	27.1 27.1	5.0 5.0	29.7 29.7	1550°C, 1 hr Second firing 1550°C, 1 hr	β s.s., δ 'S ₂ β s.s., δ 'S ₂	Densified; shrinkage = 17%
6	48.3	5.3	50.0	1550°C, 1 hr	β s.s., x ₂ , δ 'S ₂ , Y ₃ 'A ₅	Densified; shrinkage = 17%
7	72.6	5.7	61.7	1550°C, 1 hr	δ 'S ₂ , Al ₂ O ₃	Densified; shrinkage = 17%
8	5.1	14.0	36.2	1550°C, 1 hr	δ 'S ₂ , glass	Foamed
9	29.7	8.2	53.6	1550°C, 1 hr	β s.s., δ 'S ₂ , Y ₃ 'A ₅	Foamed; lot of liquid at firing temperature
10	53.6	16.4	74.0	1550°C, 1 hr	β s.s., Y ₃ 'A ₅ , glass	Foamed

TABLE I (continued)

Specimen No.	Composition			Heat Treatment	Phases Present	Remarks
	Eq. % Al	Eq. % Y	Eq. % O			
11	6.5	28.7	71.3	1550°C, 1 hr	β s.s., glass, H $\text{OY}'\text{S}_2$ and H crystallized	Foamed; evidence of lot of liquid.
11'	6.5	28.7	71.3	Devitrification at 1100°C, 20 hrs		
12	20.5	30.1	83.9	1550°C, 1 hr	glass	Shiny bead; complete melting. Classy halo increased in x-ray diffraction indicating tendency toward devitrification.
12'	20.5	30.1	83.9	Devitrification at 1100°C, 20 hrs		
13	20.0	40.0	60.0	1550°C, 1 hr	(SN)Y', β - Si_3N_4 , $\text{Y}_3'\text{A}_5$	Densified; shrinkage = 12%.
14	25.1	50.0	75.1	1550°C, 1 hr	$\text{Y}_2'\text{A}$, $\text{Y}_3'\text{A}_5$, (SN)Y'	Densified; shrinkage = 12%.
15	16.7	66.8	84.3	1550°C, 1 hr	Single phase s.s. between $\text{Y}_2'\text{A}$ and $\text{Y}_2'(\text{SNO})$	Little densification; shrinkage = 5%.
16	23.1	46.2	77.0	1550°C, 1 hr	$\text{Y}_2'\text{A}-\text{Y}_2'(\text{SNO})$ s.s., (SN)Y', $\text{Y}_3'\text{A}_5$	Densified; shrinkage = 19%.
17	28.3	33.9	71.8	1550°C, 1 hr	$\text{Y}'(\text{SNO})$, $\text{Y}_3'\text{A}_5$, glass	Deformed; lot of liquid occurred.
18	10.4	62.0	79.3	1550°C, 1 hr	Single phase s.s. between $\text{Y}_2'\text{A}$ and $\text{Y}_2'(\text{SNO})$	Little densification; shrinkage = 5%.
19	21.5	64.3	89.4	1550°C, 1 hr	Single phase s.s. between $\text{Y}_2'\text{A}$ and $\text{Y}_2'(\text{SNO})$	Little densification; shrinkage = 5%.
20	15.0	45.1	70.0	1550°C, 1 hr	$\text{Y}_2'\text{A}-\text{Y}_2'(\text{SNO})$ s.s., (SN)Y', $\text{Y}_3'\text{A}_5$, trace of $\text{Y}'(\text{SNO})$	Densified; shrinkage = 19%.
21	31.6	47.3	84.1	1550°C, 1 hr	$\text{Y}_2'\text{A}-\text{Y}_2'(\text{SNO})$ s.s., (SN)Y', $\text{Y}_3'\text{A}_5$	Densified; shrinkage = 19%.
22	18.3	32.9	63.4	1550°C, 1 hr	$\text{Y}_2'\text{A}-\text{Y}_2'(\text{SNO})$ s.s., $\text{Y}'(\text{SNO})$, glass	Deformed; lot of liquid occurred.
23	39.0	35.1	80.5	1550°C, 1 hr	$\text{Y}_3'\text{A}_5$, glass	Deformed; lot of liquid occurred.
24	6.2	6.8	7:3	1550°C, 1 hr	β s.s., (SN)Y'	No shrinkage.

