

$\text{Al}_2\text{O}_3$  and, perhaps, even more. Similar reasoning for the matrix analyses leads to the conclusion that the glass matrix in Fig. 1 has an  $\text{Al}_2\text{O}_3$  content of  $\approx 6$  mol%.

To assess the relative accuracy of the microchemical analysis, we analyzed a larger area ( $\approx 0.5 \mu\text{m}^2$ ) of the same glass sample and obtained an overall composition of  $\approx 17$  mol%  $\text{Al}_2\text{O}_3$ -83 mol%  $\text{SiO}_2$  for the glass. This value is reasonably close to the starting composition of 15 mol%  $\text{Al}_2\text{O}_3$  and suggests an experimental error of  $\pm 2$  mol% for all the quantitative data in the present work.

The compositions of the glass matrix ( $< 6$  mol%  $\text{Al}_2\text{O}_3$ ) and the droplet phase ( $> 51$  mol%  $\text{Al}_2\text{O}_3$ ) determined in the present study are consistent with the concept of a liquid miscibility gap in the binary system  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ , as predicted on thermodynamic grounds by Risbud and Pask<sup>6</sup> and as compositionally defined in the classic experimental work of MacDowell and Beall.<sup>3</sup> The experimental determination of the upper temperature limits of the miscibility gap, however, must still remain somewhat uncertain. It may, perhaps, be possible to use hot-stage STEM analysis at various temperatures to obtain chemical analysis of the separated phase in situ, thus defining the miscibility gap at each temperature. However, such experiments will be limited to less than  $\approx 1000^\circ\text{C}$  since rapid crystallization begins in binary  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  glasses at  $\approx 1000^\circ\text{C}$ .<sup>4</sup> In those cases where phase separation in glasses occurs on a scale comparable to the thickness of the electron-transparent foil, the STEM technique may provide a direct quantitative method of defining miscibility gaps in glassy systems.

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<sup>6</sup>S. H. Risbud and J. A. Pask, "Calculated Thermodynamic Data and Metastable Immiscibility in the System  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ ," *J. Am. Ceram. Soc.*, **60** [9-10] 418-24 (1977).

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<sup>10</sup>G. Cliff and G. W. Lorimer, "Quantitative Analysis of Thin Specimens," *J. Microsc. (Oxford)*, **103** [2] 203-207 (1975).

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### Subsolidus Phase Relations in Part of the System Si,Al,Y/N,O

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VARIOUS metal oxides (e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{MgO}$ ) are 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

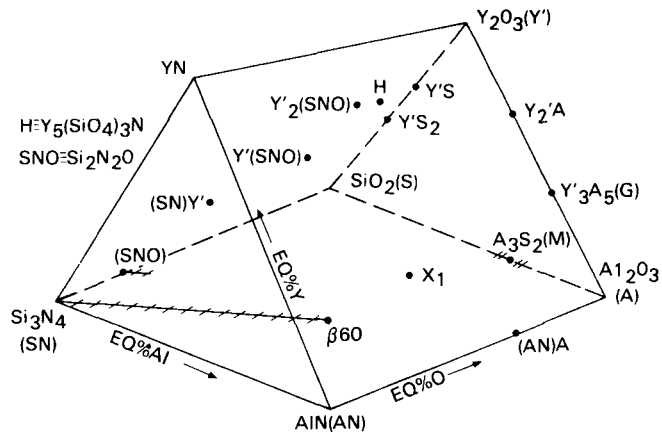


Fig. 1. Representation of the system Si,Al,Y/N,O.

$\text{Si}_3\text{N}_4$ -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 Si,M/N,O where M is a metal, e.g. Al, Y, and Mg.

Subsolidus phase equilibria in the systems Si,Al/N,O and Si,Y/N,O have been studied in detail.<sup>1-4</sup> Solid-liquid equilibria at  $1750^\circ\text{C}$  in the system Si,Al/N,O have also been reported.<sup>5</sup> The combination of these two systems gives a quasi-quaternary system Si,Al,Y/N,O. The study of phase equilibria in the system Si,Al,Y/N,O 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,<sup>†</sup> alumina,<sup>‡</sup> silica,<sup>§</sup> and yttria.<sup>¶</sup> 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  $\text{Si}_3\text{N}_4$ , 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.

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 disks over a laboratory heater and then cold-pressed into pellets 3.3 cm in diam. by 1.3 cm thick at 110 MPa. The pellets were placed in screw-top graphite crucibles which were lined with BN to avoid direct contact between the pellets and the graphite crucibles. The crucibles were placed in a large resistance-heated furnace with a graphite heating element. The specimens were fired in nitrogen at  $1550^\circ\text{C}$  and atmospheric pressure. The heating rate was  $200^\circ\text{C}/\text{min}$  and the holding time at  $1550^\circ\text{C}$  was 1 h. The specimens were cooled in the furnace at a rate of  $\approx 200^\circ\text{C}/\text{min}$  to  $800^\circ\text{C}$ . Further cooling to room temperature was somewhat slower. Samples with  $< 2\%$  weight loss on firing were considered for deriving the phase relations.

