JOURNAL OF MATERIALS SCIENCE LETTERS 4 (1985) 255–259

Phase relations of the Si_3N_4–AlN–CaO system

ZHEN-KUN HUANG, WEI-YING SUN, DONG-SHENG YAN
Shanghai Institute of Ceramics, Academia Sinica, Republic of China

Ceramics based on silicon nitride with α'-SiAlON as a major constituent are of more interest recently considering their potential high temperature properties. The structure of an α-Si_3N_4 solid solution which contains a large vacant site provides the possibility to absorb large impurity metal ions in the starting powder mixtures as sintering aids thus leading to a clean grain boundary phase which will be beneficial to the mechanical properties of ceramics at elevated temperatures.

The crystal chemistry of α'-SiAlONs which have the generalized formula $M_x(Si, Al)_{12}(O, N)_{16}$ is characterized by their content of metal cations such as lithium, calcium, yttrium and rare earth elements (except lanthanum and cerium) up to $x = 2$ present in the large interstitial holes [1]. These cations stabilize the trigonal α-Si_3N_4 structure and thereby establishing a β-Si_3N_4–α-Si_3N_4 solid solution equilibrium.

In contrast to the extensively investigated phase relations of the β-SiAlON solid solution in the quaternary system Si–Al–O–N [2–6], the information about the phase relations of the α-SiAlON solid solution in various M–Si–Al–O–N systems is scarce. This study is one of a series of phase relation studies of M–Si–Al–O–N systems following the last work on the Si_3N_4–AlN–Y_2O_3 system of one of the authors [7].

The starting powders used were Si_3N_4 (AME, total Si 60.08, N 37.72, O 1.31, free Si 1.12 wt %), AlN (Japan, total Al 64.58, N 32.78, O 1.37, others 1 wt %) and CaO (obtained by calcining $CaCO_3$ 99.99% at 1100° C for 2 h). The process of preparing and hot-pressing is the same as before [7]. Equilibrium was assumed to have been attained when no more unreacted α-Si_3N_4 was detected.

All specimens after hot-pressing at different temperatures were examined by X-ray diffraction analysis using an automatic recording X-ray diffractometer with monochromated Cu$K\alpha$ radiation. The compositions of some crystalline phases were analysed by a JCXA-733 electron probe X-ray microanalyser (JEOL).

Results obtained indicated that no binary compound is formed in this system except for $2H^{\delta}$ AlN-polytype. $2H^{\delta}$ phase was detected in all binary compositions of this system after hot-pressing at 1500 to 1700° C in N_2 for 1 h. The content of $2H^{\delta}$ phase decreased from the AlN end up to the CaO end. 2H AlN-polytype can be characterized as $Al_{11}N_9O_3$ with the ratio of cations/anions = 11/12. In fact, it is already present in the starting powder of AlN by the introduction of a small amount of oxygen during fabrication.

In some previous works concerning the phase diagram of Ca–Si–Al–O–N systems [8, 9], this

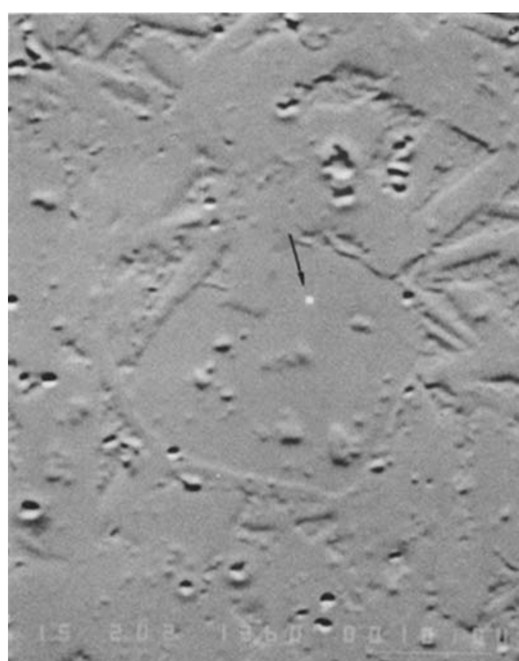

Figure 1 SEM micrograph of $2CaO{\cdot}Si_3N_4$ phase which was analysed by electron probe (arrow point) with 45.6 wt % CaO:54.4 wt % Si_3N_4 ≈ $2CaO{\cdot}Si_3N_4$ (× 2000).

