SINTERING OF BETA SILICON NITRIDE
SOLID SOLUTIONS CONTAINING METAL OXIDE

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Reaction sintering of $\beta$-Si$_3$N$_4$ solid solutions has been studied using powder mixtures of SiO$_2$, Si$_3$N$_4$, AlN, Si$_3$N$_4$, AlN, and $\alpha$-Al$_2$O$_3$, and Si$_3$N$_4$, 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.
Reaction sintered β-Si₃N₄ solid solutions with the highest densities were prepared from mixtures of Si₃N₄, AlN and Al₂O₃ powders without application of external pressure or additional densification aids. In contrast, mixtures containing SiO₂ showed less densification even with liquid present because of vaporization during sintering.
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PAPERS PRESENTED AT TECHNICAL MEETINGS

1. "1550°C Isothermal Plane in the System Si₃N₄—AlN—Al₂O₃—Y₃Al₅O₁₂,"
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2. "Reaction Sintering of β-Si₃N₄ Solid Solutions in the System Si,Al/N,O,"
   Symposium on Sintering and Related Phenomena, The University of Notre Dame.
Solid-Liquid Equilibria in the System Si₃N₄-ALN-SiO₂-Al₂O₃

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Solid-liquid equilibria at 1750°C and subsolidus phase relations in the system Si₃N₄-ALN-SiO₂-Al₂O₃ were determined for the composition region bounded by the β-Si₃N₄ 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, Si₃Al₁₀O₁₂N₂, is suggested for the Z phase. The lowest melting temperature in the system is ~1480°C and the corresponding composition is 10 eq% Al₂O₃-90 eq% O.

I. Introduction

Ceramic materials based on the system Si₃N₄-AlN 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 Si₃N₄-based ceramics can be made by pressureless sintering. Since Si₃N₄-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 Si₃AlN-O concerned the formation and nature of the β-Si₃N₄-based solid solution (β-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 SiO₂-rich side of the β-ss phase, a 2-phase region (liquid + β-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 SiO₂ corner and that there was no region where β-ss and liquid coexisted at 1800°C in their product or quasi-equilibrium diagram. They also reported that the Z phase does not melt at <1800°C. Layden⁷ proposed a tentative liquid-phase field using differential thermal analysis (DTA) and microstructure observations. The liquid field extends from the SiO₂ corner and includes the Z composition at 1750°C. The Z phase reportedly melts at ~1720°C. A large β-ss – liquid field is also indicated at 1750°C. Layden had difficulty in getting reasonable signal strengths during melting due to foaming and melting behavior observations. Therefore, an alternative method of quantitative phase analysis by X-ray powder diffraction is needed in a series of well-selected specimens to 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,¹ silicon nitride, Al₂O₃,¹ and silica.¹ The oxygen contents of the nitrides were considered in making up the compositions. Mixtures of different overall compositions in the region between the β-ss line and silica-alumina join were made using aluminum nitride-silica-

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⁴ Member, the American Ceramic Society.
⁵ Now with the Air Research and Development Center, Torrance, California 90501.
Solid-Liquid Equilibria in the System Si₃N₄-AlN-SiO₂-Al₂O₃

Fig. 1. Part of isothermal section of the system Si₃N₄-AlN-SiO₂-Al₂O₃ at 1750°C showing solid-liquid equilibria; β-s.s = β-Si₃N₄, α-Al₂O₃ based solid solution. M = mullite (3Al₂O₃·2SiO₂). L = liquid.

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 Si₃N₄) 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-weighed mixture. Tungsten carbide impurity introduced during milling was <1.5 wt%. The milled mixture was dried in shallow glass dishes 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 a 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°C/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 ~250°C/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 equilibration phase assemblages. Equilibration 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. Equilibration 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 ≤1650°C. About 50 compositions, lying in the area above the β-s.s line in Fig. 1, were fired at 1750°C to establish the isothermal section representing solid-liquid equilibria. Some selected compositions were fired at ≤1650°C to determine subsolidus phase equilibria and the temperature 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 used for the lattice parameter determination of the internal standard a-Al₂O₃. The experimental error in determining the amount of β-s.s by this method is estimated to be ±4 wt%.

A calibration curve of the peak-height ratio vs wt% β-s.s 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 β-s.s to the peak height of (012) or (113) reflection of the internal standard a-Al₂O₃. The experimental error in determining the amount of β-s.s is estimated to be ±4 wt%.

The composition of β-s.s in these selected specimens was determined from the change in the β-s.s lattice parameters. For this purpose, a calibration curve was made for lattice parameters vs β-s.s content in different hot-pressed single-phase β-s.s standards. The scanning rate on the diffractometer was 0.2°/min. Therefore, the peak heights in the diffraction patterns scanned at 0.2°/min were taken as a measure of the concentration of a given phase in a powder mixture.

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Another feature indicating that no significant amount of β-s.s crystallized during cooling in the 2-phase β-s.s + 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 compositions are identified by the numbers 5, 6, 7, 16; and 8, 30 (Table III). 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 Si₃N₄-O₂-ss + liquid field and the corresponding liquidos could not be done since liquids in this field crystallized Si₃N₄-O₂-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
Table II. Lattice Parameter Changes in Si₃N₄O Solid Solution

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

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 Na₂B₄O₇ and LiBO₂. The glass samples were then analyzed for Si and Al by the electron microprobe analyzer and for N₂ content by wet chemical analysis. In this analysis, NH₃ was liberated from the specimens by dissolving them in lithium hydroxide. The NH₃ liberated was determined volumetrically using standard H₂SO₄. The analyses showed that Si, N₂, and O were lost by vaporization but that the Al content of the specimens increased. As a result, the overall composition shifted toward the AIN 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 Layden 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 Si₃N₄O was determined from lattice parameter changes of the single-phase specimens and the appearance of secondary x₁ and β-ss phases in the neighboring compositions. The lattice parameters of Si₃N₄O-ss are given in Table II.

