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Solubility Limits of α′-SiAlON Solid Solutions in the System Si,Al,Y/N,O

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The solubility limit of α′-SiAlON solid solutions on the Si_3N_4–YN:3AlN composition join in the system Si_3N_4–YN–AlN has been determined at 1800°C. The end members of these solid solutions are $Y_{0.43}Si_{10.7}Al_{1.3}N_{16}$ and $Y_{0.8}Si_{9.6}Al_{2.4}N_{16}$. Unit-cell dimensions of the α′-SiAlON solid solutions in the system Si,Al,Y/N,O can be expressed as follows: a_0(Å) = 7.752 + 0.045m + 0.009n, c_0(Å) = 5.620 + 0.048m + 0.009n, where the α′-SiAlON solid solution has the formula $Y_xSi_{12-(m+n)}Al_{m+n}N_{16-n}O_n$. The single-phase boundary of the solid solution α′-SiAlON on the composition triangle Si_3N_4–YN:3AlN–AlN:Al_2O_3 is delineated. The present paper also reports the phase relationships involving α′-SiAlON. [Key words: solubility, SiAlON, yttrium, solid solutions, phases.]

I. Introduction

THE subsolidus phase relationships in the system Si_3N_4–AlN–YN–Al_2O_3–Y_2O_3 have been reported elsewhere.[1] In the region explored, the Y-containing compounds include melilite, $Y_3Al_5O_{12}$ (YAG), and Jss (solid solutions between $2Y_2O_3 \cdot Si_2N_2O$–$2Y_2O_3 \cdot Al_2O_3$). Both melilite and YAG were found to be compatible with α′-SiAlON. α′-SiAlON solid solutions are compatible with β′-SiAlON, AlN, and AlN-polytypoid phases (12H → 2H[δ]) forming nine α′-, β′-SiAlON and AlN-polytypoids (or AlN) compatibility tetrahedra. The presence of these tetrahedra makes possible the development of ceramic composite materials containing α′-, β′-SiAlON and AlN-polytypoids. It is believed that these ceramics may have superior properties because the AlN-polytypoid phases have a platelet morphology. In a previous paper,[1] the α′-SiAlON was considered to be a point composition. In our present work, the solubility limits will be reported.

The cell dimensions of α′-SiAlON have been reported by Hampshire *et al.*[2] as the following equations:

$$\Delta a_0(\text{Å}) = 0.045m + 0.009n \quad (1)$$

$$\Delta c_0(\text{Å}) = 0.04m + 0.008n \quad (2)$$

The relationships in these equations will be revised in the present work. Compatibility relationships involving α′-SiAlON will also be reported.

II. Experimental Procedure

The starting powders used were α-Si_3N_4,‡ AlN,§ Al_2O_3, and Y_2O_3. The oxygen content of the nitride powders was taken into account in computing the batch compositions. The batch mixtures were attrition-milled for 1.5 h in a Teflon¶-coated stainless steel jar with porcelain balls under 2-propanol. Powders were dried and put into graphite dies and then hot-pressed in a graphite-resistant furnace under a pressure of 20 MPa under static nitrogen of 1 atm pressure. The phases were identified and the unit-cell dimensions of the α′-SiAlON were determined by X-ray diffraction technique.

For the compositions in the Si_3N_4–YN–AlN system, YN was used as the starting material. The YN used was freshly prepared in this laboratory, the experimental details of which were described previously.[1] The mixtures without YN were milled under 2-propanol in an agate mortar. YN powders were then added and were dry mixed in a dry box under flowing nitrogen using an agate mortar and pestle immediately prior to firing. The firing was done at 1800°C for 2 h under a static nitrogen in a graphite-resistant furnace which was evacuated to 30×10^{-3} torr before heating to 1000°C. The entire procedure from sample preparation to X-ray analysis was carried out on the same day in order to prevent hydrolysis of YN in both the green and the fired specimens.