TABLE I X-ray data for $3CaO \cdot Si_2N_2O$ and $3CaO \cdot Al_2O_3$

$3CaO \cdot Al_2O_3$ *			$3Ca \cdot Si_2N_2O$		$3CaO \cdot Al_2O_3$ *			$3CaO \cdot Si_2N_2O$	
h k l	I/I_0	d (× 10^{-1} nm)	d_{obs} (× 10^{-1} nm)	I_{obs}	*h k l*	I/I_0	d (× 10^{-1} nm)	d_{obs} (× 10^{-1} nm)	I_{obs}
1 1 1	< 1	8.82			7 5 2	2	1.727	1.705	vw
2 1 0	6	6.83			8 4 0	< 1	1.706		
2 1 1	4	6.23			8 4 1	2	1.695	1.674	vw
2 2 0	2	5.40	5.32	mw	9 1 1	< 1	1.675	1.654	vw
2 2 1	6	5.09			9 2 1	2	1.646	1.626	w
1 1 3	4	4.604	4.539	vw	6 6 4	2	1.627	1.607	vvw
0 2 3	10	4.235	4.181	vw	9 2 2	< 1	1.618	1.598	vw
3 2 1	16	4.080	4.026	w	8 5 1	2	1.610	1.581	w
0 0 4	2	3.816	3.767	vw	8 5 2	2	1.583	1.563	vw
2 2 3	2	3.705	3.652	vw	9 3 2	2	1.574	1.553	vw
3 3 1	2	3.501	3.457	mw	8 4 4	25	1.558	1.537	m
4 2 1	6	3.332	3.288	mw	10 1 0	2	1.519	1.499	w
3 3 2	4	3.252	3.212	mw	10 2 0	2	1.497		
4 2 2	< 1	3.120	3.074	s	10 2 1	2	1.490		
4 3 0	4	3.052			9 5 1	2	1.476	1.456	vw
4 3 1	4	2.993	2.952	w	10 3 0	4	1.462	1.443	vvw
4 3 2	6	2.834	2.789	m	10 3 1	2	1.455	1.437	vvw
5 2 1	14	2.787	2.740	mw	10 3 2	1	1.436		
4 4 0	100	2.700	2.665	vs	8 7 1	< 1	1.429		
5 2 2			2.662	mw	10 4 1	2	1.411	1.392	w
5 3 1	4	2.581	2.547	w	10 3 3	2	1.405		
6 1 0	< 1	2.512	2.480	vvw	9 6 2	2	1.390	1.371	vw
6 1 1	2	2.477	2.445	mw	10 5 0	2	1.3649	1.3478	vw
6 2 0	8	2.413	2.401	vw	11 2 1	2	1.3596	1.3422	vw
6 2 1	6	2.384	2.355	vw	8 8 0	10	1.3491	1.3302	w
5 4 1	2	2.355			11 3 1	< 1	1.3336	1.3160	vw
6 3 0	4	2.277	2.247	w	11 3 2	2	1.3190	1.3022	vw
4 4 4	12	2.204	2.176	m	10 6 0	< 1	1.3087	1.2919	vw
6 3 2	2	2.181	2.155	vw	10 6 1			1.2882	vw
7 1 1	< 1	2.138	2.111	w	11 3 3	< 1	1.2948	1.2766	vw
6 4 1	4	2.097	2.071	w	11 4 2	< 1	1.2852		
7 2 1	2	2.078	2.052	w	12 1 0	2	1.2676		
6 4 2	6	2.040	2.017	vvw	12 2 1	< 1	1.2506	1.2342	vw
7 2 2	< 1	2.021	1.992	vvw	11 5 2	< 1	1.2461	1.2310	vw
7 3 1	4	1.988	1.962	w	12 2 2	2	1.2379	1.2216	vw
6 5 0	4	1.955	1.929	vvw	– – –	–	– – –	– – –	–
7 3 2	< 1	1.940	1.914	vw	– – –	–	– – –	– – –	–
0 0 8	35	1.908	1.884	s	– – –	–	– – –	– – –	–
8 1 0	4	1.893	1.871	w	– – –	–	– – –	– – –	–
7 3 3	2	1.865	1.841	vw	11 6 1	–	1.2064	1.1979	vw
8 2 1	4	1.838	1.816	vvw					
6 5 3	4	1.824	1.802	vw					
8 2 2	< 1	1.799	1.776	w					
8 3 0	< 1	1.785	1.764	vw		a_0 = 1.5262 nm		a_0 = 1.507 nm	
7 5 1	< 1	1.763	1.739	vw					
8 3 2	2	1.740	1.717	w					