The composition Si₁₋ₓAlₓOₓNₓ (i.e., 2S,N₁₋ₓAlₓOₓ; 6SIO₂) gave the highest peak intensities for the x₁ 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 x₁ as the only crystalline phase. Furthermore, when fired at 1650°C this composition gave x₁ phase only, whereas neighboring compositions contained secondary mullite or β-ss. Therefore, it is suggested that the stoichiometric composition of x₁ is Si₁₋ₓAlₓOₓNₓ. 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 x₁ 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: x₁ = Si₁₋ₓAlₓOₓNₓ.

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-as grains (estimated as < 2 vol%) which apparently precipitated from the α phase during cooling are also visible. Thus, if this is the single-phase α 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 α phase is estimated as 1720°C. This composition lies on the line joining Si₃N₄ and mullite (3Al₂O₃·2SiO₂) compositions.

Subsolidus phase equilibria in part of the system are shown in Fig. 3. The lowest-melting composition is ~ 10 eq% Al–90 eq% N which melts at 1480°C (~ 20°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.

References
Reaction Sintering Forming $\beta$-$\text{Si}_3\text{N}_4$ Solid Solutions in the System Si,Al/N,O:

I. Sintering of SiO$_2$-AlN Mixtures

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

Abstract

Reaction sintering of $\beta$-$\text{Si}_3\text{N}_4$ solid solution containing 60 equivalent percent of aluminum in the system Si,Al/N,O was investigated. The starting material used for this study was the 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 intervals, a crystalline product formed. The reaction 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.

Herstellung von $\beta$-$\text{Si}_3\text{N}_4$ Mischkristallen durch Reaktions sintern

Es wurde das Reaktions sintern von $\beta$-$\text{Si}_3\text{N}_4$, Mischkristallen mit 60 Äquivalentprozent Aluminum im System Si, AlN, O untersucht. Die Ausgangsmaterialien für diese Arbeit waren SiO$_2$ in Quarzform und AlN. Die Ergebnisse können auf der Basis der chemischen Reaktion, Verdampfung, und Verdichtung diskutiert werden. Bei Temperaturen (1400-1600°C) findet chemische Reaktion statt, die zu einer Porositätserhöhung führt. In einem mittleren Temperaturbereich (1600-1800°C) bildete sich Schmelze.

Introduction

Solid solutions formation of $\beta$-$\text{Si}_3\text{N}_4$ containing metal oxide has been reported in the system $\text{Si}_3\text{N}_4$-Al$_2$O$_3$ independently by Oyama and Kamigaito1 and Jack2. Both reported extensive solubility of Al$_2$O$_3$ in $\beta$-$\text{Si}_3\text{N}_4$. In later publications, these authors reported the extent of solid solutions in ternary systems. Jack3 studied the system $\text{Si}_3\text{N}_4$-SiO$_2$-Al$_2$O$_3$ and Oyama4 studied the system $\text{Si}_3\text{N}_4$-Al$_2$O$_3$-AlN. Both of their phase diagrams showed wide ternary solid solution regions.

The solid solution formation of Al$_2$O$_3$ in $\text{Si}_3\text{N}_4$ requires either non-metal interstitials or metal site vacancies in the $\beta$-$\text{Si}_3\text{N}_4$ 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 $\text{Si}_3\text{N}_4$-Al$_2$O$_3$ at 1760°C. They considered that at high temperatures, the reaction $\text{Si}_3\text{N}_4$-2Al$_2$O$_3$ = 3SiO$_2$+4AlN may occur. Therefore, the system $\text{Si}_3\text{N}_4$-Al$_2$O$_3$ was treated as a quasi-ternary reciprocal salt system. A representation of multi-component $\text{Si}_3\text{N}_4$-based systems containing metal oxides was given elsewhere.

Gauckler et al.6 were not able to repeat the results of Oyama4 and Jack2. According to these authors, single phase $\beta$-$\text{Si}_3\text{N}_4$ solid solution occurs between $\text{Si}_3\text{N}_4$ and Al$_2$O$_3$. Instead, single phase solutions were found to be restricted to a very narrow region along the line $\text{Si}_3\text{N}_4$-AlN-Al$_2$O$_3$. The phase diagram is given in Fig. 1. These solid solutions have a fixed metal to non-metal ratio of 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 $\text{Si}_3\text{N}_4$-SiO$_2$-Al$_2$O$_3$. All of these solid solutions have fixed metal to non-metal ratios. Between the $\beta$-$\text{Si}_3\text{N}_4$ solid solution and the SiO$_2$ corner, at 1760°C, $\beta$-phase and a liquid phase are in equilibrium. As the temperature decreases, X$_I$ crystallizes.

