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Phase relationships in Si_3N_4–AlN–M_xO_y systems and their implications for sialon fabrication

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Phase relationships in Si_3N_4–AlN–M_xO_y systems involving α′-sialon, where M represents lithium, magnesium, calcium, yttrium, neodymium, samarium, gadolinium, dysprosium, erbium and ytterbium are outlined. Their implications for the formation and fabrication of single-phase α′-sialon and two-phase β:α′ sialon ceramics are discussed.

1. Introduction

Because α′-sialon (α-Si_3N_4 solid solution) has high hardness and good thermal-shock resistance it is regarded as a possible engineering material. Many studies have been made of the formation [1–9], fabrication and properties [10–13] of α′ ceramics and the tailoring of two-phase or multiphase materials containing α′-sialon is of interest. In order to design such materials the compatible phase regions in M–Si–Al–O–N systems need to be known, and so an understanding of the phase relationships involving α′ is important.

In the $Si_{12}N_{16}$ unit cell of α-Si_3N_4 there exist two large interstitial sites that can accommodate additional metal atoms. α-Si_3N_4 solid solution is formed by partial replacement of Si^{4+} by Al^{3+}, i.e. $(m+n)$ (Si–N) by m (Al–N) and n (Al–O) resulting in a general formula $M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$ where $x < 2$ and where valency compensation is effected by additional ions (M) occupying the interstices in the (Si, Al)–(O, N) network. The additional M ions stabilize the α-Si_3N_4 structure up to higher temperatures, thereby establishing equilibrium between solid solutions based on α-Si_3N_4 and β-Si_3N_4. In the M–Si–Al–O–N Jänecke prism (shown in Fig. 1 for a trivalent metal M) there is a two-dimensional planar region of α′ stability with compositions located within the triangle formed by the β′ composition line $Si_{6-z}Al_zO_zN_{8-z}$, extended to AlN:Al_2O_3, and the composition point MN:3AlN [3–7]. The MN nitrides of yttrium (Y) and the rare-earth metals (R) are, like those of the alkali and alkali-earth metals, sensitive to hydrolysis and oxidation. Thus, for experimental convenience, the use of these metal nitrides was avoided in the present work and Si_3N_4–AlN–M_xO_y systems were studied instead of the whole range of compositions within the β′-MN:3AlN triangle. In Si_3N_4–AlN–M_xO_y systems, a one-dimensional region of α′ stability occurs on the binary join Si_3N_4–M_xO_y:AlN where the ratio M_xO_y:AlN is maintained, respectively, for univalent, divalent and trivalent metal atoms, at M_2O:3AlN (M^{1+}), MO:3AlN (M^{2+}) and $M_{2/3}O$:3AlN (M^{3+}). This composition line is the intercept of the triangle Si_3N_4–AlN–M_xO_y and the triangle β′-MN:3AlN (see Fig. 1). Phase relationships in Si_3N_4–AlN–M_xO_y systems where M includes lithium, magnesium, calcium, yttrium, neodymium, samarium, gadolinium, dysprosium, erbium and ytterbium have been established [7, 14–16], the reaction sequences under different firing conditions for Y-α′ and Y-α′:β′ sialons have been studied [17], and two-phase β:α′ composites have also been fabricated by gas pressure sintering (GPS) appropriate mixtures of nitrides plus oxides.

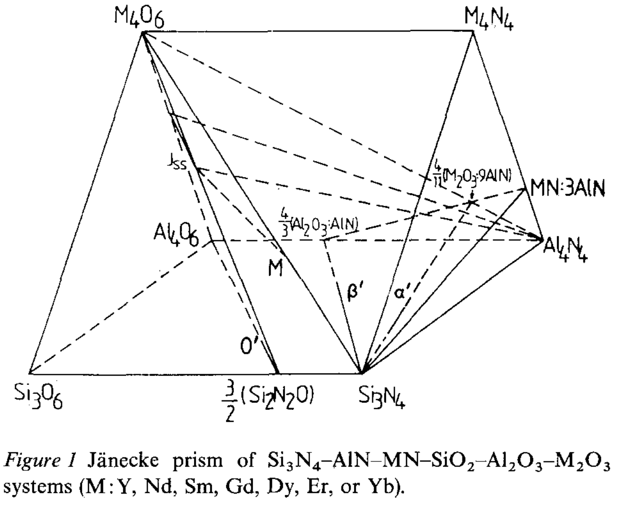

Figure 1 Jänecke prism of Si_3N_4–AlN–MN–SiO_2–Al_2O_3–M_2O_3 systems (M: Y, Nd, Sm, Gd, Dy, Er, or Yb).