*From X-ray card

binary system was characterized by a tie line of Si_3N_4—CaO in equilibrium. Some compounds may easily be missed, due to the high firing temperature conditions used. While certain compounds may only be formed at lower temperatures.

Two compounds were identified in this system by this study. The compound $3CaO \cdot Si_2N_2O$ (Z phase) with a melting temperature ~ 1580° C was synthesized by hot-pressing a composition of either $3CaO:2/3Si_3N_4$ or $3CaO:Si_2N_2O$ at 1400° C in N_2 for 0.5 h. It was characterized by a cubic structure (a_0 = 1.507 nm) being the same as that of $3CaO \cdot Al_2O_3$ (a_0 = 1.5262 nm). The X-ray data of this compound are listed in Table I, in

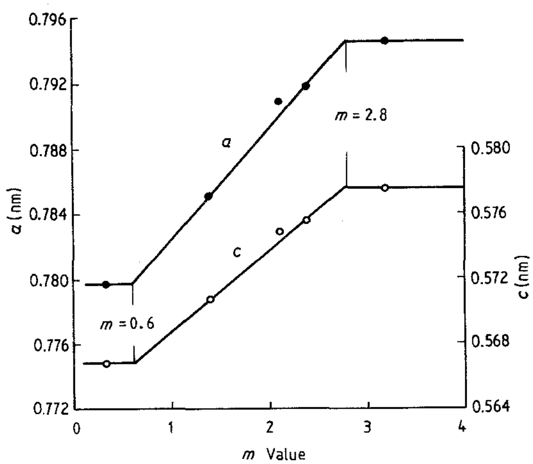

Figure 2 Lattice constants of α-SiAlON ss as a function of the *m* value of replacement of Al–N for Si–N.

comparison with those of $3CaO \cdot Al_2O_3$. Its formation is related to the introduction of a little excess of oxygen in the starting powder Si_3N_4.

Another compound of the formula $2CaO \cdot Si_3N_4$ (D phase) with a melting temperature ~ 1680° C was also found in this system in hot-pressed specimens at temperatures above 1400° C in N_2 for 1 h accompanied usually by some $3CaO \cdot Si_2N_2O$. It is difficult, however, to obtain this compound as a single phase. The quantity of $2CaO \cdot Si_3N_4$ formed was increased by elevating the

TABLE II X-ray data for $2CaO \cdot Si_3N_4$

d_{obs} ($\times 10^{-1}$ nm)	I_{obs}	d_{obs} ($\times 10^{-1}$ nm)	I_{obs}
5.163	m	1.9186	mw
4.792	w	1.8941	vw
4.609	w	1.8620	w
3.471	mw	1.7951	w
3.314	vs	1.7717	w
3.251	m	1.7390	w
3.197	m	1.7211	w
2.955	s	1.6676	w
2.883	vw	1.6570	m
2.803	w	1.6236	w
2.770	m	1.5640	w
2.583	mw	1.4940	mw
2.542	vs	1.4780	m
2.437	m	1.4261	vw
2.422	m	1.4037	mw
2.396	ms	1.3952	m
2.379	mw	1.3406	w
2.305	m	1.3306	w
2.288	m	1.2711	mw
2.2108	m	1.2472	w
2.1445	w		
2.1091	w		
2.0157	vw		
1.9947	mw		

temperature. Up to 1650° C for 1 h, a nearly pure phase of this compound could be obtained. Its real composition was determined by electron probe microanalysis (Fig. 1). Its X-ray data are listed in Table II without indexing.