In a recent review, Jack7 revised the phase diagram for the system $\text{Si}_3\text{N}_4$-Al$_2$O$_3$. The diagram was presented as a reciprocal salt system. In the diagram agrees with that of Gauckler’s as shown in Fig. 1 except that the locations of the AlN rich “polypoly phases” are slightly different. Similar “polypoly phases” were also reported by Land et al.8 in the system Si/Al/N/O (Fig. 2). However, the compositions of these phases are again different from both of those reported by Gauckler et al.8 and by Jack7.
I. \[\text{Si}_3\text{N}_4 \cdot \text{Al}_{2}\text{O}_3 \cdot \text{Si}_3\text{N}_4\text{Al}_2\text{O}_3\] hence different sintering kinetics. This paper reports the results of reaction position, and \[\text{Si}_3\text{N}_4 \cdot \text{Al}_2\text{O}_3 \text{ powders or Si}_3\text{N}_4 \text{ and Si}_3\text{N}_4 \text{Al}_2\text{O}_3 \text{ powders. For one particular corn-}
\]
\[\text{Compositions Si}_5\_ \times \_\text{Al}_0\_\text{N}_9\_ \text{ can be formulated by mixing either Si}_3\text{N}_4, \text{ Si}_3\text{N}_4 \text{Al}_2\text{O}_3, \text{ or Si}_3\text{N}_4 \text{Al}_2\text{O}_3 \text{ powders. For one particular composition, Si}_3\text{N}_4 \text{Al}_2\text{O}_3 \text{ powders can be sintered and densified during sintering of Si}_3\text{N}_4 \text{ solid solution using SiO}_2 \text{ and Al}_2\text{O}_3 \text{ as starting materials. The sintering behavior using other sets of starting mate-}
\]
\[\text{rials will be reported separately. Single phase Si}_3\text{N}_4 \text{ solid solution powders were also sintered and the results are reported in this paper.}
\]

**Experimental**

One mole of quartz form of SiO\(_2\) and 2 moles of AlN powders (where \(x = 4\) in the formula \(\text{Si}_3\text{N}_4 \cdot \text{Al}_2\text{O}_3 \cdot \text{Si}_3\text{N}_4 \text{Al}_2\text{O}_3\)) were mixed in a hard metal mill under fluid. The mixtures were dried and then compacted under an isotropic pressure of 650 MN/m\(^2\) 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 450°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 skeletal 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 SiO\(_2\)-AlN Mixture:** Nitrogen concentration of the powder mixture (1 mole of SiO\(_2\) and 2 moles of AlN) after milling was analyzed\(^a\) 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 \(\beta\)-Si\(_3\)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 specimens heated at 1400, 1500 and 1600°C. Large shrinkage occurred between 1850 and 1950°C. Weight losses during 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-
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 angle phase material prepared earlier. Peak heights were used to compare the quantities of phases in the specimens. The results are given in Fig. 8.

The results showed that the reaction $\text{SiO}_2 - 4\text{AIN} \Rightarrow 3\text{Si}_3\text{N}_4 + 2\text{Al}_2\text{O}_3$ took place at the beginning of the process. At 1400°C, the amount of crystalline $\text{SiO}_2$ decreased rapidly and $\beta$-$\text{Si}_3\text{N}_4$ and $\text{Al}_2\text{O}_3$ formed already during heating intermediate phases appeared during the reaction. $X_5$ 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 $\beta$-phase and increase of $X_4$ 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 $\text{Si}_{1-x}\text{Al}_x\text{N}_y\text{O}_{1-z}$ should have been observed during the reaction between $\text{SiO}_2$ and AIN. Probably, because of kinetic reasons, some of the phases were not observed. Low melting liquid (<1 500°C) has been observed to exist in the system at about 80 eq. % Si and 60 eq. % O. 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 temperature behavior.

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

Fig. 7 Microstructure of sintered compacts.

Fig. 8 Phases present after sintering.

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.
temperature behaviour. The results showed that the $\beta$-Si$_3$N$_4$ 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 $\beta$-Si$_{5.25}$Al$_x$N$_{4}$O$_{16}$ are also plotted.

X-ray diffraction line broadening of $\beta$-Si$_3$N$_4$ 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 prolonged heating, the x-ray diffraction lines became sharper again. The initial broad peaks for the 1500°C sintered samples can be explained as small particle size of $\beta$-phase during sintering. The results shown in Fig. 9 (lattice parameter) and Fig. 10 (line broadening) can be interpreted as homogenization of the $\beta$-Si$_3$N$_4$ solid solution. In the beginning of the reaction, very fine particles of $\beta$-Si$_3$N$_4$, 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 $\beta$-Si$_3$N$_4$ 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 $\beta$-Si$_3$N$_4$ solid solution lattice. However, in diffusion couple experiments no measurable homogenization could be observed when different aluminium containing $\beta$-Si$_3$N$_4$ solid solution slabs were fused together and heated for one hour at 1500°C. These results seem to be in conflict with the sintering results.

Glass Formation in the System Si$_3$Al/N$_2$: The SiO$_2$-Al$_2$O$_3$ 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 $\beta$-phase are plotted in Fig. 12. No other crystalline phase present in the specimens was observed after cooling. The relative amount of $\beta$-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.
Grain growth was observed in these samples as shown in Fig. 14. The crystals in these mixtures are $\beta$-$\text{Si}_3\text{N}_4$ 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 $\beta$-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 $\beta$-$\text{Si}_3\text{N}_4$ Solid Solution Powder: Hot pressed $\beta$-$\text{Si}_3\text{N}_4$ solid solution having the same composition as the SiO$_2$-AIN mixture ($x = 4$) was pulverized and compacted. The x-ray diffraction pattern showed the hot pressed material is a well crystallized single phase $\beta$-$\text{Si}_3\text{N}_4$ 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 $\text{Si}_3\text{N}_4$ compacts are also shown in the same figure for comparison. The pure $\text{Si}_3\text{N}_4$ 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$_2$-AIN mixture is replotted in the same figure for specimens heated for one hour at different temperatures.

Conclusion

The sintering behaviour of SiO$_2$-AIN mixture can be discussed on the basis of "chemical reaction", "vaporization" and "densification". The moderate density decrease at low temperatures (1 400–1 600°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 (1 600–1 800°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 (>1 800°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 (1 800°C and above), crystalline $\beta$-phase and liquid only existed and the amount and composition of $\beta$ 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 Layden. This is very reasonable because for this composition liquid should be one of the intermediate phases during reaction.