This paper gives an overview of work at Shanghai Institute of Ceramics on phase relationships and their implication for sialons fabrication. There are, of course, inherent limitations in studying "one-dimensional" compositions of Si_3N_4–MqO:3AlN systems compared with the full range of "two-dimensional" α′ and "three-dimensional" α′:β′ compositions that require synthesis from nitride plus oxide mixtures of Si_3N_4–AlN–MpN–Al_2O_3–MqO.

2. Experimental procedure

The starting powders used were Si_3N_4, AlN, Li_2O (produced by decomposing Li_2CO_3), MgO (produced by decomposing $Mg(OH)_2 \cdot 4MgCO_3 \cdot 5H_2O$), Y_2O_3 and rare-earth oxides (99.9% purities). Selected compositions were made by mixing the required amounts

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of the starting powders in an agate mortar under absolute alcohol for 1.5–2.0 h. Dried mixtures were isostatically pressed into a cylinder (diameter 5 mm × 10 mm) under 200 MPa for measuring the melting point and liquid-phase region in the Li_2O-, MgO-, CaO-containing systems. For the determination of phase compositions, the samples were prepared by firing or hot-pressing (under a pressure of 30 MPa) at different temperatures 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 $\sim 200\,^{\circ}\mathrm{C\,min^{-1}}$ in the high-temperature region. Samples that underwent $< 2\%$ weight loss on firing were considered in deriving the phase relations. It was assumed that equilibrium was attained when unreacted α-Si_3N_4 was no longer detected.

X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA) were used for phase composition analysis, determination of lattice parameters and observation of microstructure.

3. Results and discussion

3.1. Phase relationships

All Si_3N_4–AlN–M_xO_y systems investigated have similar phase relationships as shown by Figs 2–6. Single-phase α' occurs on the lines Si_3N_4–Li_2O:3AlN, Si_3N_4–CaO:3AlN and Si_3N_4–$R_{2/3}O$:3AlN but not for Mg-α'-sialon. The lower solubility limits (x) in the α'-$M_x(Si, Al)_{12}(O, N)_{16}$ structure are all near $x = 0.3$ cations per cell and the upper limits are 1.5 (Li), 1.4 (Ca), 0.67 (Y) and 0.6–1.0 (Nd–Yb; see Fig. 7), indicating that ions with lower valency or, for rare-earth elements all with the same valency, smaller size, are accommodated more easily in the interstices. The corresponding replacement of Si^{4+} by Al^{3+} is, of course, in the reverse order because each interstitial cation (M) requires the replacement of 1 Si atom by 1.5 Al for Li_2O:3AlN, 3.0 Al for CaO:3AlN and 4.5 Al for $R_{2/3}O$:3AlN.

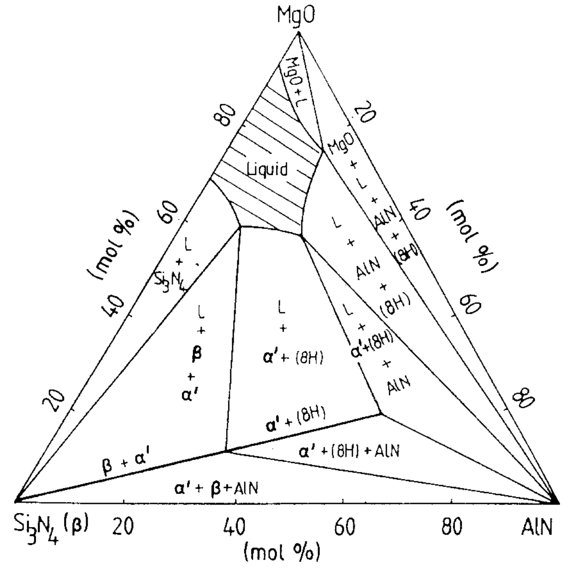

Figure 3 Isothermal section at 1750 °C of the Si_3N_4–AlN–MgO system [16].