Selected specimens, some of which showed the continued presence of  $\alpha$ - $\text{Si}_3\text{N}_4$  after the 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 on grinding and refiring. This procedure indicated that, when the amount of silicon nitride in the overall composition was  $< 60$  wt%, equilibrium was readily ob-

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\*HCST 2633, combined oxygen = 2.9%, H. C. Starck, Goslar, Federal Republic of 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-Berylco Industries, Inc., Reading, Pa.

‡Linde A or calcined alumina A-16,  $> 99.5\%$   $\text{Al}_2\text{O}_3$ ; Aluminum Company of America, Pittsburgh, Pa.

§Flint No. 25,  $> 99.5\%$   $\text{SiO}_2$ ; Rovin Ceramics, Dearborn Heights, Mich.

¶No. 5600 yttrium oxide, 99.9% pure; Molycorp, Inc., White Plains, N.Y.

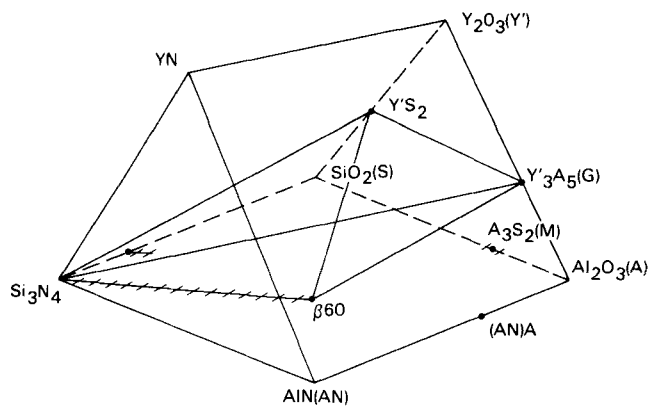


Fig. 2. Compatibility tetrahedron  $\text{Si}_3\text{N}_4\text{-}\beta 60\text{-Y}_2\text{O}_3\cdot 2\text{SiO}_2(\text{Y}'\text{S}_2)\text{-}3\text{Y}_2\text{O}_3\cdot 5\text{Al}_2\text{O}_3(\text{Y}'_3\text{A}_5)$ .

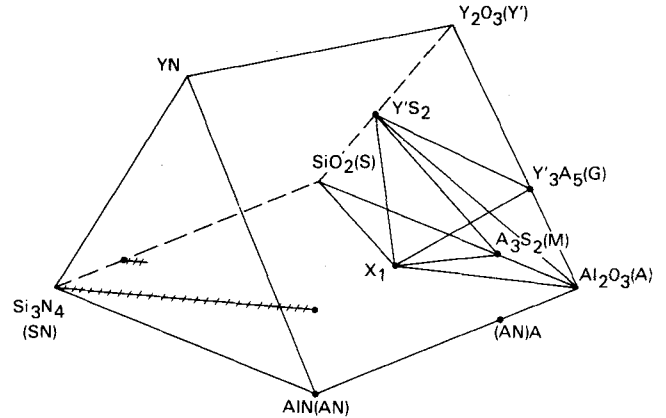


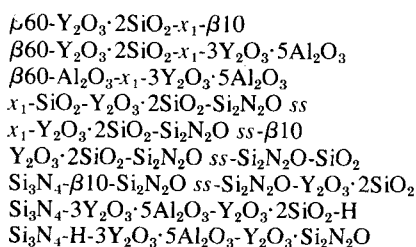
Fig. 3. Compatibility tetrahedra  $x_4\cdot 3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2(\text{A}_3\text{S}_2)\text{-Al}_2\text{O}_3\cdot \text{Y}_2\text{O}_3\cdot 2\text{SiO}_2(\text{Y}'\text{S}_2)$  and  $x_4\cdot 3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2(\text{A}_3\text{S}_2)\text{-Y}_2\text{O}_3\cdot 2\text{SiO}_2(\text{Y}'\text{S}_2)\text{-SiO}_2$ .

tained in the first firing, as was also the case when some liquid ( $> 10\%$ ) was formed in the samples at the firing temperature.

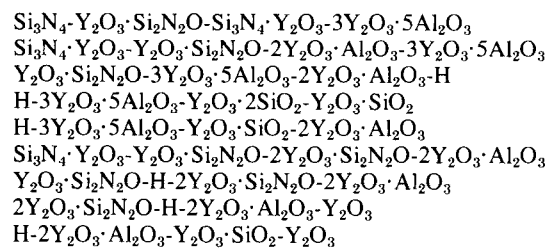
About 50 compositions were fired at  $1550^\circ\text{C}$  to obtain the phase relations. The compositions that contained substantial amounts of glass after firing were annealed at  $1150^\circ$  to  $1250^\circ\text{C}$  for an extended time ( $\approx 24$  h) to devitrify the glass. Subsolidus phase relations in the region that is liquid at  $1550^\circ\text{C}$  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  $\text{CuK}\alpha$  radiation was used to scan the powdered samples between  $10^\circ$  and  $80^\circ 2\theta$  at a rate of  $2^\circ/\text{min}$ . Standard optical microscopy was used for microstructure observation. The compositions made, heat treatment used, and the phases observed are listed in Table I.\*

