J. Am. Ceram. Soc., **69** [10] C-241-C-242 (1986)

Subsolidus Phase Relationships in Si_3N_4–AlN–Rare-Earth Oxide Systems

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The subsolidus phase relationships in Si_3N_4–AlN–rare-earth oxide (Me_2O_3 where Me=Nd, Sm, Gd, Dy, Er, and Yb) systems were studied. Solid-solution regions with the α-Si_3N_4 structure were delineated along the Si_3N_4–"Me_2O_3:9AlN" joins for all of the rare-earth oxide systems studied. The solubility limits of these solid solutions increased with decreasing size of the rare-earth ions.

THE EXISTENCE of silicon nitride solid solutions with the α structure (α-sialon) has been reported by Jack and his associates.[1,2] This series of solid solutions can be regarded as the stuffed derivatives of α-Si_3N_4 which is analogous to that of the stuffed derivatives of the SiO_2 structure.[3] The concept of stuffed derivatives of the SiO_2 structure can be described as Al^{3+} ion substitution for Si^{4+} ions in the SiO_2 structure; the charge deficiencies are compensated by locating large alkaline or alkaline-earth ions in the interstitial sites of the silica structure.

Single-phase α-Si_3N_4 solid-solution compositions should be located in the composition triangle between sialon compositions ($Si_{6-x}Al_xN_{8-x}O_x$ where x=0 to 4) and the composition point "MeN:3AlN" (where Me is a trivalent rare-earth ion) in the system Si_3N_4–SiO_2–AlN–Al_2O_3–MeN–Me_2O_3 as shown in Fig. 1. The compositions on the binary join Si_3N_4 and the composition point Me_2O_3:9AlN in the triangle Si_3N_4–AlN–Me_2O_3 contain compositions of α-Si_3N_4 solid solutions $Me_x(Si, Al)_{12}(N, O)_{16}$. This composition line is the intercept of the triangle Si_3N_4–AlN–Me_2O_3 and the triangle sialon–"MeN:3AlN." These relationships are illustrated in Fig. 1.

The relative size of the rare-earth ions and the size of the interstitial sites in the α-silicon nitride structure should be a factor determining the solubility limit of the α-sialon solid solutions in systems containing different rare-earth ions. The α-Si_3N_4 solid solutions on the join Si_3N_4–Me_2O_3:9AlN containing Y_2O_3 have been reported previously by one of the authors.[4] This paper will discuss the results in Si_3N_4–AlN–Me_2O_3 systems where "Me" is Nd, Sm, Gd, Dy, Er, and Yb.

Sample Preparation

The starting powders used were Si_3N_4 (LC10),[‡] AlN,[§] and rare-earth oxides. Since both the silicon nitride and the aluminum nitride powders contained oxygen as an impurity, the compositions studied should be regarded as richer in oxygen than the compositions on the plane Si_3N_4–AlN–Me_2O_3. The purities of the rare-earth oxides were 99.9% or better. Powders of silicon nitride, aluminum nitride, and rare-earth oxides were weighed and mixed in an agate jar under absolute ethyl alcohol on a rotating mill for 2 h. Dried mixtures were hot-pressed at 1700°C under a pressure of 30 MPa in BN-coated graphite dies in a graphite resistance furnace under a mild flow of nitrogen. After hot-pressing, the furnace was cooled at a rate of ≈200°C/min in the high-temperature region. Average weight loss was lower than 2% for all of the runs. Temperature and time used for hot-pressing are given in Table I.[¶]

End points for hot-pressing were obtained where no further phase change was observed when specimens were heated for longer times.

Results

Subsolidus Phase Relationships

Hot-pressed specimens were examined using X-ray diffraction with monochromated Cu$K\alpha$ radiation. The results used to construct the subsolidus phase relationships are given in Table I. In these systems, the following compatibility triangles were observed for Si_3N_4–AlN–Me_2O_3 systems where Me=Gd, Dy, Er, and Yb: three-phase regions—(1) α-Si_3N_4($s.s.$)–β-Si_3N_4–AlN, (2) α-Si_3N_4($s.s.$)–β-Si_3N_4–Si_3N_4·Me_2O_3, (3) α-Si_3N_4($s.s.$)–AlN–Si_3N_4·Me_2O_3, (4) Si_3N_4·Me_2O_3–AlN–Si_2N_2O·2Me_2O_3, (5) Si_2N_2O·2Me_2O_3–AlN–Me_2O_3; two-phase regions—(1) α'-Si_3N_4($s.s.$)–AlN, (2) α'-Si_3N_4($s.s.$)–Si_3N_4·Me_2O_3. The above subsolidus phase relationships are the same as reported in the system Si_3N_4–AlN–Y_2O_3.[4] The subsolidus phase relationships of these systems are plotted in Fig. 2. It should be noted that the compound Si_2N_2O·2Me_2O_3 does not lie in the plane sialon–MeN:3AlN.

