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Solid–Liquid Reaction in the Si_3N_4–AlN–Y_2O_3 System under 1 MPa of Nitrogen

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The melting behaviors of selected compositions in the Si_3N_4–AlN–Y_2O_3 system were determined under 1 MPa of nitrogen. The phase diagrams of the ternary and their binary systems are presented. The lowest melting composition of the ternary system contains 15 mol% Si_3N_4, 25 mol% AlN, and 60 mol% Y_2O_3 and has a melting temperature of 1650°C. The binary eutectic compositions and temperatures are 15 mol% Si_3N_4 and 85 mol% Y_2O_3 at 1720°C, and 20 mol% AlN and 80 mol% Y_2O_3 at 1730°C.

I. Introduction

THE densification of silicon nitride ceramics always occurs in the presence of a reaction liquid. The reaction liquid is a eutectic melt, which forms from the reaction between the surface layer of the silicon nitride powder and the oxide sintering additives used. Therefore, the solid–liquid reaction in Si_3N_4–metal oxide systems must be determined. Previous studies of subsolidus phase equilibria in the Y-Si-Al-O-N system found 68 compatibility tetrahedra.[1] Phase regions in this system which are useful for production of Si_3N_4 ceramics have been indicated. Hohnke and Tien[2] were the first to study the solid–liquid reactions in the Si_3N_4–β_{60}–YAG region. The 1650° and 1750°C isotherms in this system have also been reported by Wisnudel and Tien.[3] As a part of a series of studies on solid–liquid reactions in the Y-Si-Al-O-N system, we reported the solid–liquid reaction in the system Si_3N_4–$Y_3Al_5O_{12}$–$Y_2Si_2O_7$ under 1 MPa of nitrogen in a previous paper.[4]

The section Si_3N_4–AlN–Y_2O_3 of the Y-Si-Al-O-N system has been used to develop β–α' sialon composites. The compositions of these β–α' sialon composites are located on the composition line Si_3N_4–Y_2O_3:9AlN. These composites have the highest strength[5,6] among silicon nitride ceramics. The subsolidus phase equilibrium in the Si_3N_4–AlN–Y_2O_3 system was published by one of the authors.[7] The focus of this research is to clarify the solid–liquid reactions in the system Si_3N_4–AlN–Y_2O_3.

II. Experimental Procedure and Results

The starting powders used were Si_3N_4 (UBE-SN-E10, Japan), AlN (MAN-05, Japan), and Y_2O_3 99.99% (Aldrich Chemical Co., U.S.A.). More than 50 compositions were prepared in the system, among which the smallest interval between compositions was 5 wt%. The starting powders of different compositions were weighed and mixed in an agate mortar and pestle under isopropyl alcohol for 1.5 h. The mixtures were dried and pressed into pellets (0.25 cm × 1 cm in diameter) and then isostatically pressed under 300 MPa. The pellets were placed in a BN powder-bed in a graphite die with a screw cap and were sintered in a graphite furnace under 1 MPa of nitrogen at different temperatures for 2 h. The natural cooling rate of the samples after sintering was 40°C/min from power-off until 1000°C. The weight loss of the samples was measured by weighing the samples before and after sintering. The experimental procedures are the same as those used in a previous study.[4]

X-ray diffraction was used for phase identification. The melting behavior of the compositions was determined by visual observation and scanning electron microscopy. The liquid phase was crystallized after densification to verify the location of the starting composition. The compositions, firing conditions, and phases are listed in Tables I through III.† These data were used to construct the phase diagrams in Figs. 1 through 4.

III. Discussion

(1) The Binary System Si_3N_4–Y_2O_3

Only one compound—$Y_2O_3 \cdot Si_3N_4$, melilite (M-phase)—exists in this system. It melts at 1850°C and separates the system into two parts (Fig. 1). On the Si_3N_4-rich side, considerable weight loss was observed. The starting Si_3N_4 powder contains 1.4 wt% oxygen, which is equivalent to 3.86 wt% SiO. Beyond this amount the higher weight loss would correspond to the decomposition of Si_3N_4 to Si and N, except for exhaust-internal SiO. It shows that a gas-phase region formed from Si,

†For Tables I, II, and III, order ACSD-239 from the Data Depository Service, American Ceramic Society, 735 Ceramic Place, Westerville, OH 43081.

