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Formation of N-phase and Phase Relationships in $MgO–Si_2N_2O–Al_2O_3$ System

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Formation of N-phase in the system Mg,Si,Al/N,O was studied. Its composition was confirmed to be $MgAl_2Si_4O_6N_4$ ($2Si_2N_2O·MgAl_2O_4$). Subsolidus phase relationships in the $MgO–Si_2N_2O–Al_2O_3$ system were determined. The results are discussed by comparing with two similar systems, CaO– and $Y_2O_3–Si_2N_2O–Al_2O_3$.

I. Introduction

Drew *et al.*[1] reported a compound "N-phase" with a proposed composition of Mg_2AlSiO_4N. These authors described this compound as a nitrogen-containing petalite having an orthorhombic structure with a = 5.6282, b = 14.331, and c = 4.9682 Å.

Nunn *et al.*[2,3] found a phase in the system Mg,Si,Al/N,O with an X-ray diffraction pattern very similar to the one reported for N-phase by Drew. The compound found by Nunn lies on the join $MgAl_2O_4–Si_2N_2O$ in the system Mg,Si,Al/N,O. Nunn *et al.*[2,3] reported that this nitrogen-containing compound has a composition of $2Si_2N_2O·MgAl_2O_4$ ($MgAl_2Si_4O_6N_4$). This compound crystallizes in an orthorhombic structure with a = 14.1213, b = 4.9387, and c = 5.5746 Å. The thermal expansion coefficient of the compound was also characterized with high-temperature X-ray diffraction equipment in the range from room temperature up to 1200°C. The thermal expansion coefficients along the a, b, and c axes were reported as 1.46×10^{-6}, 3.39×10^{-6}, and 2.08×10^{-6}, respectively. Table I lists the X-ray data from both Nunn and Drew for comparison. Both Nunn and Drew designated this phase as N-phase.

It should be indicated that the compositions reported by Nunn and Drew are quite different, even though they have very similar X-ray diffraction patterns. Therefore, there is need for further work to clarify the composition of this phase. Like cordierite, N-phase has a very low linear thermal expansion coefficient, 2.31×10^{-6}/°C, low melting temperature, 1450°C (incongruently), and is compatible with Si_3N_4.[3] This implies the possibility of using N-phase as the second phase in a silicon nitride composite for lowering the sintering temperature and strengthening the combination between matrix and second phase. For this reason, an understanding of the compatible relationships of N-phase and neighboring phases is necessary. The present work studied the formation of N-phase and the phase relationships in the $MgO–Si_2N_2O–Al_2O_3$ system.

II. Experimental Procedure

Two compositions, $MgAl_2Si_4O_6N_4$ (NN, proposed by Nunn[2,3]) and Mg_2AlSiO_4N (ND, proposed by Drew[1]), were prepared and studied. Starting powders used were MgO (99.9%, Baikowski International), Al_2O_3 (Sumitomo, AKP-50), SiO_2 (99.9%), Si_3N_4 (Ube, SN-E10, N > 38.0 wt%, O = 1.4 wt%), and AlN (Starck, N 33.5%). Powders were weighed and mixed in an agate mortar under isoprenyl for 1.5 h. The mixtures were dried and then isostatically pressed into a pellet (5 mm × 10 mm in diameter) under pressure of 300 MPa. Solid-state reaction was carried out by firing the pellets embedded in BN powder for 2 h. Some pellets were also fired for 2 h in a BN powder bed under 1.5 MPa nitrogen pressure (GPS) at 1640°C. Some of the compositions were hot pressed in a BN-lined graphite die for 1 h in flowing nitrogen under a pressure of 35 MPa at temperatures 1400° or 1550°C. After firing, some melted samples were annealed at 1300°C for 20 h to crystallize the crystal phase. The samples with weight loss <4 wt% after firing and <2 wt% after hot pressing were used for analysis. The X-ray diffraction technique was used for phase identification. The N-phase composition was also verified using electron probe microanalysis (EPMA).

