

# Insolubility of Mg in $\beta$ - $\text{Si}_3\text{N}_4$ in the System Al-Mg-Si-O-N

L. J. GAUCKLER,\* J. WEISS,\* and T. Y. TIEN\*

Department of Materials and Metallurgical Engineering, The University of Michigan, Ann Arbor, Michigan 48109

G. PETZOW\*

Max-Planck-Institut fuer Metallforschung, Institut fuer Werkstoffwissenschaften, 7 Stuttgart 80, Federal Republic of Germany

**Solid-solution formation of magnesium in  $\beta$ - $\text{Si}_3\text{N}_4$  containing AlN: $\text{Al}_2\text{O}_3$  was investigated. Samples were hot-pressed at 1700°C. Under the condition studied, very little or no magnesium entered the  $\beta$ - $\text{Si}_3\text{N}_4$  lattice.**

## I. Introduction

EXTENSIVE solid-solution formation in  $\beta$ - $\text{Si}_3\text{N}_4$  has been established in literature in the systems Al-Si-O-N,<sup>1</sup> Be-Si-O-N,<sup>2</sup> and Al-Be-Si-O-N.<sup>3,4</sup> In these solid solutions aluminum and/or beryllium replace silicon in tetrahedral sites of the  $\beta$ - $\text{Si}_3\text{N}_4$  lattice and the stoichiometry is preserved by replacing nitrogen with oxygen. It has been demonstrated that extrinsic lattice defects in the  $\beta$ - $\text{Si}_3\text{N}_4$  lattice do not exist under the conditions studied.<sup>3</sup> Based on these data, a lattice tolerance factor was suggested to estimate the extent of the substitutional solid solution in  $\beta$ - $\text{Si}_3\text{N}_4$ .<sup>4</sup> Using this calculation, magnesium could be accommodated in the lattice up to 5 eq%. However, substitutional magnesium solid solution in pure  $\beta$ - $\text{Si}_3\text{N}_4$  has never been experimentally demonstrated<sup>5-7</sup> even though magnesium should fit in the tetrahedral sites.<sup>8</sup> Oyama and Kamigaito<sup>9</sup> reported a solubility up to 30 mol% of MgO in  $\beta$ - $\text{Si}_3\text{N}_4$  at 1750°C; however, the present writers feel this conclusion was not justified.

Substitutional solid solution of magnesium in  $\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$  (Ref. 1) requires the replacement of  $\text{Si}^{4+}$  and/or  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}$  and nitrogen by appropriate amounts of oxygen to maintain the charge balance and stoichiometry. Solid solutions of this kind have been reported by Jack,<sup>10-13</sup> who found that up to 6 eq% of magnesium can be dissolved in  $\beta$ - $\text{Si}_3\text{N}_4$  containing aluminum. Unfortunately, no detailed experimental data were presented and the phase relations shown by Jack in the corresponding systems  $\text{Si}_3\text{N}_4$ -MgO- $\text{Al}_2\text{O}_3$  (Ref. 13) and  $\text{Si}_3\text{N}_4$ -AlN: $\text{Al}_2\text{O}_3$ -Mg $\text{Al}_2\text{O}_4$ -Mg $_2\text{SiO}_4$  (Ref. 11) are inconsistent.

It is also possible that magnesium, together with aluminum, enters the  $\beta$ - $\text{Si}_3\text{N}_4$  lattice forming an interstitial solid solution similar to that of the stuffed derivatives of silica.<sup>14</sup> In these compounds,  $\text{Al}^{3+}$  replaces  $\text{Si}^{4+}$  in tetrahedral sites and positive charge deficiencies are compensated by stuffing large ions, e.g.  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{2+}$  (Ref. 15), in interstitial sites. Since the  $\beta$ - $\text{Si}_3\text{N}_4$  structure is built by ( $\text{SiN}_4$ ) tetrahedra which are similar to that of silicate, the possibility of this solid solution formation should not be ignored.