Acknowledgment

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References

12. J. K. Nak, L. J. Gaulckler and T. Y. Tien, "Liquids Surface in Part of the Systems Si,$\text{Al}/\text{N}$", to be published.
Reaction Sintering Forming $\beta$-$\text{Si}_3\text{N}_4$ Solid Solutions in the System Si, Al/N, O

II. Sintering of $\text{Si}_3\text{N}_4$ – $\text{SiO}_2$ – AlN Mixtures

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

Abstract

Reaction sintering of $\beta$-$\text{Si}_3\text{N}_4$ 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 $\alpha$-$\text{Si}_3\text{N}_4$, AlN and quartz form of $\text{SiO}_2$. Specimens of compositions could be densified via transient liquid phase sintering to densities greater than 96% of theoretical density. Increasing amounts of $\alpha$-$\text{Si}_3\text{N}_4$ in the starting materials reduced weight losses to less than 2 wt.% for one hour sintering time.

Introduction

In a previous paper 1, we have reported that high density $\beta$-$\text{Si}_3\text{N}_4$, solid solution ceramics (having a formula $\beta$-$\text{Si}_3\text{N}_4$-$\text{AlO}_x\text{N}_{4-x}$, where $x = 4$) could be obtained by reaction sintering without applied pressure. The starting materials used for that experiment were one mole of $\text{SiO}_2$ 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 $\text{SiO}_2$. The $\beta$-$\text{Si}_3\text{N}_4$ solid solution grains were formed by double exchange reaction between the $\text{SiO}_2$ 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. 1 that the mechanical properties of the $\beta$-$\text{Si}_3\text{N}_4$-$\text{AlO}_x\text{N}_{4-x}$ ceramics with lower $x$ values are superior to those of the higher $x$ values. This investigation was designed to test if additional $\text{Si}_3\text{N}_4$ can be dissolved in a $\text{SiO}_2$-AlN mixture forming $\beta$-$\text{Si}_3\text{N}_4$ solid solution ceramics with lower $x$ values.

The compositions studied were [330] and [50/5] ($x = 2.18$ and $x = 3.14$ respectively when $x = 4.1$, i.e. [60]). These compositions can be regarded as [60] plus various amounts of $\text{Si}_3\text{N}_4$

Experimental

Appropriate amounts of $\text{Si}_3\text{N}_4$, $\text{SiO}_2$ 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.

Results and Discussion

Relative apparent densities after sintering at different temperatures are given in Fig. 1. For comparison, the results for [60] from the previous paper 1 are also plotted in this figure. These results showed that high density $\beta$-$\text{Si}_3\text{N}_4$ solid solution ceramics containing 30 and 50 equivalent percent of aluminium (I330 and I500 respectively) could be obtained by reaction sintering without applied pressure. As shown in Fig. 1, the sintered density of [330] ceramics is higher than that of [50] and [50] is higher than that of [60] for the same heat treatment. At the highest temperatures 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) $\text{SiO}_2$ and AlN react to form $\text{SiO}_2$ rich liquid, 2) liquid reacts with AlN and $\text{Si}_3\text{N}_4$, and 3) $\beta$-$\text{Si}_3\text{N}_4$ solid solutions precipitate. Densification can only be accomplished when vaporization is low. Vaporization and liquid phase sintering. The reaction steps should have been as follows: 1) $\text{SiO}_2$ and AlN react to form $\text{SiO}_2$ rich liquid, 2) liquid reacts with AlN and $\text{Si}_3\text{N}_4$, and 3) $\beta$-$\text{Si}_3\text{N}_4$ solid solutions precipitate. Densification can only be accomplished when vaporization is low. The phases present after sintering are given in Fig. 3. The phase $x$, appeared in some of the specimens after sintering. As shown by Naik et al. 2, the pre-
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°C.

The higher the SiO₂ content in the starting mixture (in the SiO₂, Si₃N₄, AlN series), the larger the quantities of SiO₂ rich liquid which will be formed upon heating. Therefore, higher weight losses will be observed. This explains the higher weight losses observed for the 160 versus 150 and 150 versus 130.

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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References


Fig. 3 Quantities of phases /β-N₃, as determined by x-ray diffraction. Specimens were sintered for one hour at different temperatures.
Reaction Sintering Forming $\beta$-$\text{Si}_3\text{N}_4$ Solid Solutions in the System $\text{Si,Al}/\text{N,O}$

III. Sintering of $\text{Si}_3\text{N}_4$, $\text{AlN}$, $\text{Al}_2\text{O}_3$ Mixtures

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At the time this work was done, S. Boskovic was a Humboldt Fellow at Max-Planck Institut, Stuttgart, BRD.
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 $\text{SiO}_2$ and $\text{AlN}$. The same composition can also be prepared by using a mixture of $\text{Si}_3\text{N}_4$, $\text{AlN}$ and $\text{Al}_2\text{O}_3$.

The results obtained from the reaction sintering of $\text{SiO}_2$ and $\text{AlN}$ 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 $\text{SiO}_2$ (4). $\beta$-$\text{Si}_3\text{N}_4$ solid solutions were formed by double exchange reaction between the liquid and $\text{AlN}$ 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 $\text{Si},\text{Al}/\text{N},\text{O}$ is located at the $\text{SiO}_2$ corner containing 10 eq.% of aluminum and 10 eq.% of nitrogen. This composition lies on the line connecting the $\text{SiO}_2$ and $\text{AlN}$ corners in the phase diagram (5). During the reaction of $\text{SiO}_2$ with $\text{AlN}$, 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 Si₂N₂O - X₃. Two iso-
thermal planes of the Si,Al/N₂O diagram are shown in Figure 1.

At temperatures above 1700°C, X₁ melted and the liquid
dissolved more AlN and became aluminum rich and the join X₁ -
Si₂N₂O disappeared. These aluminum rich liquids are then at
equilibrium with the β phase.