III. Results and Discussion

(1) Formation of N-phase

Table II lists the firing conditions and phase compositions analyzed by X-ray diffraction. For the NN composition, the sample after firing at 1450°C started to produce liquid. This NN composition melted at 1650°C. Reaction at <1450°C formed only a medium amount of N-phase even under hot-pressing conditions. Nearly single-phase material could be obtained by firing for 2 h at >1450°C or by annealing the melted samples for 20 h at 1300°C. It seems that the formation reaction of N-phase occurs rapidly when liquid emerges. Some neighboring compositions also showed the existence of N-phase. Table III lists the EPMA results from the NN samples fired under nitrogen overpressure after crystallization, showing a composition close to that of $MgAl_2Si_4O_6N_4$ for N-phase.

For the ND composition, two different batches of starting powder mixtures with and without AlN (Table II) were prepared and studied. This ND composition melted at 1600°C. Under all firing conditions or after crystallization from melted samples, no N-phase was observed, but a multiphase assemblage composed of forsterite (Mg_2SiO_4), spinel ($MgAl_2O_4$), 12 H′-polytypoid, and a trace of magnesia was obtained. The existence of the phase 12H′ ($Mg_{2.3}Al_{0.7}Si_3O_{2.3}N_{4.7}$ or $2.3MgO·0.7AlN·Si_3N_4$) had been reported by Kuang *et al.*[4] in the $MgO–Si_3N_4–AlN$ system.

These results support the composition $MgAl_2Si_4O_6N_4$ for N-phase, instead of Mg_2AlSiO_4N. The composition Mg_2AlSiO_4N reported by Drew was located in a four-phase region, Mg_2SiO_4, $MgAl_2O_4$, 12H′-polytypoid, and MgO.

(2) Phase Relationships

Nunn *et al.*[2,3] has established the subsolidus phase relationships in an oxygen-rich region of the Mg-Al-Si-O-N system bound by the compounds SiO_2, Mg_2SiO_4, $MgAl_2O_4$, Al_2O_3, and β′-SiAlON. The N-phase can be compatible with Si_3N_4, Si_2N_2O, Mg_2SiO_4, $MgAl_2O_4$, $2MgO·2Al_2O_3·5SiO_2$ (cordierite), and X_1 phase. The present work checked some compositions

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Table I. Comparative X-ray Data of N-phase