III. Results and Discussion

(1) Solid Solubility Limits of α′-SiAlON

The α′-SiAlON solid solution has a two-dimensional composition region lying on the plane Si_3N_4–AlN:Al_2O_3–YN:3AlN, as illustrated in Fig. 1. The compositions of α′-SiAlON solid solutions can be expressed by the formula $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$. Based on their experimental data, Hampshire *et al.*[2] established an empirical relationship to express the change of cell dimension of the α′-SiAlON phase containing different metals (M) in the interstitial sites (see Eqs. (1) and (2)).

These equations do not differentiate the type of M ions in the interstitial sites. With the experimental data accumulated in our investigations, however, it became clear that the c/a ratio varied slightly in α′-SiAlON containing different metal ions in the interstitial sites. For Y-containing α′-SiAlON, the change in cell dimensions in the c direction is always higher for a given $m + n$ value than that in the a direction. Y-containing and rare-earth-containing α′-SiAlONs always have a c/a ratio in the range of 0.728 to 0.729.[2–7] The c/a ratios for the Ca- and Li-containing α′-SiAlONs are 0.727 and 0.724, respectively.[2] Our results indicate that the Y-containing α′-SiAlON has a steeper slope in the c direction than that in the a direction and that the c/a ratio in Y-containing α′-SiAlON has a range from 0.728 to 0.729 (see Table I). Therefore, for different α′-SiAlONs containing different metal ions, the above relationships need to be revised. From the published data[2–4] (which are considered to be more accurate because the compositions of α′-SiAlON were determined by EDAX),

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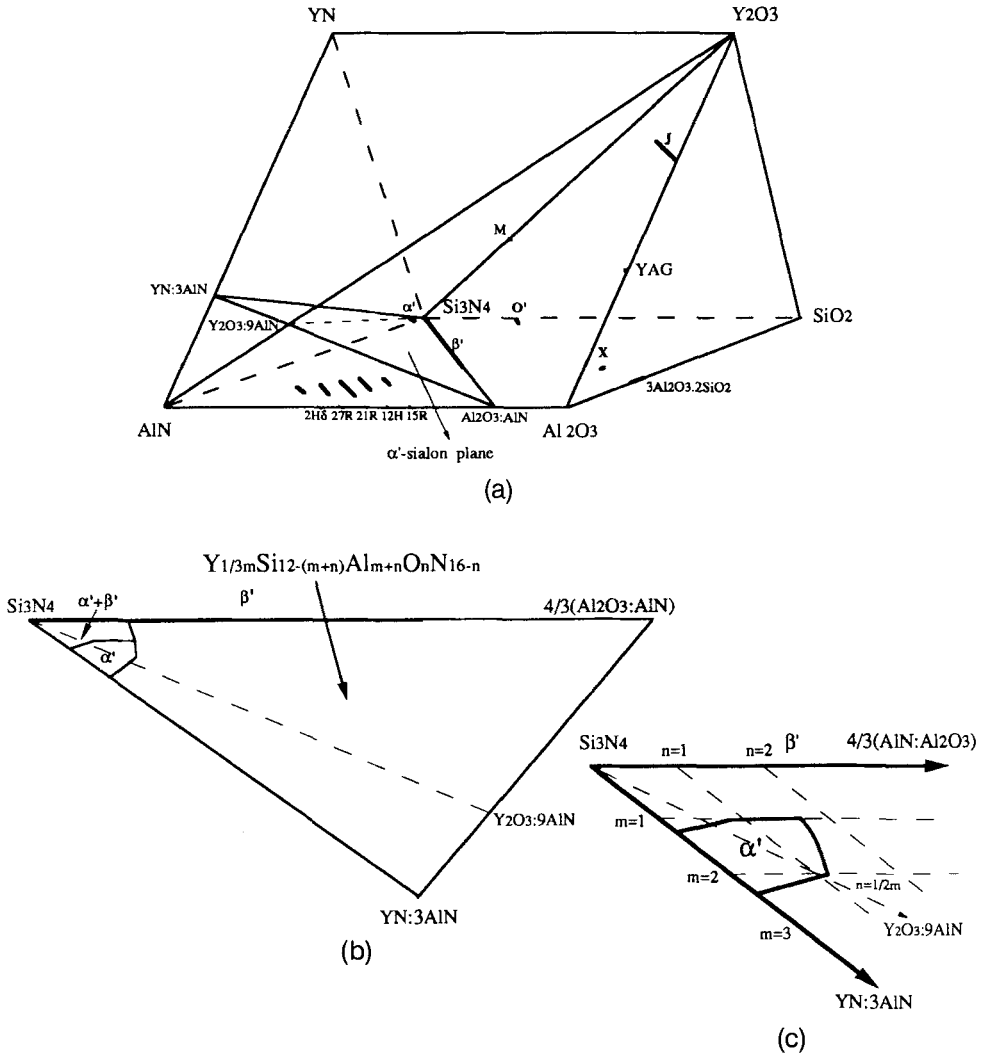