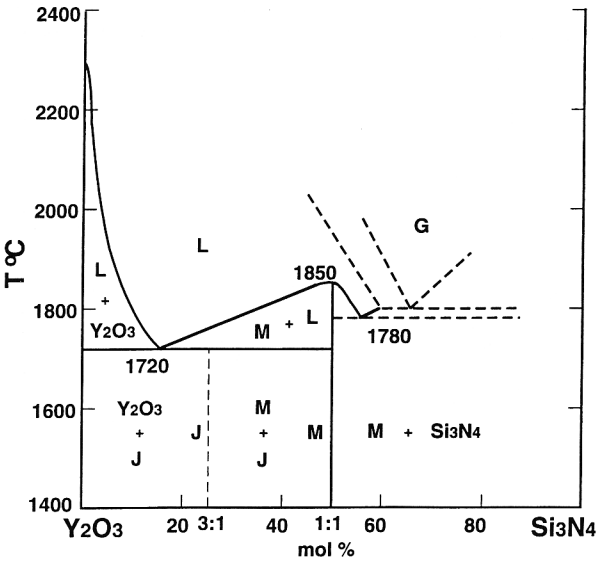

Fig. 1. Y_2O_3–Si_3N_4 system under 1 MPa of N_2 (M: $Y_2Si_3O_3N_4$, melilite; J: $Y_4Si_2O_7N_2$).

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N, Y, O, SiO, or NO species at temperatures above 1800°C. Si_3N_4 is compatible with melilite, and sometimes also with $Y_2Si_3N_6$ at around 1800°C. It is obvious that $Y_2Si_3N_6$ forms under high nitrogen pressure when the composition moves a little bit into the Si_3N_4–M–$Y_2Si_3N_6$ triangle area.[1]

On the Y_2O_3-rich side, the severe reaction between Si_3N_4 and Y_2O_3 promoted the formation of a larger liquid region with steep liquidus line from Y_2O_3 (Fig. 1). $2Y_2O_3{\cdot}Si_2N_2O$ (J-phase) always formed and was compatible with either melilite or Y_2O_3. As a result, the crystalline phases were either J-phase and Y_2O_3 or J-phase and melilite, instead of the equilibrium between melilite and Y_2O_3. J-phase forms because impurity oxygen is present at the surface of Si_3N_4 powder. The composition 15 mol% Si_3N_4:85 mol% Y_2O_3 has the lowest melting temperature (1720°C), which shows the melting behavior of a composition containing J-phase rather than the eutectic.

(2) The Binary System AlN–Y_2O_3

Some of the phase diagrams in AlN–R_2O_3 (rare-earth oxides) systems have been published previously.[8] Compared with these systems, the AlN–Y_2O_3 system has a similar phase diagram which contains a liquid region with a steep liquidus line from Y_2O_3 and a gaseous region on the AlN side (Fig. 2). No binary compound exits in this system, indicating similar chemical properties for Y_2O_3 and heavy rare-earth oxides.[8]

The compositions in the AlN–Y_2O_3 system showed much lower weight loss at high temperatures than did the compositions in the Si_3N_4–Y_2O_3 system. This is why AlN ceramics always densify more easily than Si_3N_4 ceramics. The binary eutectic composition contains 20 mol% AlN and 80 mol% Y_2O_3 with a eutectic temperature of 1730°C. These experimental results revise our previous work[9] where the AlN–Y_2O_3 subsystem was tentative in no melting up to 1850°C.

(3) The Ternary System Si_3N_4–AlN–Y_2O_3

Subsolidus phase relationships in the Si_3N_4–AlN–Y_2O_3 system have been reported previously.[7] In earlier studies the existence of liquid phase was not determined. Figure 3 shows the isothermal section of this system at 1750°C including a liquid-phase region. The tie line between AlN–melilite (M) separates the system into two parts: an AlN–M–Y_2O_3 triangle with a liquid region and an AlN–M–Si_3N_4 triangle with an α′-sialon line. In the AlN–M–Y_2O_3 triangle, the composition of 60 mol% Y_2O_3, 15 mol% Si_3N_4, and 25 mol% AlN has the lowest melting temperature, 1650°C. J-phase solid solutions often occurred in the AlN–M–Y_2O_3 triangle, forming a tetrahedron of AlN–M–Y_2O_3–J_{SS} just as similar J-phase formed in the Y_2O_3–melilite subsystem (Fig. 1). For the AlN-rich compositions, YAM also occurred. It was caused by Al_2O_3 impurity in AlN powder,

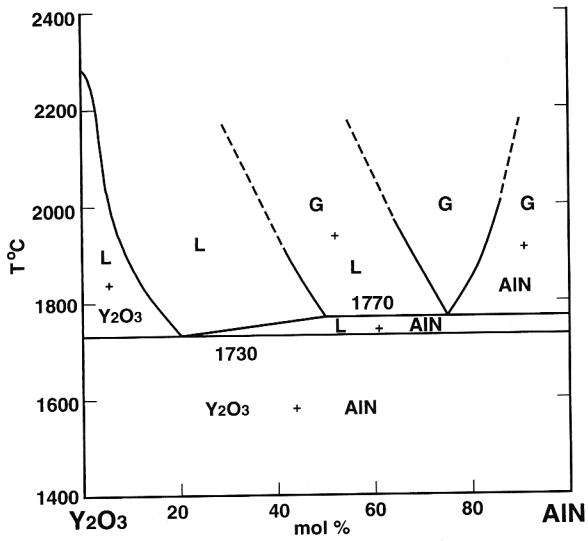

Fig. 2. Y_2O_3–AlN system under 1 MPa of N_2.