$MgAl_2Si_4O_6N_4$ $a = 14.1213, b = 4.9387, c = 5.5764$				Mg_2AlSiO_4N* a = 5.6282, b = 14.331, c = 4.9682			
d (calc)	*d* (obsv)	I/I1	*h k l*	*d* (calc)	*d* (obsv)	*I* (obsv)†	*h k l*
7.0606	7.0548	3	2 0 0	7.164	7.192	vvw	0 2 0
5.1866	5.1820	5	1 0 1	5.239	5.232	vw	1 1 0
3.5970	3.5973	85	3 0 1	3.642	3.648	ms	1 3 0
3.5766	3.5739	80	1 1 1	3.605	3.606	s	1 1 1
3.5303	3.5298	100	4 0 0	3.582	3.586	ms	0 4 0
2.9075	2.9068	40	3 1 1	2.937	2.941	m	1 3 1
2.7882	2.7867	9	0 0 2	2.814	2.817	w	2 0 0
2.7354	2.7395	3	1 0 2				
2.5933	2.5916	4	2 0 2				
2.5195	2.5189	4	5 0 1				
2.4694	2.4695	39	0 2 0	2.484	2.486	m	0 0 2
2.4280	2.4275	41	0 1 2	2.449	2.451	m	2 0 1
2.3989	2.3995	4	3 0 2				
2.3929	2.3928	6	1 1 2				
2.3309	2.3321	8	2 2 0	2.347	2.351	vw	0 2 2
2.2960	2.2957	10	2 1 2	2.317	2.316	mw	2 2 1
2.2443	2.2441	4	5 1 1	2.271	2.270	vw	1 5 1
2.0358	2.0363	20	3 2 1	2.052	2.054	m	1 3 2
2.0005	2.0005	4	4 1 2	2.022	2.023	w	2 4 1
1.8970	1.8975	18	7 0 1	1.924	1.925	m	1 7 0
1.8486	1.8480	7	0 2 2	1.863	1.863	w	2 0 2/3 1 0
1.7709	1.7711	18	7 1 1	1.794	1.793	mw	1 7 1/0 8 0
1.7636	1.7629	2	5 2 1				
1.7289	1.7285	22	3 0 3	1.746	1.746	m	3 3 0
1.7207	1.7218	2	3 2 2				
1.7037	1.7045	2	6 2 0				
1.6318	1.6317	3	3 1 3				
1.6293	1.6294	2	6 2 1				
1.5104	1.5101	2	9 0 1				
1.5043	1.5046	9	7 2 1	1.521	1.522	mw	1 7 2
1.4969	1.4973	14	3 3 1	1.508	1.508	w	1 3 3
1.4914	1.4913	3	8 0 2				
1.4851	1.4857	2	0 2 3				
1.4812	1.4810	3	5 1 3				
1.4769	1.4768	6	1 2 3	1.489	1.488	vw	3 1 2
1.4443	1.4440	4	9 1 1				
1.4360	1.4361	4	8 2 0	1.453	1.453	vvw	0 8 2
1.4277	1.4282	9	8 1 2	1.446	1.445	vw	2 8 1
1.4176	1.4172	23	0 3 2				
1.4121	1.4117	10	10 0 0				
1.3941	1.3948	7	0 0 4				
1.3898	1.3897	3	2 3 2				
1.3670	1.3666	14	7 0 3				
1.3629	1.3623	2	7 2 2				
1.3577	1.3579	6	10 1 0				
1.3417	1.3413	3	0 1 4				
1.3181	1.3185	4	2 1 4				
1.3155	1.3151	9	4 3 2				
1.2967	1.2969	4	4 0 4				
1.2433	1.2434	9	7 3 1				
1.2207	1.2211	5	10 1 2				
1.2140	1.2137	3	0 2 4				
1.2011	1.2011	1	1 4 1				

*Private communication. †v = very, w = weak, m = medium, s = strong.

around the N-phase and studied the compositions located in the MgO-rich region of $MgO–Si_2N_2O–Al_2O_3$ system (Fig. 1).

As for the results, combining them with those reported previously by other authors,[5–8] the subsolidus phase relationships of $MgO–Si_2N_2O–Al_2O_3$ system are presented in Fig. 2, in which 12H′-polytypoid is located at the $MgO–Si_3N_4$–AlN section. Kuang *et al.*[4] reported the subsolidus phase relationships of the $MgO–Si_3N_4$–AlN system. Within this system, there exists only one phase, 12H′, which is compatible with three members of the system. This 12H′-polytypoid is still compatible with forsterite, spinel, MgO, or N-phase, forming two compatible tetrahedra, F–Sp–12H′–MgO and F–Sp–12H′–N-phase.

Cao *et al.*[9,10] had reported the phase relationships of two systems, $CaO–Si_2N_2O–Al_2O_3$ and $Y_2O_3–Si_2N_2O–Al_2O_3$. For comparison, these two phase diagrams are presented in Figs. 3 and 4. The decomposition reaction of Si_2N_2O with CaO or Y_2O_3 occurring in the Si_2N_2O-rich side of binary subsystems Si_2N_2O–CaO or $–Y_2O_3$ had been described. Similarly, the decomposition reaction of Si_2N_2O with MgO in the present system occurred as follows:

$$2Si_2N_2O + 2MgO \longrightarrow Mg_2SiO_4 + Si_3N_4$$

It seems that MgO reacts only with SiO_2, but not with Si_3N_4 under subsolidus conditions, when SiO_2 and Si_3N_4 are used as starting powders instead of Si_2N_2O.