Fig. 1. (a) Representation of α'-sialon plane in Y–sialon system. (b) α'-Sialon plane. (c) Enlarged corner of α'-sialon plane.

the following empirical equations were suggested for the unit-cell dimensions in the Y-containing α'-SiAlONs:

$$a_0(\text{Å}) = 7.752 + 0.045m + 0.009n \quad (3)$$

$$c_0(\text{Å}) = 5.620 + 0.048m + 0.009n \quad (4)$$

Table II lists a comparison of the observed and calculated unit-cell dimensions for Y-containing and rare-earth-ion-containing α'-SiAlONs using the new proposed formulas given in Eqs. (3) and (4). Compared to Eqs. (1) and (2), the new relationships in these equations give a better fit.

Thompson[8] reported that the α'-SiAlON in the YN–Si_3N_4–AlN system has a range of composition extending from $m = 1.8$ to $m = 3.4$ in the general formula $Y_{m/3}Si_{12-m}Al_mN_{16}$. However, Slasor[9] found that the single-phase region of the Y-containing α'-SiAlON extends from the pure silicon nitride toward aluminum oxide. The boundary facing β'-SiAlON is approximately at $m = 1.0$ and $n = 0$ to $n = 1.7$ ($Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, where $n = (1/2)m$). Huang *et al.*[3] determined that the solubility limits of the α'-SiAlON on the join Si_3N_4–Y_2O_3:9AlN had an "m" value that ranged from 1 to 2. Stutz *et al.* reported that the solubility limit of α'-SiAlON in the oxygen-rich direction is as follows: $x = 0.33$ to 0.67 ($x = (1/3)m$) for Y, $m + n = 1.5$ to 3.0 for Al, and $n = 0.5$ to 1.24 for O.[6] Table II gives the cell dimensions of some of the α'-SiAlON compositions. The lower limit of the cell dimensions of pure nitride α'-SiAlON ($n = 0$), which coexists with β'-SiAlON, has a value of $a = 7.810$ (Å) and $c = 5.681$ (Å). The upper limit of the pure nitride α'-SiAlON, which is in equilibrium with AlN and $Y_2Si_3N_6$,[1] is at $a = 7.863$ (Å) and

Table I. Comparison between Observed and Calculated Unit-Cell Dimensions

Compositions	Observed			Calculated*			Calculated†		
	a (Å)	c (Å)	c/a	a (Å)	c (Å)	c/a	a(Å)	c(Å)	c/a
$Y_{0.4}Si_{1.0}Al_2O_{0.8}N_{15.2}$[2]	7.81	5.69	0.729	7.813	5.674	0.726	7.813	5.685	0.728
$Y_{0.6}Si_{9.2}Al_{2.8}O_{1.1}N_{14.9}$[2]	7.83	5.71	0.729	7.843	5.701	0.727	7.843	5.716	0.729
$Y_{0.5}Si_{9.3}Al_{2.7}O_{0.9}N_{15.1}$[4]	7.83	5.71	0.729	7.823	5.687	0.727	7.823	5.701	0.729
$Nd_{0.6}Si_{8.5}Al_{3.5}O_{1.7}N_{14.3}$[3]	7.85	5.72	0.729	7.848	5.706	0.727	7.848	5.723	0.729
$Sm_{0.6}Si_{9.2}Al_{2.8}ON_{15}$[3]	7.85	5.72	0.729	7.842	5.700	0.727	7.842	5.715	0.729
$Gd_{0.6}Si_{9.2}Al_{2.8}ON_{15}$[3]	7.85	5.72	0.729	7.842	5.700	0.727	7.842	5.715	0.729
$Dy_{0.67}Si_9Al_3ON_{15}$[3]	7.86	5.73	0.729	7.851	5.708	0.727	7.851	5.725	0.729