For Si_3N_4–AlN–Me_2O_3 systems where Me=Nd and Sm, an additional compound (AlN·Me_2O_3 or Me_2AlO_3N) has

CONTRIBUTING EDITOR—K. G. FRASE

Received February 18, 1986; revised copy received May 13, 1986; approved June 9, 1986.

Supported by the National Science Foundation (U.S.A.) under the U.S.-China Cooperative Research program (Grant No. INT 8311995).

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¶Available both from University Microfilms, Ann Arbor, MI 48106, and from the Data Depository Service (ACSD-201), The American Ceramic Society, 65 Ceramic Drive, Columbus, OH 43214.

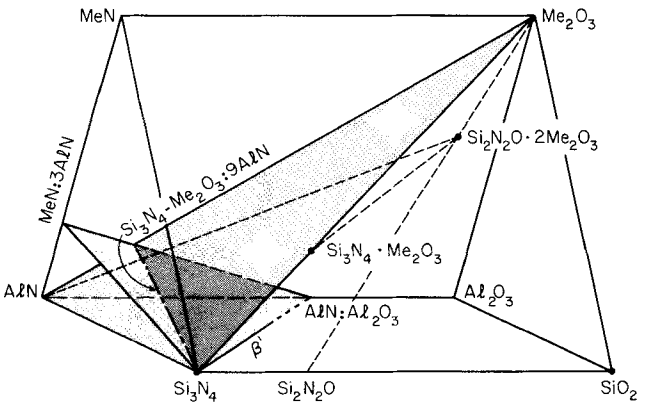

Fig. 1. The system Si_3N_4–SiO_2–AlN–Al_2O_3–MeN–Me_2O_3 (Me=Yb, Er, Dy, Gd, Sm, and Nd).

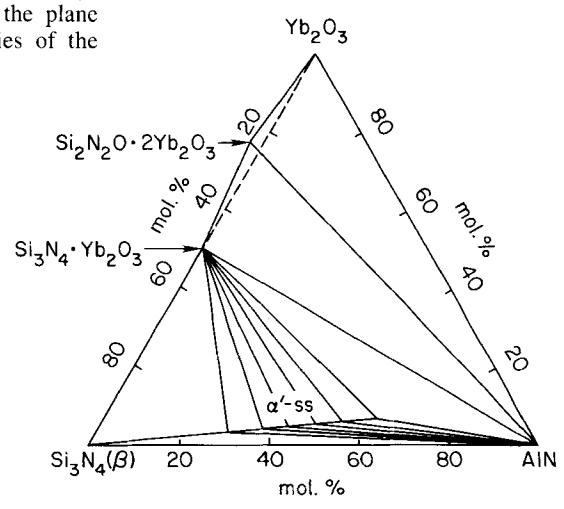

Fig. 2. The system Si_3N_4–AlN–Yb_2O_3. (Note: Systems with Er_2O_3, Dy_2O_3, or Gd_2O_3 have the same behavior.)

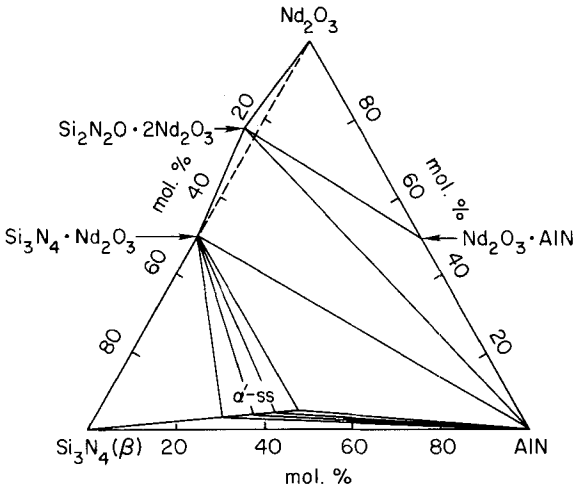

Fig. 3. The system Si_3N_4–AlN–Nd_2O_3. (Note: The system with Sm_2O_3 has similar behavior.)