TABLE 1 (continued)

Specimen No.	Composition				Heat Treatment	Phases Present	Remarks
	Eq. % Al	Eq. % Y	Eq. % Zr	Eq. % O			
25	0	9.5	11.8	11.8	1550°C, 1 hr	β - Si_3N_4 , (SN)Y'	No shrinkage.
26	6.9	8.0	25.4	25.4	1550°C, 1 hr	β s.s., glass	Densified; shrinkage = 14%.
26'	6.9	8.9	25.4	25.4	Devitrification at 1250°C, 21 hrs	Y_3A_5 , $\delta\text{Y}'\text{S}_2$ and β - Si_3N_4 crystallized	
27	7.6	2.6	11.1	11.1	1550°C, 1 hr	β s.s.	Some densification; shrinkage = 9%.
27'	7.6	2.6	11.1	11.1	Devitrification at 1250°C, 21 hrs	Y_3A_5 and β - Si_3N_4 crystallized	
28	32.8	19.7	52.4	52.4	1550°C, 1 hr	β - Si_3N_4 , α - Si_3N_4 (trace), Y_3A_5 , Al_2O_3 (trace)	Densified; shrinkage = 16%.
29	0	12.0	100	100	1550°C, 1 hr	Y_2SiO_5 , $\delta\text{Y}'\text{S}_2$, small amount of H	No densification; shrinkage = 2%.
30	0	29.2	88.8	88.8	1550°C, 1 hr	H	Some densification; shrinkage = 10%; 2.5% wt. gain due to oxidation.
31	38.1	15.6	62.0	62.0	1550°C, 1 hr	β -30, Y_3A_5 , glass	Foamed and deformed; some liquid occurred.
32	60.9	13.7	61.9	61.9	1550°C, 1 hr	β -50, Y_3A_5 , some Al_2O_3	Some densification; shrinkage = 8%.
33	0	22.5	52.5	52.5	1550°C, 1 hr	β - Si_3N_4 , α - Si_3N_4 , $\delta\text{Y}'\text{S}_2$, H	Some foaming.
34	0	27.0	50.2	50.2	1550°C, 1 hr	β - Si_3N_4 , H	Densified; shrinkage = 18%.
35	41.9	9.0	81.4	81.4	1550°C, 1 hr	x_1 , glass	Foamed.
36	41.6	17.1	100	100	1550°C, 1 hr	glass, some Al_2O_3	Glassy bead, lot of liquid.
37	31.2	40.2	100	100	1550°C, 1 hr	Y_3A_5 , $\beta\text{Y}'\text{S}_2$, $\alpha\text{Y}'\text{S}_2$, glass	Lot of liquid occurred.
38	33.6	47.9	100	100	1550°C, 1 hr	Y_3A_5 , $\text{Y}'\text{S}$, glass	Deformed; some liquid occurred.

TABLE 1 (continued)

Specimen No.	Composition			Heat Treatment	Phases Present	Remarks
	Eq. % Al	Eq. % Y	Eq. % O			
39	4.0	14.6	53.5	1550°C, 1 hr	Si ₂ N ₂ O s.s., glass	Deformed; some liquid occurred.
40	4.8	7.8	42.3	1550°C, 1 hr	Si ₂ N ₂ O s.s., traces of β-Si ₃ N ₄ and α-Si ₃ N ₄ , glass	Some densification; shrinkage = 10%.
40'	4.8	7.8	42.3	Devitrification at 1200°C, 16 hrs	Y ₂ Si ₂ O ₇ crystallized	
41	7.6	40.6	48.0	1550°C, 1 hr	Y ₂ A, (SN)Y'	Little densification; shrinkage = 4%.
42	16.3	34.4	50.7	1550°C, 1 hr	Y'(SNO), Y ₃ A ₅	Some densification; shrinkage = 10%.
43	49.0	10.2	49.0	1550°C, 1 hr	Y ₃ A ₅ , β-40, trace of x ₂	Foamed; 4% weight gain.
44	76.0	14.0	62.3	1550°C, 1 hr	Y ₃ A ₅ , x ₂ , Al ₂ O ₃ , trace of β-40	Sample burst into many pieces.
45	85.4	16.6	79.7	1550°C, 1 hr	Y ₃ A ₅ , Al ₂ O ₃ , AlN	Sample burst into many pieces.