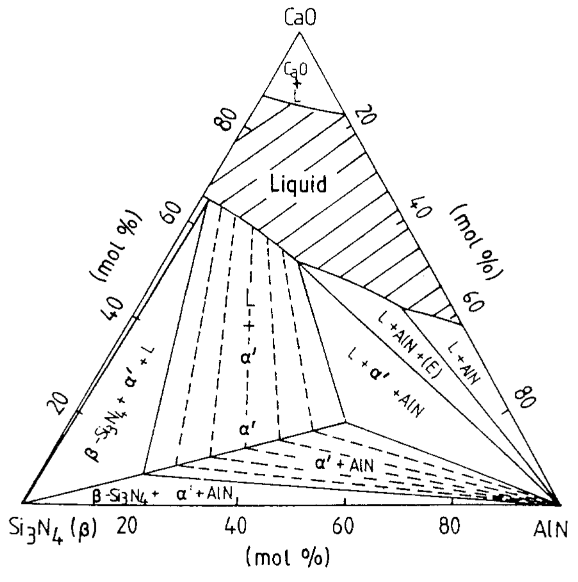

Figure 4 Isothermal section at 1700 °C of the Si_3N_4–AlN–CaO system [14].

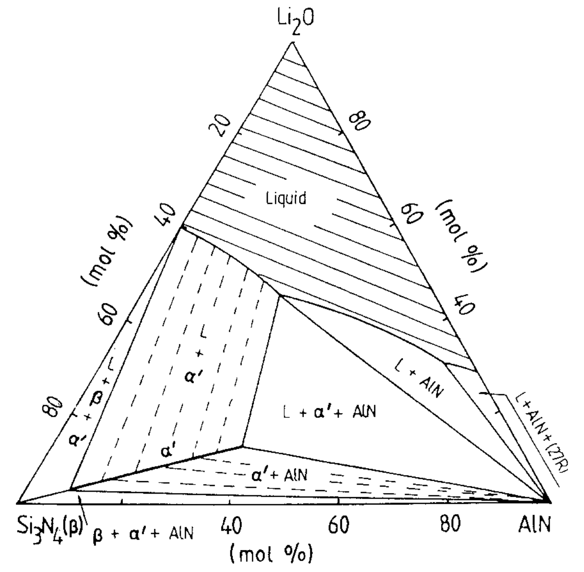

Figure 2 Isothermal section at 1750 °C of the Si_3N_4–AlN–Li_2O system [15].

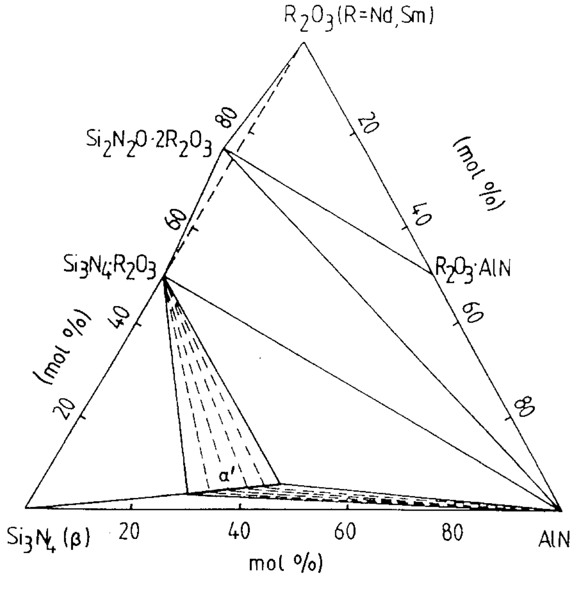

Figure 5 Subsolidus phase diagram of the Si_3N_4–AlN–R_2O_3 (R: Nd, Sm) systems (after [7]).