Naik et al. (4) have shown that the weight loss for SiO₂
rich liquids was much higher than that of the aluminum rich
liquids at all temperatures. The formation of the SiO₂ rich
liquids must have been the cause of the heavy weight losses and
low sintered densities of some of the SiO₂, AlN mixtures.

The composition, Si₂Al₄O₄N₄ blended by mixing Si₃N₄, AlN
and Al₂O₃ 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 Si₃N₄, AlN and Al₂O₃ would be different from that of
the mixture SiO₂ and AlN. The weight loss for the Si₃N₄, AlN,
Al₂O₃ mixture should be lower than that of SiO₂ and AlN mixture
because the SiO₂ rich liquid is not in the triangle formed by
these three chemicals. This experiment was designed to test
this postulation.

Appropriate amounts of Si₃N₄, AlN and Al₂O₃ powders giving
composition Si₂Al₄O₄N₄ 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/m². 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 SiO₂—AlN. For the SiO₂—AlN mixture, the reaction already began at 1400°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Surface Area (m²g⁻¹)</th>
<th>Mean Particle Size</th>
<th>Content (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>2.0</td>
<td>2.5</td>
<td>1.4 32.1</td>
</tr>
<tr>
<td>α-Si₃N₄</td>
<td>9.0</td>
<td>--</td>
<td>2.5 27.0</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>7.8</td>
<td>0.5</td>
<td>--</td>
</tr>
</tbody>
</table>
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 Si₂Al₄O₄N₄ did not densify at all. Densification was observed above 1800°C for SiO₂ and AlN mixture. For the specimens using Si₃N₄, AlN and Al₂O₃ as starting materials, noticeable densification was observed at 1700°C.

The lack of low melting SiO₂ rich liquid may have been the major cause of this difference in sintering behavior. The low melting SiO₂ rich liquid could only form from the surface oxygen on the Si₃N₄ particles. The low melting liquid could have vaporized before the chemical reaction proceeded further. The presence of X₂ and the absence of X₁ confirmed the vaporization of the high SiO₂ 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 SiO₂ layer on the Si₃N₄ crystals to form liquid. At the same time, α-Si₃N₄ converted to β-Si₃N₄ in the presence of the low melting liquid. Si₂N₂O was never formed (as shown by the x-ray data because of the kinetic reaction, therefore, the tie line between X₁ and Si₂N₂O did not exist. The formation of X₂ could be interpreted as an intermediate phase formed between AlN and the liquid.

At 1700°C and above, Si₃N₄ and Al₂O₃ 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

The authors wish to acknowledge the partial financial support of this work by AFOSR and BMFT.
References


Fig. 1. Isothermal Sections of the System Si$_3$N$_4$-SiO$_2$-AlN-Al$_2$O$_3$.

After Naik et. al. (4).
The specimen was noted as a mixture of $X_2$, $X_3$, and $AlN$ (see phase diagram in Fig. 1). This result indicates that $SO_3$ was lost 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.

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.

Figure 1. Relative Apparent Densities of Specimens Sintered for one hour at Different Temperatures.

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

Where $f_i$ is the amount of each phase, and \( \text{sp.gr.}_i \) 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 $\text{Al}_2\text{O}_3$, $\text{Y}_2\text{O}_3$ and $\text{MgO}$ have been shown to be useful densifying aids in fabricating high-density ceramics from $\text{Si}_3\text{N}_4$ powder. It is necessary to know the phase equilibria in these $\text{Si}_3\text{N}_4$-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 $\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$ 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 $\text{Si}_3\text{N}_4$, $\text{AlN}$, $\text{Al}_2\text{O}_3$, $\text{SiO}_2$ and $\text{Y}_2\text{O}_3$ 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; $\alpha-$Si$_3$N$_4$ = 85%; $\beta-$Si$_3$N$_4$ = 12%; combined oxygen = 1.8%; Kawecki-Beryleo Industries, Reading, Pennsylvania.
§ Linde A or calcined alumina A-16; >99.5% $\text{Al}_2\text{O}_3$; Aluminum Company of America, Pittsburgh, Pennsylvania.
‡‡ Flint #25; >99.5% $\text{SiO}_2$; 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 α-Si₃N₄ 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 CuKα radiation was used to scan the powdered samples between 10 and 80° 2θ 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 Y2O3-Al2O3-SiO2 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 Si1.3N1.4-860-Y2O3·2SiO2-3Y2O3·5Al2O3 tetrahedron in Fig. 2 and x1-3Al2O3·2SiO2-Al2O3-Y2O3·2SiO2 and x1-3Al2O3·2SiO2-Y2O3·2SiO2-SiO2 tetrahedra in Fig. 3. Here 860 is 8Si6Al2O12 solid solution containing 60 eq.% Al, i.e., x = 4.00.

3Y2O3·5Al2O3 is the well-known cubic yttrium-aluminum garnet. The yttrium disilicate Y2O3·2SiO2 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.