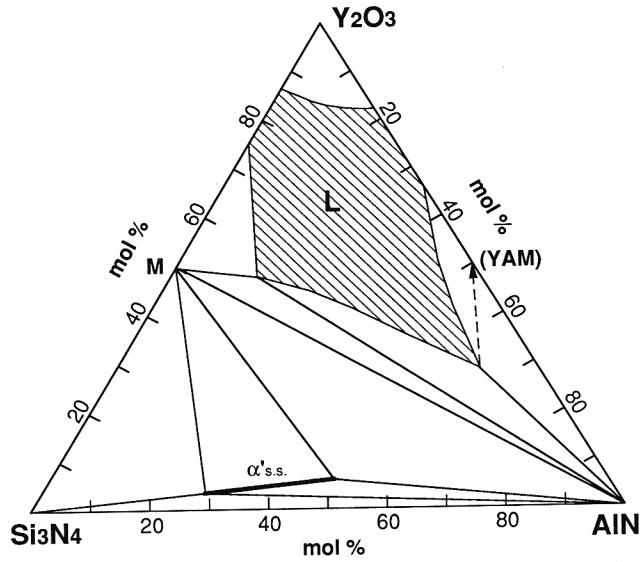

Fig. 3. Si_3N_4–AlN–Y_2O_3 system at 1750°C under 1 MPa of N_2 (M: $Y_2Si_3O_3N_4$; YAM: $Y_4Al_2O_9$).

because the starting AlN contains a small amount of oxygen impurity corresponding to 1.9 wt% Al_2O_3. The liquid phase is compatible with these four phases (Fig. 4): AlN, melilite, Y_2O_3, and J_{SS}, respectively. The liquid-phase region may extend toward the oxygen-rich area. In addition, a nitride-phase $Y_2Si_3N_6$ also appeared. Since the Si_3N_4–AlN–Y_2O_3 section crosses the tie line of J–$Y_2Si_3N_6$, the compositions investigated often fall into neighboring areas, such as AlN–Y_2O_3–J–$Y_2Si_3N_6$, AlN–M–J–$Y_2Si_3N_6$ tetrahedra, or their triangular subsystems.[1]

In the AlN–melilite–Si_3N_4 triangle, α′-sialon is compatible with β-Si_3N_4, melilite, and AlN, respectively, except for the appearance of $Y_2Si_3N_6$ or J_{SS}. A minor amount of β′-sialon could also be detected, due to unavoidable oxygen impurity in the starting powders.

An attempt to melt compositions along the Si_3N_4–α'_{SS}–Y_2O_3:9AlN line under 5 MPa of nitrogen at 1900°C for 1.5 h and under 1 MPa of nitrogen at 2000°C for 2 h, respectively, failed because of excessive vaporization (Table III). The samples, however, remained as α′-sialon phase, indicating α′-sialon could be stable until 1900°C or higher. A much higher nitrogen pressure would be required to restrain the vaporization and permit melting of α′-sialon compositions.

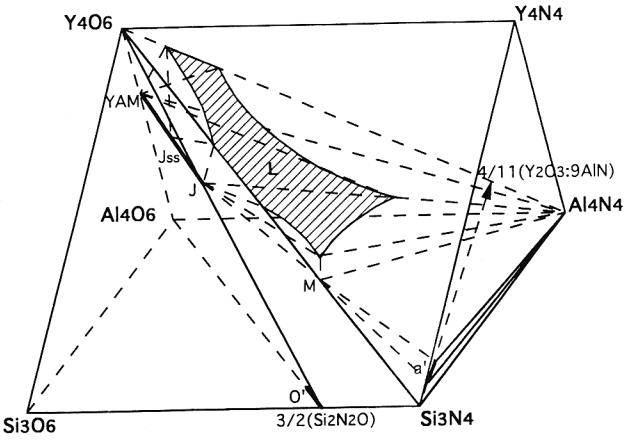

Fig. 4. Relations of liquid phase in the system Si_3N_4–AlN–Y_2O_3 and neighboring phases.

IV. Summary

The melting behaviors in the system Si_3N_4–AlN–Y_2O_3 were determined under 1 MPa of nitrogen. The behavior phase diagrams of the ternary and their binaries have been presented. The ternary composition of 15 mol% Si_3N_4, 25 mol% AlN, and 60 mol% Y_2O_3 has the lowest melting temperature of 1650°C.

The binary compositions with the lowest melting points are 15 mol% Si_3N_4 and 85 mol% Y_2O_3 at 1720°C, and 20 mol% AlN and 80 mol% Y_2O_3 at 1730°C.

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