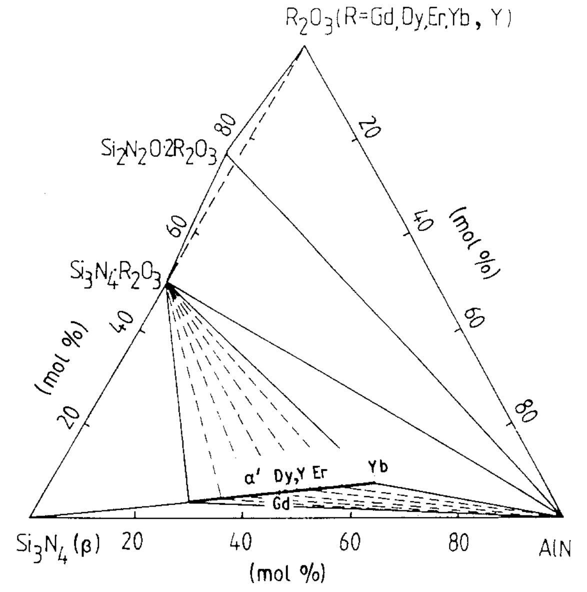

Figure 6 Subsolidus phase diagram of the Si_3N_4–AlN–R_2O_3 (R:Gd, Dy, Er, Yb, and Y) systems (after [7]).

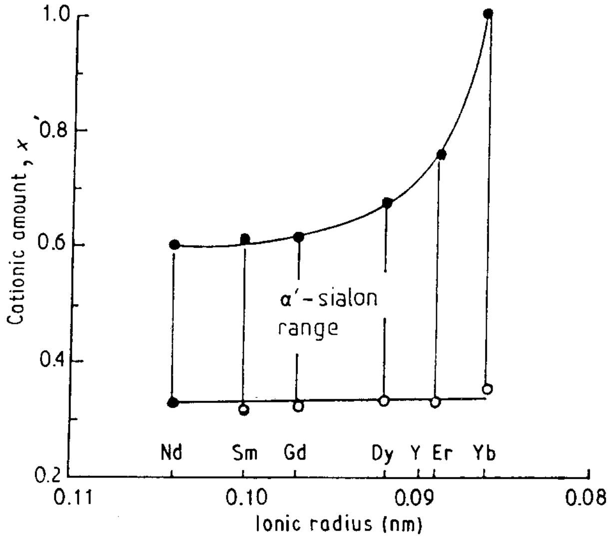

Figure 7 Solid solubility limits of α′ along the join Si_3N_4–$M_{2/3}O$:3AlN (after [7]).

Li-α′, Ca-α′ and R(Y)-α′ are compatible with β-Si_3N_4 and AlN forming two-phase regions of α′ plus β-Si_3N_4 and α′ plus AlN, respectively. Surface oxides of both Si_3N_4 and AlN often cause the nominal composition to deviate slightly from the "one-dimensional" line towards "two-dimensional" plane where α′ forms. Although the small and variable amounts of Al_2O_3 and SiO_2 impurities in the system might produce minor amounts of β′, it cannot be controlled and thus cannot change the equilibrium between β-Si_3N_4 and α′ with lower solubility limit. According to one-dimensional compositions used with Si_3N_4 + AlN (without Al_2O_3) and with a ratio of MqO:AlN fixed at 1:3 (i.e. M_2O:3AlN, MO:3AlN, $R_{2/3}O$:3AlN), the uppermost theoretical limits of α′ are $M_2(Si_9Al_3ON_{15})$ for M^{1+}, $M_2(Si_6Al_6O_2N_{14})$ for M^{2+} or $M_2(Si_3Al_9O_3N_{13})$ for M^{3+}, respectively. In practice, they are never achieved. So far, the biggest solubility limit obtained by Jack [4] is $x = 1.8$ (Ca) in the α′-$M_2(Si, Al)_{12}(O, N)_{16}$ structure by using Ca_3N_2, compared with 1.4 (Ca) by using CaO, and 1.5 (Li) by using Li_2O. With further increasing M in nominal compositions, AlN as the rest occurs and is compatible with α′ at an upper limit.