\[
\begin{align*}
\beta60-Y_2O_3 \cdot 2SiO_2 - x_1 - \beta10 \\
\beta60-Y_2O_3 \cdot 2SiO_2 - x_1 - 3Y_2O_3 \cdot 5Al_2O_3 \\
\beta60-Al_2O_3 - x_1 - 3Y_2O_3 \cdot 5Al_2O_3 \\
x_1 - SiO_2 - Y_2O_3 \cdot 2SiO_2 - Si_2N_2O \text{ s.s.} \\
x_1 - Y_2O_3 \cdot 2SiO_2 - Si_2N_2O \text{ s.s.} - \beta10 \\
Y_2O_3 \cdot 2SiO_2 - Si_2N_2O \text{ s.s.} - Si_2N_2O - SiO_2 \\
Si_3N_4 - 3Y_2O_3 - Si_2N_2O \text{ s.s.} - Si_2N_2O - Y_2O_3 \cdot 2SiO_2 \\
Si_3N_4 - 3Y_2O_3 \cdot 5Al_2O_3 - Y_2O_3 \cdot 2SiO_2 - H \\
Si_3N_4 - H - 3Y_2O_3 \cdot 5Al_2O_3 - Y_2O_3 \cdot Si_2N_2O \\
Si_3N_4 - Y_2O_3 \cdot Si_2N_2O - Si_3N_4 \cdot Y_2O_3 - 3Y_2O_3 \cdot 5Al_2O_3 \\
Si_3N_4 \cdot Y_2O_3 - Si_2N_2O - 2Y_2O_3 \cdot Al_2O_3 - 3Y_2O_3 \cdot 5Al_2O_3 \\
Y_2O_3 \cdot Si_2N_2O - 3Y_2O_3 \cdot 5Al_2O_3 - 2Y_2O_3 \cdot Al_2O_3 - H \\
H - 3Y_2O_3 \cdot 5Al_2O_3 - Y_2O_3 \cdot 2SiO_2 - Y_2O_3 \cdot SiO_2 \\
H - 3Y_2O_3 \cdot 5Al_2O_3 - Y_2O_3 \cdot SiO_2 - 2Y_2O_3 \cdot Al_2O_3 \\
Si_3N_4 \cdot Y_2O_3 - Si_2N_2O - 2Y_2O_3 \cdot Si_2N_2O - 2Y_2O_3 \cdot Al_2O_3 \\
Y_2O_3 \cdot Si_2N_2O - H - 2Y_2O_3 \cdot Si_2N_2O - 2Y_2O_3 \cdot Al_2O_3 \\
2Y_2O_3 \cdot Si_2N_2O - H - 2Y_2O_3 \cdot Al_2O_3 - Y_2O_3 \\
H - 2Y_2O_3 \cdot Al_2O_3 - Y_2O_3 \cdot SiO_2 - Y_2O_3.
\end{align*}
\]

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°C. It is reported to be stable only above 1835°C (8). H phase has the apatite structure and its formula is $Y_5(SiO_4)_3N$ which can also be represented as $(Y_2O_3\cdot Si_2N_2O)_4(Y_2O_3\cdot SiO_2)$. 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,0 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 $\beta-Si_3N_4$-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.
References


8. Phase Diagrams for Ceramists, Editors: E. M. Levin, C. R. Robbins and H. F. McMurdie, American Ceramic Society, Columbus, Ohio, 1969 (Figure 2344, p.)
Fig. 1. Representation of the system Si,Al,Y/N,O.
Fig. 2.

Compatibility tetrahedron \( \text{Si}_3\text{N}_4 - \beta 60 - \text{Y}_2\text{O}_3 - 2\text{SiO}_2(\text{Y}'S_2) - 3\text{Y}_2\text{O}_3 - 5\text{Al}_2\text{O}_3(\text{Y}'3\text{A5}) \).
Compatibility tetrahedra $x_{1}3\text{Al}_{2}\text{O}_{3} \cdot 2\text{SiO}_{2}(\text{A}_{3}\text{S}_{2}) - \text{Al}_{2}\text{O}_{3} \cdot \text{Y}_{2}\text{O}_{3} \cdot 2\text{SiO}_{2}(\text{Y}'\text{S}_{2})$

and $x_{1}3\text{Al}_{2}\text{O}_{3} \cdot 2\text{SiO}_{2}(\text{A}_{3}\text{S}_{2}) - \text{Y}_{2}\text{O}_{3} \cdot 2\text{SiO}_{2}(\text{Y}'\text{S}_{2}) - \text{SiO}_{2}$. 

Fig. 3.
<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Composition</th>
<th>Heat Treatment</th>
<th>Phases Present</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. Z Al</td>
<td>Eq. Z Y</td>
<td>Eq. Z O</td>
<td></td>
</tr>
<tr>
<td>1</td>
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<td>0</td>
<td>10.4</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td>1'</td>
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<td>0</td>
<td>10.4</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td>2</td>
<td>31.2</td>
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</tr>
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<td>2'</td>
<td>31.2</td>
<td>0</td>
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<td>1550°C, 1 hr</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>0</td>
<td>66.7</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td>3'</td>
<td>100</td>
<td>0</td>
<td>66.7</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td>4</td>
<td>38.8</td>
<td>21.4</td>
<td>23.0</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td>4'</td>
<td>38.8</td>
<td>21.4</td>
<td>23.0</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td>4''</td>
<td>38.8</td>
<td>21.4</td>
<td>23.0</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Densified; shrinkage = 15%</td>
</tr>
<tr>
<td>5</td>
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<td>29.7</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td>5'</td>
<td>27.1</td>
<td>5.0</td>
<td>29.7</td>
<td>1550°C, 1 hr</td>
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<td>48.3</td>
<td>5.3</td>
<td>50.0</td>
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<tr>
<td>7</td>
<td>72.16</td>
<td>5.7</td>
<td>61.7</td>
<td>1550°C, 1 hr</td>
</tr>
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<td>9</td>
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<td>53.6</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td>10</td>
<td>53.6</td>
<td>16.4</td>
<td>74.0</td>
<td>1550°C, 1 hr</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Foamed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Foamed; lot of liquid at firing temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Foamed</td>
</tr>
<tr>
<td>Specimen No.</td>
<td>Eq. % Al</td>
<td>Eq. % Y</td>
<td>Eq. % O</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>6.5</td>
<td>28.7</td>
<td>71.3</td>
<td></td>
</tr>
<tr>
<td>11'</td>
<td>6.5</td>
<td>28.7</td>
<td>71.3</td>
<td></td>
</tr>
<tr>
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<td>20.5</td>
<td>30.1</td>
<td>83.9</td>
<td></td>
</tr>
<tr>
<td>12'</td>
<td>20.5</td>
<td>30.1</td>
<td>83.9</td>
<td></td>
</tr>
<tr>
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<td>40.0</td>
<td>60.0</td>
<td></td>
</tr>
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<td>50.0</td>
<td>75.1</td>
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</tr>
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<td>16.7</td>
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<td>86.3</td>
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</tr>
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<td>46.2</td>
<td>77.0</td>
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</tr>
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<td>17</td>
<td>28.3</td>
<td>33.9</td>
<td>71.8</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>10.4</td>
<td>62.0</td>
<td>79.3</td>
<td></td>
</tr>
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<td>21.5</td>
<td>64.3</td>
<td>89.4</td>
<td></td>
</tr>
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<td>15.0</td>
<td>45.1</td>
<td>70.0</td>
<td></td>
</tr>
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<td>31.6</td>
<td>47.3</td>
<td>84.1</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>18.3</td>
<td>32.9</td>
<td>63.4</td>
<td></td>
</tr>
<tr>
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<td>39.0</td>
<td>35.1</td>
<td>80.5</td>
<td></td>
</tr>
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<td>24</td>
<td>6.2</td>
<td>6.8</td>
<td>7.3</td>
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**TABLE I (continued)**