A limited range of solid solutions of Ca–α-SiAlON was determined to exist extending on the tie line Si_3N_4–CaO:3AlN. The generalized formula of the Ca–α-SiAlON solid solution can be represented as $Ca_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$ [1], where the replacement of Al–O (0.175 nm) for Si–N (0.174 nm) and the fill of calcium in interstitial holes would cause no structural change. But the replacement of Al–N (0.187 nm) for Si–N (0.174 nm) would give rise to a large structural change. The results of analysis of two compositions of Ca–α′-SiAlONs as examples by electron probe are

$$Ca_{0.7}Si_{9.4}Al_{2.6}O_{1.2}N_{14.8} \quad (m = 1.4)$$

and

$$Ca_{1.2}Si_8Al_4O_{1.6}N_{14.4} \quad (m = 2.4)$$

with

$$a = 0.7851\,\text{nm} \quad c = 0.5708\,\text{nm} \quad c/a = 0.727$$

and

$$a = 0.7917\,\text{nm} \quad c = 0.5756\,\text{nm} \quad c/a = 0.727$$

respectively. It was found that only ~ 70% of the calcium in the starting compositions could fill in the interstitial holes. The change of unit cell parameters of Ca–α-SiAlON ss in relation to the *m* value of replacement of Al–N for Si–N is shown in Fig. 2. It can be postulated that the solubility of calcium in α-SiAlON ss spans from 0.3 to 1.4 Ca per unit cell ($m = 0.6$ to 2.8) at 1700° C, which is less than the highest content, $Ca_{1.83}Si_{8.34}Al_{3.66}N_{16}$, as determined by Jack [10] and is considerably higher than that of Y–α-SiAlON ss [7].

In this quasiternary system, a metastable phase of $2CaO \cdot Si_3N_4 \cdot AlN$ (M phase) was synthesized by hot-pressing at only 1450° C. Its *d* spacing data are listed in Table III without indexing. By elevating the temperature it decomposes to two crystalline phases, $CaAlSiN_3$ (E phase) and AlN, and with some glass phase. The different phases appeared with a starting composition of $2CaO:Si_3N_4:AlN$ by treating at different temperatures which are also listed in Table IV. The $CaAlSiN_3$ phase was characterized to be orthorhombic (Table V). In fact the E phase does not occur on the plane of this system. It is interesting to note that $CaAlSiN_3$

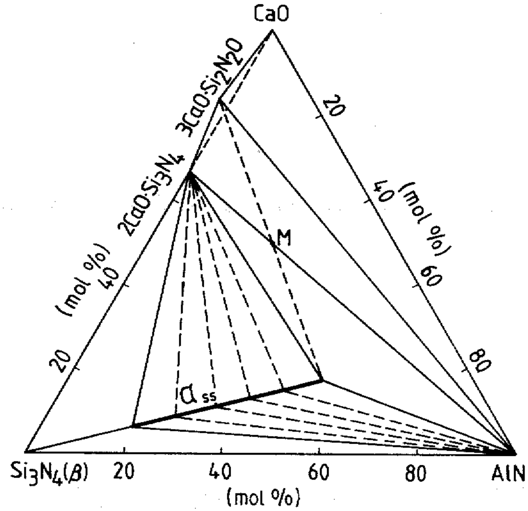

Figure 3 Subsolidus diagram of Si_3N_4–AlN–CaO system.