The purpose of the present investigation was to delineate solid-solution formation of  $\beta$ - $\text{Si}_3\text{N}_4$  in the system Al-Mg-Si-O-N. The substitutional solid solutions should be confined in the plane of a constant metal to nonmetal ratio of 3:4. This plane is defined by  $\text{Si}_3\text{N}_4$ -AlN: $\text{Al}_2\text{O}_3$ -Mg $\text{Al}_2\text{O}_4$ -Mg $_2\text{SiO}_4$ . The compositions in this plane can be expressed by  $\text{Si}_{6-x-y}\text{Mg}_y\text{Al}_x\text{O}_{x+2y}\text{N}_{8-x-2y}$ . The solid solution of interstitial type should exist in the plane  $\text{Si}_3\text{N}_4$ -AlN: $\text{Al}_2\text{O}_3$ -Mg $_3\text{Al}_6\text{N}_8$  and the compositions are defined by  $\text{Mg}_{x/2}\text{Si}_{6-x-z}\text{Al}_{x+z}\text{O}_x\text{N}_{8-x}$ . The system Al-Mg-Si-O-N is graphically represented<sup>16</sup> in Fig. 1; the planes of interest are shaded areas in the graph. Compositions located on these two planes were prepared and studied.

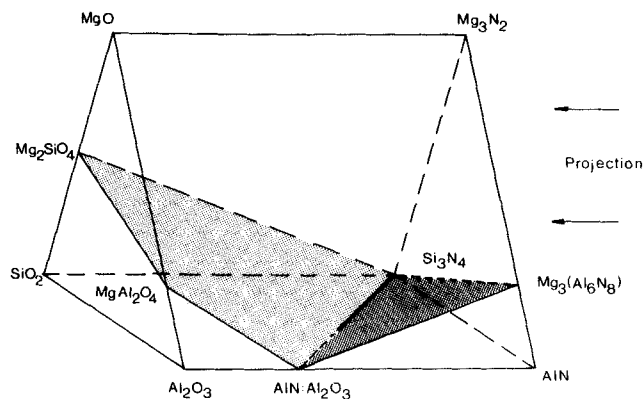


Fig. 1. The system Al-Mg-Si-O-N in eq% (Ref. 16).

## II. Experimental Procedure

Specimens in the system Al-Mg-Si-O-N were hot-pressed under a pressure of 30 MN/m<sup>2</sup> and/or sintered under 1 atm N<sub>2</sub> at 1700° to 1800°C. The compositions studied and their heat-treatment conditions are listed in Table I.\*

The starting materials used were  $\alpha$ - $\text{Si}_3\text{N}_4$ ,<sup>†</sup> AlN,<sup>‡</sup> MgO,<sup>§</sup>  $\alpha$ - $\text{Al}_2\text{O}_3$ ,<sup>¶</sup> and  $\text{SiO}_2$ .<sup>||</sup> The powders were mixed for 120 min in agate jars using dry methanol. The  $\text{SiO}_2$  pickup from the agate balls was <0.5 wt% of the total powder mix and could, therefore, be neglected. The dried powders were hot-pressed and/or sintered in graphite dies with BN liners until no further phase change was observed (usually  $\approx$ 20 to 150 min). Temperatures were measured using a Pt6Rh-Pt30Rh thermocouple or an optical pyrometer calibrated against a W-wire standard lamp. Samples were weighed before and after heat treatment. Only samples with <1 wt% loss were used for further analysis.

Selected specimens were chemically analyzed after heat treatment. Nitrogen was extracted from the specimens as NH<sub>3</sub> by dissolving the nitrides in lithium hydroxide; the NH<sub>3</sub> liberated was determined volumetrically using standard H<sub>2</sub>SO<sub>4</sub>. Nitrogen content was also determined by microprobe techniques.<sup>17</sup> The analysis was performed with a lead stearate pseudocrystal, using a standard flow proportional detector with P-10 gas (10 vol% CH<sub>4</sub>-90 vol% Ar) at atmospheric pressure. The metal contents were also determined by microprobe and by X-ray fluorescence after porous specimens were dissolved in borate glass (LiBO<sub>2</sub>:Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 1:1).<sup>18</sup> In some specimens, the metal contents were determined by atomic absorption in acidic solution after the material was dissolved in HF/HNO<sub>3</sub> under 200 atm pressure in a Teflon tube.<sup>19</sup> Crystalline phases were detected by X-ray diffraction using LiF-monochromated CuK $\alpha$  radiation. Lattice parameters were determined using high-angle

\*For Tables I, II, and III, order ACSD-145 from Data Depository Service, The American Ceramic Society, 65 Ceramic Drive, Columbus, Ohio 43214.