Table II. Firing Conditions and Phase Analysis by X-ray for Two N-compositions

	Compositions (mole ratios)					Firing conditions (in flowing N_2)		Phase compositions* (X-ray diffraction)			Melting behavior
	MgO	Al_2O_3	SiO_2	Si_3N_4	AlN	Temp (°C)	Time (h)	Main	Medium	Little	
NN	1	1	1	1		1400(Hp)	1	Sp,α	N		
						1500	2	N		α,Sp	Little pore
						1550	2				Bubble
						1600	2				Bubble
						1650	2				Melted
						+1300	20	N		α,β	
						1640(GPS)	2			β	Melted
						+1300	20	N		β	
ND	8	2	1	1		1500	2	F,12H′,Sp			
						1550	2	F,8H′,Sp			
						1550(Hp)	1	F,12H	Sp	MgO	
						1600	2				Melted
						1650	1				Melted
						+1300	20	F,12H′,Sp		MgO	
						1640(GPS)	2			F,12H′	Melted
						+1300	20	F	12H′		
	2		1		1	1550(Hp)	1	F	12H′,Sp		
						1650	1				Melted
						+1300	20	F,Sp	12H′		

*N: $MgAl_2Si_4O_6N_4$; Sp: $MgAl_2O_4$ (spinel); α or β: Si_3N_4; F: Mg_2SiO_4 (forsterite); 12H′: $Mg_{2.3}Al_{0.7}Si_3O_{2.3}N_{4.7}$(12H′-polytypoid);[4] 8H: $Mg_{3.29}Si_{1.89}Al_{2.82}O_{4.41}N_{4.59}$ (8H-polytypoid).[11]

Table III. EPMA Results on N-phase

Elements	Atomic fraction	Ratio	NN
Mg	0.06	1.0	1
Al	0.10	1.7	2
Si	0.23	3.8	4
O	0.38	6.3	6
N (by difference)	0.23	3.8	4

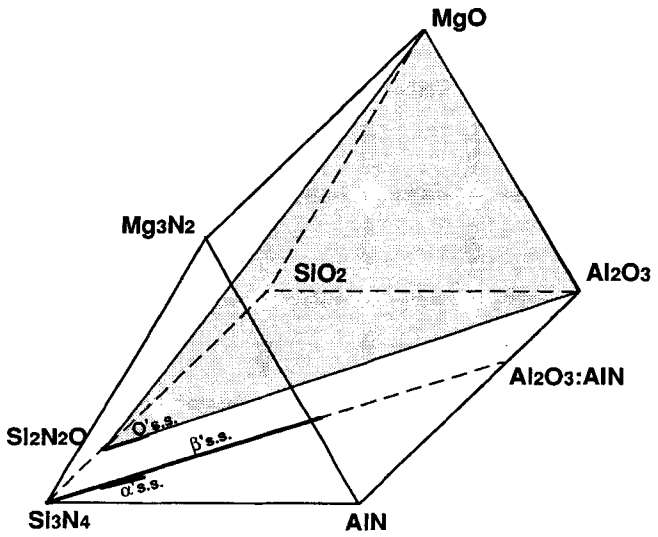

Fig. 1. Mg-Si-Al-N-O system prism.

It is well known that Ca (1.0 Å) and Y (0.9) ions have bigger radii and require high coordinations, so they cannot enter into structural tetrahedra forming polytypoid in SiAlON systems. For much smaller Mg (0.57), many Mg-polytypoids in the Mg–SiAlON system have been reported.[11] Their compositions would be located in the nitrogen-rich regions of the Mg–SiAlON system prism. They would also be compatible with other neighboring phases, forming some compatible tetrahedra.

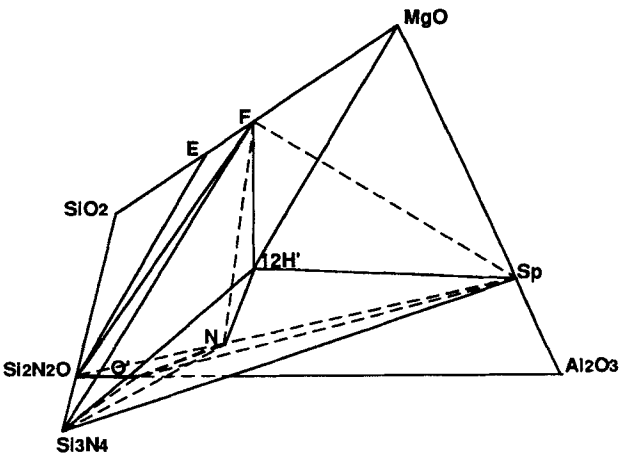

Fig. 2. Subsolidus phase relationships in the $MgO–Si_2N_2O–Al_2O_3$ system.