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Phases Present</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1550°C, 1 hr</td>
<td>Ø s.s., glass, H</td>
<td>Foamed; evidence of lot of liquid.</td>
</tr>
<tr>
<td>Devitrification</td>
<td>ØY'S2 and H crystallized</td>
<td></td>
</tr>
<tr>
<td>1100°C, 20 hrs</td>
<td>glass</td>
<td></td>
</tr>
<tr>
<td>Devitrification</td>
<td>glass</td>
<td></td>
</tr>
<tr>
<td>1550°C, 1 hr</td>
<td>(SN)Y', Ø-S13N4, Y3'AN5</td>
<td>Shiny bead; complete melting.</td>
</tr>
<tr>
<td>Devitrification</td>
<td>Y2'AN2, Y3'AN5, (SN)Y'</td>
<td>Glassy halo increased in x-ray diffraction</td>
</tr>
<tr>
<td>1550°C, 1 hr</td>
<td>Single phase s.s. between Y2'AN2 and Y2'(SN0)</td>
<td>indicating tendency toward devitrification.</td>
</tr>
<tr>
<td>Devitrification</td>
<td>Y2'-Y2'(SN0) s.s., (SN)Y', Y3'AN5</td>
<td></td>
</tr>
<tr>
<td>1550°C, 1 hr</td>
<td>Y'(SN0), Y3'AN5, glass</td>
<td>Densified; shrinkage = 12%.</td>
</tr>
<tr>
<td>Devitrification</td>
<td>Single phase s.s. between Y2'AN2 and Y2'(SN0)</td>
<td></td>
</tr>
<tr>
<td>1550°C, 1 hr</td>
<td>Single phase s.s. between Y2'AN2 and Y2'(SN0)</td>
<td></td>
</tr>
<tr>
<td>Devitrification</td>
<td>Y2'AN2-Y2'(SN0) s.s., (SN)Y', Y3'AN5, trace of Y'(SN0)</td>
<td></td>
</tr>
<tr>
<td>1550°C, 1 hr</td>
<td>Y2'AN2-Y2'(SN0) s.s., (SN)Y', Y3'AN5</td>
<td>Densified; shrinkage = 19%.</td>
</tr>
<tr>
<td>Devitrification</td>
<td>Y2'AN2-Y2'(SN0) s.s., (SN)Y', Y3'AN5</td>
<td></td>
</tr>
<tr>
<td>1550°C, 1 hr</td>
<td>Y2'AN2-Y2'(SN0) s.s., Y'(SN0), glass</td>
<td>Densified; shrinkage = 19%.</td>
</tr>
<tr>
<td>Devitrification</td>
<td>Y3'AN5, glass</td>
<td></td>
</tr>
<tr>
<td>1550°C, 1 hr</td>
<td>Ø s.s. (SN)Y'</td>
<td>Deformed; lot of liquid occurred.</td>
</tr>
<tr>
<td>Devitrification</td>
<td>Ø s.s. (SN)Y'</td>
<td></td>
</tr>
<tr>
<td>1550°C, 1 hr</td>
<td>Ø s.s. (SN)Y'</td>
<td>Deformed; lot of liquid occurred.</td>
</tr>
</tbody>
</table>