†HCST 3733, H. C. Starck-Berlin, Goslar, Federal Republic of Germany.

‡HCST 3168, Starck-Berlin.

§No. 5866, E. Merck AG, Darmstadt, Federal Republic of Germany.

¶Alcoa A16, Aluminum Co. of America, Pittsburgh, Pa.

||No. 7536, E. Merck AG.

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\*Member, the American Ceramic Society.

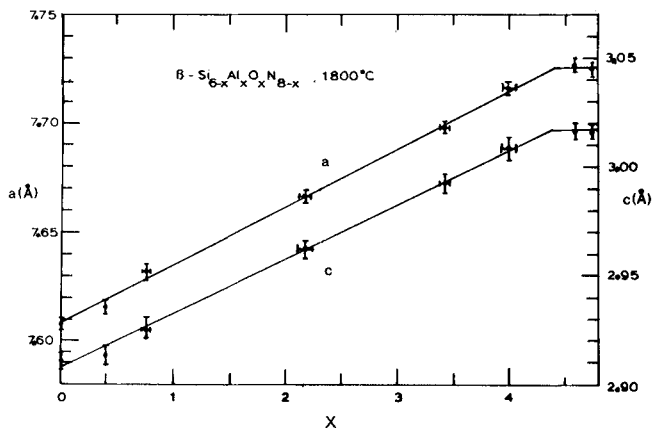


Fig. 2. Lattice parameters of  $\beta$ - $\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$  vs composition.

reflection lines obtained at a goniometer scanning speed of  $0.5^\circ 2\theta/\text{min}$ . Optical microscopy was used to detect phases  $<5 \text{ vol}\%$  as well as glass in the microstructure.

### III. Results and Discussion

Substitutional solid solution in  $\beta$ - $\text{Si}_3\text{N}_4$  should be expected in the 3:4 plane (Fig. 1). Compositions studied, heat treatments, and phase analyses are listed in Table I. Extensive solid solution was found only along the magnesium-free line  $\text{Si}_3\text{N}_4$ -AlN: $\text{Al}_2\text{O}_3$ , as reported previously.<sup>1,3</sup> Lattice parameter measurements of hot-pressed specimens with compositions  $\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$  showed a linear increase with increasing  $x$  values (Fig. 2). Vertical error bars are standard deviations from at least six measurements. After hot-pressing some of the single-phase specimens were chemically analyzed; the results are listed in Table II. Good agreement was achieved between wet chemical analysis and microprobe methods. Compositions with  $x=2.18$  and  $x=4$  showed a small silicon and oxygen loss. This shift in composition is shown by the horizontal error bars in Fig. 2.

For verifying the substitutional solid solution formation, samples having compositions  $\text{Si}_{6-x-y}\text{Al}_x\text{Mg}_y\text{O}_{x+2y}\text{N}_{8-x-2y}$  with  $x$  values of 1, 2, 3, and 4 (aluminum concentrations) and  $y=0, 0.2, 0.4, 0.6$ , and 0.8 (magnesium concentrations) were studied. The specimens of  $y=0.2$  for all of the  $x$  values showed other phases as well as  $\beta$ - $\text{Si}_3\text{N}_4$  (*ss*). The secondary phases were mainly  $x_2$  (15R, AlN polytype) and liquid, detected by X-ray and light microscopy. (For composition of  $x_2$  (15R) and other AlN polytypes, see Refs. 1 and 10. The solubility of Mg in the polytypes was not investigated.) A typical microstructure is shown in Fig. 3. Elongated light grains (probably platelets) of  $x_2$  (15R) and small  $\beta$ - $\text{Si}_3\text{N}_4$  (*ss*) grains are shown evenly distributed in the liquid phase (dark gray).