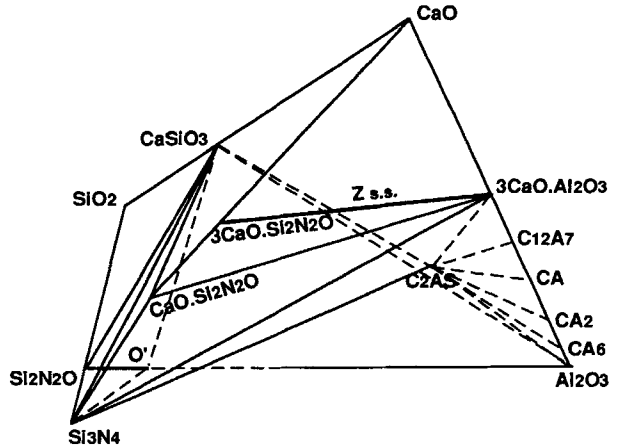

Fig. 3. Subsolidus phase relationships in the $CaO–Si_2N_2O–Al_2O_3$ system.[9]

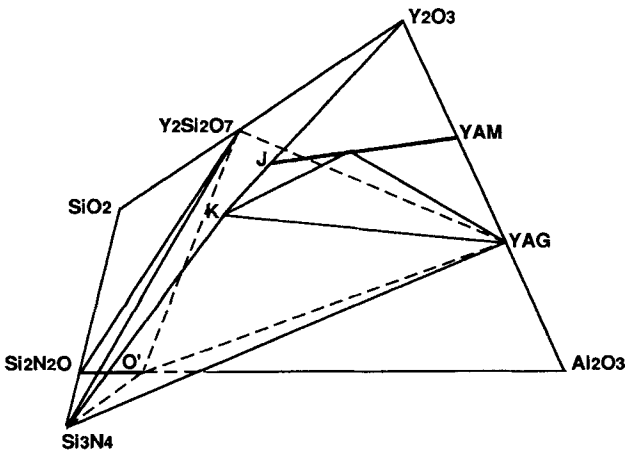

Fig. 4. Subsolidus phase relationships in the Y_2O_3–Si_2N_2O–Al_2O_3 system.[10]

F–Sp–12H′–MgO and F–Sp–12N′–N-phase tetrahedra established in this present work are two types of such compatible tetrahedra.

Quinary phases consisted of the quinary solid solutions, J-phase *ss* (i.e., $2Y_2O_3 \cdot Si_2N_2O$–$2Y_2O_3 \cdot Al_2O_3$ solid solution), Z-phase *ss* (i.e., $3CaO \cdot Si_2N_2O$–$3CaO \cdot Al_2O_3$ solid solution), and α'-SiAlON reported in M-Si-Al-O-N (M = Y, Ca, or Mg) systems. Besides, two quinary phases, Y_2SiAlO_5N (B-phase)[12] and $2CaO \cdot Si_3N_4 \cdot AlN$[13] with more or less metastability had also been reported in Y-SiAlON and Ca-SiAlON systems, respectively. They formed at lower temperatures or by crystallizing from melt. Therefore, it is unlikely that they would be compatible with neighboring high-temperature phases under subsolidus conditions. N-phase might be the only quinary compound so far reported in the Mg-SiAlON system, except for Mg-polytypoids or possibly Mg-α'-SiAlON. N-phase forms more easily in the presence of liquid and should be more stable than B-phase and $2CaO \cdot Si_3N_4 \cdot 4AlN$.

IV. Conclusions

The composition of N-phase was confirmed to be $MgAl_2Si_4O_6N_4$ instead of Mg_2AlSiO_4N, which forms a four-phase assemblage. Subsolidus phase relationships of the MgO–Si_2N_2O–Al_2O_3 system were presented. Within this system, two compatible tetrahedra, F–Sp–12H′–MgO and F–Sp–12H′–N-phase, were constructed.

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