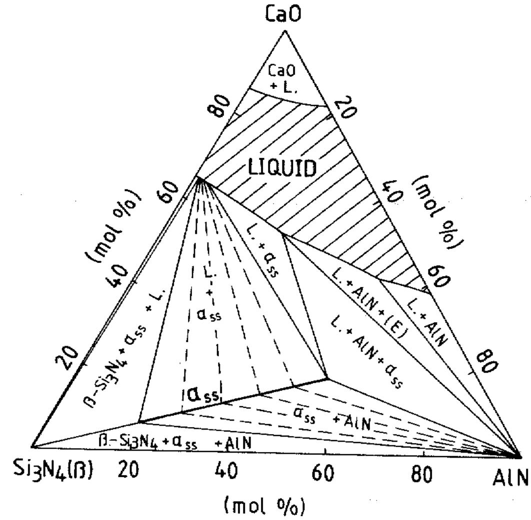

Figure 4 Isothermal section of Si_3N_4–AlN–CaO system at 1700° C.

and AlN phases appear simultaneously at 1500° C in almost all compositions restricted in the $3CaO \cdot Si_2N_2O$–$2CaO \cdot Si_3N_4$–AlN subsystem. Up to 1700° C the composition $2CaO:Si_3N_4:AlN$ forms α-solid solution with glass.

No calcium-containing polytype was found.

By phase analysis and varying heat treatment conditions of about forty compositions within this quasiternary system, the subsolidus phase diagram of the Si_3N_4–AlN–CaO system was constructed (Fig. 3). The following compatible phase equilibria were established, respectively.

β-Si_3N_4–α-SiAlON ss–AlN

β-Si_3N_4–α-SiAlON ss–$2CaO \cdot Si_3N_4$

α-SiAlON ss–AlN

α-SiAlON ss–$2CaO \cdot Si_3N_4$

CaO–$3CaO \cdot Si_2N_2O$–AlN

$2CaO \cdot Si_3N_4$–$3CaO \cdot Si_2N_2O$–AlN,

$2CaO \cdot Si_3N_4$–α-SiAlON ss–AlN

Considering the metastability of the $2CaO \cdot Si_3N_4 \cdot AlN$ phase, the tie lines starting from it are joined by the dotted lines.

The upper part of this system presents a low melting temperature region. The isothermal section of this system at 1700° C was determined as shown in Fig. 4. For all compositions studied, the composition Si_3N_4:9CaO:10AlN possesses the

TABLE III X-ray data for $2CaO \cdot Si_3N_4 \cdot AlN$

d_{obs} ($\times 10^{-1}$ nm)	I_{obs}	d_{obs} ($\times 10^{-1}$ nm)	I_{obs}
5.19	w	2.421	ms
4.85	vw	2.393	mw
4.706	w	2.366	ms
4.436	w	2.343	m
4.308	mw	2.289	vw
4.101	w	2.163	m
3.555	m	2.0823	w
3.457	vw	2.0526	w
3.376	w	2.0234	vw
3.149	s	2.0014	w
3.100	w	1.9762	vw
3.054	w	1.9201	mw
3.005	w	1.8922	m
2.943	vw	1.8280	w
2.883	w	1.8050	mw
2.861	w	1.7317	vw
2.820	mw	1.6834	w
2.720	m	1.6603	w
2.696	s	1.6132	vw
2.659	mw	1.5898	vw
2.611	vs	1.5657	mw
2.535	w	1.5527	ms
2.512	w		
2.485	m		
2.440	w		

TABLE IV Crystalline phases formed at different temperatures for the composition $2CaO:Si_3N_4:AlN$

T(° C) (HP. for 1 h)	Crystalline phases *
1400	M + D
1450	M
1500	E + AlN
1600	E + AlN + α′
1600 (for 1.5 h)	α′ + D + E + AlN
1700	α′

*M: $2CaO \cdot Si_3N_4 \cdot AlN$, D: $2CaO \cdot Si_3N_4$, E: $CaAlSiN_3$, α′: α-SiAlON ss.