The quasi-quaternary system  $\text{Si, Al, Y/N, O}$  has three independent composition variables. Therefore, the subsolidus phase relations in the system can be represented in a triangular prism (Fig. 1). The known compounds in the oxide ternary  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$  and the quasi-ternaries  $\text{Si, Al/N, O}$  and  $\text{Si, Y/N, O}$  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 an 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 the  $\text{Si}_3\text{N}_4\text{-}\beta 60\text{-Y}_2\text{O}_3\cdot 2\text{SiO}_2\text{-}3\text{Y}_2\text{O}_3\cdot 5\text{Al}_2\text{O}_3$  tetrahedron (Fig. 2) and the  $x_4\cdot 3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Y}_2\text{O}_3\cdot 2\text{SiO}_2$  and  $x_4\cdot 3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{-Y}_2\text{O}_3\cdot 2\text{SiO}_2\text{-SiO}_2$  tetrahedra (Fig. 3). Here  $\beta 60$  is a  $\beta\text{Si}_{3-x}\text{Al}_x\text{O}_x\text{N}_{4-x}$  solid solution containing 60 eq. % Al, i.e.  $x=2.00$ . The  $3\text{Y}_2\text{O}_3\cdot 5\text{Al}_2\text{O}_3$  is the well-known cubic yttrium-aluminum garnet. The yttrium disilicate  $\text{Y}_2\text{O}_3\cdot 2\text{SiO}_2$  has four polymorphic forms ( $\alpha, \beta, \gamma$ , and  $\delta$ ) and they were identified using the work of Ito and Johnson.<sup>6</sup>  $x_1$  is a compound  $2\text{Si}_3\text{N}_4\cdot 9\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$  in the system  $\text{Si, Al/N, O}$ . Other compatibility tetrahedra in the system are:



\*For Table I, order ACSD-158 from Data Depository Service, The American Ceramic Society, 65 Ceramic Drive, Columbus, Ohio 43214.



No quinary, i.e. five-component, compounds were found in the part of the system investigated;  $2\text{Y}_2\text{O}_3\cdot \text{Si}_2\text{N}_2\text{O}$  and  $2\text{Y}_2\text{O}_3\cdot \text{Al}_2\text{O}_3$  are isostructural, with a monoclinic structure. They form a complete series of solid solutions involving interchange of  $\text{Si-N}$  and  $\text{Al-O}$  pairs.<sup>7</sup> The  $\text{Y}_2\text{O}_3\cdot \text{Si}_2\text{N}_2\text{O}$  probably has the same structure as the high-temperature phase  $\text{Y}_2\text{O}_3\cdot \text{Al}_2\text{O}_3$ . However,  $\text{Y}_2\text{O}_3\cdot \text{Al}_2\text{O}_3$  was not observed in the specimens made at  $1550^\circ\text{C}$ . It is reported to be stable only above  $1825^\circ\text{C}$ .<sup>8</sup> The H phase has the apatite structure and its formula is  $\text{Y}_5(\text{SiO}_4)_3\text{N}$ , which can also be represented as  $(\text{Y}_2\text{O}_3\cdot \text{Si}_2\text{N}_2\text{O})\cdot 4(\text{Y}_2\text{O}_3\cdot \text{SiO}_2)$ . The homogeneity ranges of the phases  $\text{Y}_2\text{O}_3\cdot \text{Si}_2\text{N}_2\text{O}$ ,  $\text{Si}_3\text{N}_4\cdot \text{Y}_2\text{O}_3$ , and  $\text{Y}_4(\text{SiO}_4)_3\text{N}$  are limited. This aspect of the phase diagram needs further investigation. There is no phase in the  $\text{Si, Y/N, O}$  plane corresponding to the garnet  $3\text{Y}_2\text{O}_3\cdot 5\text{Al}_2\text{O}_3$ .

The high-temperature mechanical properties of hot-pressed and sintered  $\text{Si}_3\text{N}_4$  ceramics fabricated using  $\text{MgO}$  or  $\text{Y}_2\text{O}_3$  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  $\beta\text{-Si}_3\text{N}_4$ -based ceramics which have a more refractory crystalline second phase instead of the glassy grain-boundary phase. Such a development will significantly improve the high-temperature mechanical properties of these ceramics.

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<sup>2</sup>L. J. Gauckler, H. Hohnke, and T. Y. Tien, "The System  $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Y}_2\text{O}_3$ "; to be published in the *Journal of the American Ceramic Society*.

<sup>3</sup>R. R. Wills, S. Holmquist, J. M. Wimmer, and J. A. Cunningham, "Phase Relations in the System  $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-SiO}_2$ ," *J. Mater. Sci.*, **11** [7] 1305-1309 (1976).

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<sup>8</sup>E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagrams for Ceramists*, 1969. Edited by M. K. Reser. American Ceramic Society, Columbus, Ohio; Fig. 2344.