These results indicated that the substitutional solid solution of magnesium in pure  $\beta$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$  (*ss*) containing aluminum, if any, is  $<1.5 \text{ at.}\%$  (0.88 eq% at  $x=1$  and 1.01 eq% at  $x=4$ ). Because the  $\beta$ -phase which is in equilibrium with the second phase contains varying amounts of Al, the lattice parameter change of  $\beta$  phase cannot be used to determine the solid solution formation in the system Al-Mg-Si-O-N.

Interstitial solid solution of magnesium with aluminum in  $\text{Si}_3\text{N}_4$ , if formed, should occur in the plane  $\text{Si}_3\text{N}_4$ -AlN: $\text{Al}_2\text{O}_3\text{Mg}_2\text{Al}_6\text{N}_8$ . Compositions on this plane have a formula  $\text{Si}_{6-x-z}\text{Al}_{x+z}\text{Mg}_{2z}\text{N}_{8-x}\text{O}_x$ . Compositions of  $x=1, 2, 3$ , and 4 with varying amounts of  $z$  were studied. Heat treatment and phase analysis of these specimens are listed in Table III. As shown in the table, secondary phases appeared in all magnesium-containing samples studied, e.g. for  $x=2$  and  $z=0.12$  (0.4 at. % Mg),  $\beta$ - $\text{Si}_3\text{N}_4$  solid solution and  $x_2$  (15R) were detected. No single-phase material was obtained for the  $x$  values when  $z>0$ , indicating that magnesium solubility is  $<0.4 \text{ at.}\%$  (0.55 eq%  $\text{Mg}^{2+}$ ), if any.

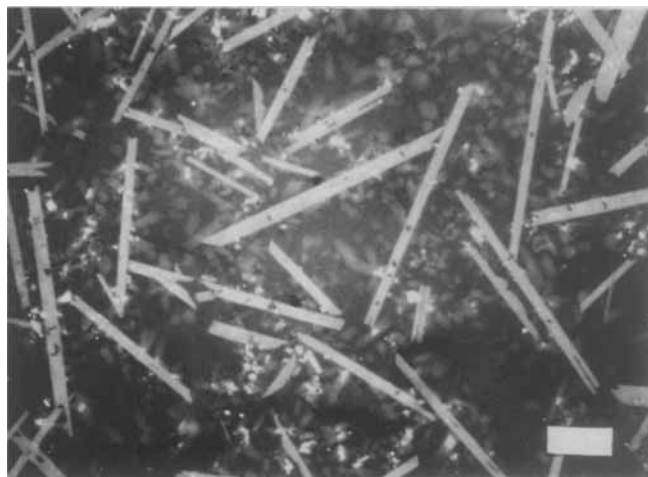


Fig. 3. Microstructure of composition containing 25Al-25Mg-50Si (eq%) in 3:4 plane (1750°C). Elongated grains are  $x_2$  phase (15R), medium gray regions  $\beta$ - $\text{Si}_3\text{N}_4$  (*ss*), and dark gray regions liquid (bar = 10  $\mu\text{m}$ ).

The absence of noticeable substitutional and interstitial solid solution of magnesium does not exclude the possibility of a combined solution of both types. If this combined solid solution exists, the composition would be between the two shaded planes shown in Fig. 1. However, the occurrence of multiphase specimens in the 3:4 plane in which  $\beta$ - $\text{Si}_3\text{N}_4$  solid solution,  $x_2$  (15R), and liquid coexist, indicates that tie lines from the  $\text{SiO}_2$ -rich liquid region to the aluminum- and nitrogen-rich  $x_2$  (15R) phase cross the composition region of a hypothetical  $\beta$ - $\text{Si}_3\text{N}_4$  solid solution of the combined type in the concentration prism. Therefore, this possibility can be ruled out.

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