No shrinkage.
<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Eq. % Al</th>
<th>Eq. % Y</th>
<th>Eq. % O</th>
<th>Heat Treatment</th>
<th>Phases Present</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0</td>
<td>9.5</td>
<td>11.8</td>
<td>1550°C, 1 hr</td>
<td>β-Si₃N₄, (SN)Y</td>
<td>No shrinkage.</td>
</tr>
<tr>
<td>26</td>
<td>6.9</td>
<td>8.0</td>
<td>25.4</td>
<td>1550°C, 1 hr</td>
<td>β s.s., glass</td>
<td>Densified; shrinkage = 14%.</td>
</tr>
<tr>
<td>26'</td>
<td>6.9</td>
<td>8.9</td>
<td>25.4</td>
<td>Devitrification at 1250°C, 21 hrs</td>
<td>Y₃A₅, 6Y'S₂ and β-Si₃N₄ crystallized</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>7.6</td>
<td>2.6</td>
<td>11.1</td>
<td>1550°C, 1 hr</td>
<td>β s.s.</td>
<td>Some densification; shrinkage = 9%.</td>
</tr>
<tr>
<td>27'</td>
<td>7.6</td>
<td>2.6</td>
<td>11.1</td>
<td>Devitrification at 1250°C, 21 hrs</td>
<td>Y₃A₅ and β-Si₃N₄ crystallized</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>32.8</td>
<td>19.7</td>
<td>52.4</td>
<td>1550°C, 1 hr</td>
<td>β-Si₃N₄, α-Si₃N₄ (trace, Y₃A₅, Al₂O₃ (trace)</td>
<td>Densified; shrinkage = 16%.</td>
</tr>
<tr>
<td>29</td>
<td>0</td>
<td>12.0</td>
<td>100</td>
<td>1550°C, 1 hr</td>
<td>Y₂SiO₃, 6Y'S₂, small amount of H</td>
<td>No densification; shrinkage = 2%.</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>29.2</td>
<td>88.8</td>
<td>1550°C, 1 hr</td>
<td>H</td>
<td>Some densification; shrinkage = 10%; 2.5% wt. gain due to oxidation.</td>
</tr>
<tr>
<td>31</td>
<td>38.1</td>
<td>15.6</td>
<td>62.0</td>
<td>1550°C, 1 hr</td>
<td>β-30, Y₃A₅, glass</td>
<td>Foamed and deformed; some liquid occurred.</td>
</tr>
<tr>
<td>32</td>
<td>60.9</td>
<td>13.7</td>
<td>61.9</td>
<td>1550°C, 1 hr</td>
<td>β-50, Y₃A₅, some Al₂O₃</td>
<td>Some densification; shrinkage = 8%.</td>
</tr>
<tr>
<td>33</td>
<td>0</td>
<td>22.5</td>
<td>52.5</td>
<td>1550°C, 1 hr</td>
<td>β-Si₃N₄, α-Si₃N₄, 6Y'S₂, H</td>
<td>Some foaming.</td>
</tr>
<tr>
<td>34</td>
<td>0</td>
<td>27.0</td>
<td>50.2</td>
<td>1550°C, 1 hr</td>
<td>β-Si₃N₄, H</td>
<td>Densified; shrinkage = 18%.</td>
</tr>
<tr>
<td>35</td>
<td>41.9</td>
<td>9.0</td>
<td>81.4</td>
<td>1550°C, 1 hr</td>
<td>x₁, glass</td>
<td>Foamed.</td>
</tr>
<tr>
<td>36</td>
<td>41.6</td>
<td>17.1</td>
<td>100</td>
<td>1550°C, 1 hr</td>
<td>glass, some Al₂O₃</td>
<td>Glassy bead, lot of liquid.</td>
</tr>
<tr>
<td>37</td>
<td>31.2</td>
<td>40.2</td>
<td>100</td>
<td>1550°C, 1 hr</td>
<td>Y₃A₅, 6Y'S₂, 4Y'S₂, glass</td>
<td>Lot of liquid occurred.</td>
</tr>
<tr>
<td>38</td>
<td>33.6</td>
<td>47.9</td>
<td>100</td>
<td>1550°C, 1 hr</td>
<td>Y₃A₅, Y'S, glass</td>
<td>Deformed; some liquid occurred.</td>
</tr>
<tr>
<td>Specimen No.</td>
<td>Eq.2 Al</td>
<td>Eq.2 Y</td>
<td>Eq.2 O</td>
<td>Heat Treatment</td>
<td>Phases Present</td>
<td>Remarks</td>
</tr>
<tr>
<td>-------------</td>
<td>---------</td>
<td>--------</td>
<td>--------</td>
<td>----------------</td>
<td>--------------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>39</td>
<td>4.0</td>
<td>14.6</td>
<td>53.5</td>
<td>1550°C, 1 hr</td>
<td>Si₃Na₂O s.s., glass</td>
<td>Deformed; some liquid occurred.</td>
</tr>
<tr>
<td>40</td>
<td>4.8</td>
<td>7.8</td>
<td>42.3</td>
<td>1550°C, 1 hr</td>
<td>Si₃Na₂O s.s., traces of β-Si₃N₄ and α-Si₃N₄, glass</td>
<td>Some densification; shrinkage = 10%.</td>
</tr>
<tr>
<td>40'</td>
<td>4.8</td>
<td>7.8</td>
<td>42.3</td>
<td></td>
<td>Devitrification at 1200°C, 16 hrs</td>
<td>YY'S₂ crystallized</td>
</tr>
<tr>
<td>41</td>
<td>7.6</td>
<td>40.6</td>
<td>48.0</td>
<td>1550°C, 1 hr</td>
<td>Y₂'Al₂' (SN)Y'</td>
<td>Little densification; shrinkage = 4%.</td>
</tr>
<tr>
<td>42</td>
<td>16.3</td>
<td>34.4</td>
<td>50.7</td>
<td>1550°C, 1 hr</td>
<td>Y'(SNO), Y₁'Al₂</td>
<td>Some densification; shrinkage = 10%.</td>
</tr>
<tr>
<td>43</td>
<td>49.0</td>
<td>10.2</td>
<td>49.0</td>
<td>1550°C, 1 hr</td>
<td>Y₁'Al₂, β-40, trace of x₂</td>
<td>Foamed; 4% weight gain.</td>
</tr>
<tr>
<td>44</td>
<td>76.0</td>
<td>14.0</td>
<td>62.3</td>
<td>1550°C, 1 hr</td>
<td>Y₁'Al₂, x₂, Al₂O₃, trace of β-40</td>
<td>Sample burst into many pieces.</td>
</tr>
<tr>
<td>45</td>
<td>85.4</td>
<td>16.6</td>
<td>79.7</td>
<td>1550°C, 1 hr</td>
<td>Y₁'Al₂, Al₂O₃, AlN</td>
<td>Sample burst into many pieces.</td>
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</tbody>
</table>