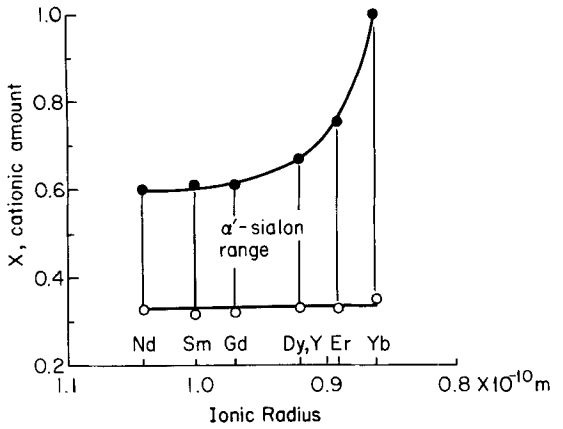

Fig. 4. Solid solubility limit of α-Si_3N_4 solid solutions $Me_x(Si, Al)_{12}(N, O)_{16}$.

been observed. The X-ray patterns of these compounds are given in Table II.[1] The subsolidus phase relationships in these two systems are similar to those of the other systems. However, in addition to the three-phase and two-phase regions given above, the subternary system Si_2N_2O·$2Me_2O_3$–Me_2O_3–AlN was divided into two subternary systems: Si_2N_2O·$2Me_2O_3$–AlN–AlN·Me_2O_3 and Si_2N_2O·$2Me_2O_3$–AlN·Me_2O_3–Me_2O_3. The subsolidus phase diagrams of these systems are given in Fig. 3.

α-Si₃N₄ Solid Solutions

The α-Si_3N_4 solid solutions investigated in this study can be considered as solid solutions formed between Si_3N_4 and the composition "Me_2O_3·9AlN" or "$Me_{2/3}(Al_3N_3O)$" as mentioned in the previous section. Therefore, the solid solution of the α-Si_3N_4 structure in these systems can be written as $Me_x(Si_{12-4.5x}Al_{4.5x})$-$(N_{16-1.5x}O_{1.5x})$, i.e., $Me_x(Si, Al)_{12}(N, O)_{16}$. As shown in Fig. 4, the lower limits of the solid solutions for all rare-earth ions started at $x=0.33$ with the same hexagonal lattice parameter of $a=7.80$ Å and $c=5.69$ Å. The upper limit of the α-Si_3N_4(*s.s.*) region increased as the size of the rare-earth ions became smaller. The values of x are plotted as a function of size of the rare-earth ions in Fig. 4. The lattice parameters of the solid solutions at their upper solubility limits are given in Table III. It shows that the lattice parameters of the limiting compositions are almost the same for compositions containing different amounts of different rare-earth ions. These results indicated that the α-silicon nitride structure can only tolerate a certain amount of distortion. Figure 4 can be used to extrapolate solid solubilities for other rare-earth ions. However, it is not known whether this curve can be used to predict the solubility of alkaline-earth and alkaline metal ions in α-Si_3N_4 solid solutions.

Table III. Compositions and Unit-Cell Dimensions of α'-Sialons with the Most Extensive Solubility

Compositions	*a* (nm)	*c* (nm)	*c*/*a*
$Nd_{0.6}Si_{8.5}Al_{3.5}O_{1.7}N_{14.3}$	0.785	0.572	0.729
$Sm_{0.6}Si_{9.2}Al_{2.8}ON_{15}$	0.785	0.572	0.729
$Gd_{0.6}Si_{9.2}Al_{2.8}ON_{15}$	0.785	0.572	0.729
$Dy_{0.67}Si_9Al_3ON_{15}$	0.786	0.573	0.729
$Er_{0.75}Si_{8.5}Al_{3.5}O_{1.25}N_{14.75}$	0.787	0.574	0.729
$YbSi_7Al_5O_2N_{14}$	0.789	0.575	0.729

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