These phase relationships mentioned provide the possibility of producing β:α′, α′ or α′:AlN ceramics. These phase regions are all in equilibrium with the liquid-phase region, although the liquid region in the R_2O_3- or Y_2O_3-containing systems was not fully determined. Experiments confirmed that the liquid phase is compatible with R(Y)-α′ at 1700 °C or higher.

Single-phase Mg-α′ cannot be obtained on the join Si_3N_4–MgO:3AlN. The phase compositions along the line with increasing MgO:3AlN are composed of a mixture of the phases β + α′, α′ + 8H (or 12H) polytypoid or α′ + 8H (or 12H) + AlN, respectively. The formation of magnesium-polytypoid can be understood from subsolidus phase relationships of the Si_3N_4–AlN–MgO system without α′ formation [16], but cannot explain the phase relationships of the section at 1750 °C of this system involving liquid phase and thus is bracketed (see Fig. 3). It seems that the effects of the temperatures and kinetics of magnesium-polytypoid formation on phase relationships are significant. The nominal composition point showed that the transfer of β-Si_3N_4 disappearing and polytypoid occurring is located at about $x = 1.75$ Mg. The failure to obtain a single-phase region of Mg-α′ on the "one-dimensional" line Si_3N_4–MgO:3AlN could be a cause of the homogeneous Mg-α′ phase region being located only at more nitrogen-rich compositions in the "two-dimensional" phase field.

These phase regions provide the possibility to fabricate composites of Mg-α′ plus β or polytypoid. These compatible regions are all in equilibrium with the liquid-phase region as shown in Fig. 3.

3.2. Sialon fabrication based on phase relationships

According to the phase relationships mentioned in the α′-containing systems investigated, compositional design of the single-phase α′ or the two-phase α′:β as the major crystalline phases of materials can be made along the line Si_3N_4–MqO:3AlN (where M is lithium, calcium, yttrium, neodymium, samarium, gadolinium, dysprosium, erbium or ytterbium. These sialon materials can be fabricated by forming and sintering appropriate mixtures of Si_3N_4, AlN plus M_xO_y at 1700 °C or higher in a nitrogen atmosphere. Below 1650 °C, these compositions could not form sufficient α′ to be a major phase in the materials. Li–O′-sialon (LiAlSi-N_2O) often occurred as a transitional phase at 1200–1650 °C before the formation of Li-α′ [15]. For Mg-sialon [16], only a polytypoid 12H with a formula of about $Mg_{2.3}Al_{0.7}Si_3O_{2.3}N_{4.7}$ was obtained below 1700 °C (its melting point is 1730 °C) without Mg-α′ which could form with polytypoid at a higher temperature, say 1750 °C. Above 1750 °C, α′ often starts to transform into β′ with accompanying liquid. The ratio

α':β' decreases with increasing temperature. The transformation of α' to β' and the volatilization from the liquid phase at grain boundaries can be reduced by embedding the samples in AlN-packing powder by providing a nitrogen-rich environment [17].

In the phase relationships mentioned, it is obvious that a large liquid area existing in the lithium- and calcium-containing systems might facilitate the densification of Li- and Ca-α'-sialon materials, but should not be good for their high-temperature strength, because of the existence of liquid phase with low melting temperature in the grain boundaries. Although this case should also be the same for the Mg-α'-sialon system, Mg-α' or Mg-α' plus polytypoid, all with more nitrogen-rich compositions, should be obtained with possibly a small amount of liquid phase. However, the more nitrogen-rich the composition, the smaller the amount of liquid phase produced, and the more difficult it is to densify. In practice, so far, yttrium-α' is the best choice for fabrication. Rare-earth-α' is also the same, if the cost price is not considered.

A two-phase ceramic of β': α' with a ratio of 60:40, as an example, was fabricated using a pre-synthesized β' powder plus AlN, Y_2O_3 and α-Si_3N_4 by pressureless sintering at 1800 °C for 2 h in nitrogen [18]. The compositions of the two phases were analysed by EDX as $\beta' = Si_{5.4}Al_{0.6}O_{0.6}N_{7.4}$ and $\alpha' = Y_{0.42}Si_{10.1}$-$Al_{1.9}O_{0.64}N_{15.36}$. Compared with the designed composition, the β' content in the material is increased by $\sim 5\%$ and the Z-value is decreased slightly.