TABLE V X-ray data for $CaAlSiN_3$ phase

hkl	d_{cal} ($\times 10^{-1}$ nm)	d_{obs} ($\times 10^{-1}$ nm)	I_{obs}
110	4.853	4.839	vw
020	4.792	4.789	vw
111	3.478	3.482	vw
200	2.814	2.819	m
130	2.778	2.773	s
002	2.493	2.495	s
201	2.451	2.453	s
131	2.427	2.422	s
040	2.396	2.394	vw
223	2.182	2.183	w
202	1.866	1.866	vw
132	1.855	1.854	w
330	1.618	1.618	m
060	1.597	1.598	vw
331	1.539	1.539	vw
203	1.431	1.433	mw
133	1.426	1.426	w
223	1.371	1.371	vw
332	1.357	1.356	mw
261	1.338	1.339	vw

Orthorhombic $a_0 = 0.5629(2)$ nm $b_0 = 0.9584(3)$ nm $c_0 = 0.4986(1)$ nm.

lowest melting temperature with $T_m \sim 1450°$ C, although the exact eutectic point has not been determined thoroughly.

The following conclusions can be made.

1. In the Si_3N_4–CaO system, two compounds, $2CaO \cdot Si_3N_4$ and $3CaO \cdot Si_2N_2O$ were identified and the latter was characterized by a cubic structure ($a_0 = 1.507$ nm) same as that of $3CaO \cdot Al_2O_3$ ($a_0 = 1.5282$ nm).

2. In the AlN–CaO system, no compound was found except for the $2H^{\delta}$ AlN-polytype introduced by the AlN starting powder.

3. The subsolidus phase diagram and the isothermal section at 1700° C of the Si_3N_4–AlN–CaO system were determined. Within this system the extent of Ca–α-SiAlON ss was determined to have a solubility of calcium in α-SiAlON ss within a range of 0.3 to 1.4 Ca per unit cell. The α-SiAlON ss is in equilibrium with β-Si_3N_4 and/or AlN as well as with $2CaO \cdot Si_3N_4$. A metastable phase of $2CaO \cdot Si_3N_4 \cdot AlN$ at 1450°C was found. No calcium-containing polytype could be identified. Within the low melting region, the composition of Si_3N_4:9CaO:10AlN possesses the lowest melting temperature with $T_m \sim 1450°$ C.

References

1. S. HAMPSHIRE, H. K. PARK, D. P. THOMPSON and K. H. JACK, *Nature* **274** (1978) 880.
2. K. H. JACK, in "High Temperature Chemistry of Inorganic and Ceramic Materials," edited by F. P. Glasser and P. E. Potter (The Chemical Society, Burlington House, London, 1976) pp. 204–21.
3. L. J. GAUCKLER, H. L. LUKAS and G. PETZOW, *J. Amer. Ceram. Soc* **58** (1975) 346.
4. L. J. GAUCKLER, H. L. LUKAS and T. Y. TIEN, *Mater Res. Bull.* **11** (1976) 503.
5. I. K. NAIK, L. J. GAUCKLER and T. Y. TIEN, *J. Amer. Ceram. Soc* **61** (1978) 332.
6. G. PETZOW, L. J. GAUCKLER, T. Y. TIEN and S. BOSKOVIC, in Proceedings of the International Symposium on Sintering of Oxide and Non Oxide Ceramics, edited by S. Somiya and S. Saito (Gakujutsu Fukyu-Kai, Tokyo, 1979) pp. 28–39.
7. Z. K. HUANG, P. GREIL and G. PETZOW, *J. Amer. Ceram. Soc.* **66** (1983) C96.
8. T. Y. TIEN, G. PETZOW, L. J. GAUCKLER and J. WEISS, private communication (1982).
9. W. Y. SUN, T. S. YEN and T. Y. TIEN, "Subsolidus Phase Relationships in Part of the System Si, Al, Ca/N, O" (1983).
10. K. H. JACK, in Second Annual and Final Technical Report, European Research Office, United States Army, London W. 1, England (1979) p. 60.

Received 6 June
and accepted 3 July 1984