Compared with β', α' is a more nitrogen-rich solid solution and thus more difficult to densify. In addition to the use of AlN-packing powder for embedding the samples, La_2O_3 was often used and proved to be a good additive in our work [16, 17, 19]. La_2O_3 cannot be accommodated in the α-structure, but remains completely in the glassy phase, thus enhancing diffusion and densification with also the possible effect of transferring more Li_2O, CaO, or Y_2O_3 into the α' phase from the grain-boundary glassy phase.

Other two-phase ceramics of β:Y-α' designed from the nominal compositions located on the "one-dimensional" line by using Si_3N_4, AlN and Y_2O_3 with La_2O_3 as additive, were obtained by GPS at 1900 °C for 1.5 h in 1.5 MPa nitrogen [19]. The phase compositions of two products are β:α' (80:20 and 60:40) with a grain-boundary glassy phase. After annealing at 1400 °C for 10 h, a small amount of wohlerite (J-phase) or apatite (H-phase) crystallized from lanthanium-containing liquid at the grain boundaries. The bending strength of these two compositions before and after annealing remains high at high temperature, as shown in Fig. 8. High strength at high temperature could be caused by the intergranular vitreous or crystalline phases which all have high melting temperatures. The subsolidus phase relationships in Si_3N_4–AlN–R(Y)$_2O_3$ systems investigated showed that β:α' are in equilibrium with melilite R(Y)$_2O_3 \cdot Si_3N_4$ (M-phase). Instead of melilite, however, J- or H-phase occurs here after annealing. It might be caused by a greater oxygen content in lanthanium-containing liquid at the grain boundaries, even though GPS was used.

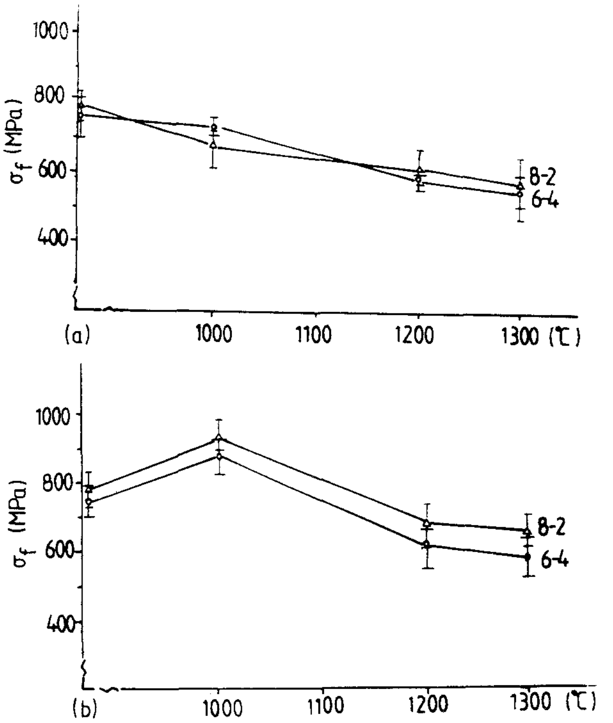

Figure 8 Bend strength of GPS β:α' composites versus temperature: (a) before annealing; (b) after annealing) [19].

4. Conclusions

Phase relationships in the Si_3N_4–AlN–M_xO_y systems, where M = lithium, magnesium, calcium, yttrium, neodymium, samarium, dysprosium, erbium or ytterbium, have been established. Within these systems, a "one-dimensional" region of α' stability exists, except for magnesium along the binary join Si_3N_4–MgO:3AlN and is compatible with β-Si_3N_4, AlN, polytypoid and liquid phase, respectively. The single-phase M-α' region and the two-phase fields in the systems investigated, provide the basis for the compositional design and fabrication of M-α'-containing materials. Formation and phase composition change of some sialon materials have been discussed. Examples of two composites designed have been fabricated, one by pressureless sintering and the other by GPS under high nitrogen pressure. Further work along these lines of material design, fabrication, as well as property studies is worthwhile.

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