*By using the equations $\Delta a(\text{Å}) = 0.045m + 0.009n$ and $\Delta c(\text{Å}) = 0.040m + 0.008n$ (Ref. 2). †By using the equations $\Delta a(\text{Å}) = 0.045m + 0.009n$ and $\Delta c(\text{Å}) = 0.048m + 0.009n$.

Table II. Results of XRD Determination: Phases Present and Unit-Cell Dimensions

No.	Compositions (wt%)					Phases present	Unit-cell dimensions					Compositions of α'- and β'-sialon		
							α'-sialon			β'-sialon				
	Si_3N_4*	AlN†	Al_2O_3	Y_2O_3	YN‡		a (Å)	c (Å)	c/a	a	c	m	n	β
1	61.70	21.13			17.17	α', AlN, $Y_2Si_3N_6$	7.863	5.731	0.729			2.4	0	
2	77.87	12.04			10.08	α'	7.821	5.693	0.728			1.5	0	
3	82.00	12.68			5.31	α', β-Si_3N_4	7.810	5.681	0.727			1.3	0	
4	60.53	11.65	2.94	24.88		α', melilite	7.813	5.691	0.728			1.2	1.7	
5	47.65	44.66	3.47	4.22		α', AlN, 2H[δ], 27R	7.816	5.699	0.729			1.2	1.7	
6	67.37	21.65	7.98	3.00		β', α', 12H	7.805	5.687	0.729	7.627	2.923	1.0	1.6	β_{10}
7	76.61	8.37	0.07	14.95		α', β', melilite	7.799	5.677	0.728	7.608	2.910	1.0	1.0	β_0
8	72.33	11.70	6.01	9.96		β', α', YAG, 12H	7.804	5.682	0.728	7.626	2.923	1.0	1.5	β_{10}

*Containing 2 wt% O. †Containing 1.3 wt% O. ‡Containing 9 wt% free C.

c = 5.731 (Å). These compositions correspond to m = 1.3 and 2.4, respectively.

α'-SiAlON, which can be prepared by using Si_3N_4, AlN, Al_2O_3, and Y_2O_3, without the use of the compound YN, would have a composition whose oxygen content is higher than that of the compositions on the join Si_3N_4–Y_2O_3:9AlN ($n = (1/2)m$).

Using the empirical relationships given in Eqs. (3) and (4), a series of parallel lines can be constructed, as shown in Figs. 2 and 3. These lines represent the composition dependence of the lattice parameters of Y–α'-SiAlON. Combined with our previous results,[1] the entire α'-SiAlON solid solution region $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ can now be outlined. The single-phase α'-SiAlON begins on the pure nitride ternary system Si_3N_4–YN–AlN with a single-phase region ranging from m = 1.3 to m = 2.4 and extends toward the alumina side with the limit gradually decreasing until m = 1.0. The low limit facing the β'-SiAlON changes very slowly from m = 1.3 to m = 1.0. The maximum oxygen content of α'-SiAlON is approximately n = 1.7. The solid lines in Figs. 2 and 3 represent the data determined in this laboratory. Considering the oxygen content in the nitrides, the solubility region of m = 1 to m = 2 determined on the join Si_3N_4–Y_2O_3:9AlN[3] should be somewhere above the line $n = (1/2)m$. The dotted lines indicate the boundary of the α'-SiAlON facing alumina, estimated by combining the literature data.[9]

(2) Subsolidus Phase Relationships

Compositions listed in Table I were designed to establish the subsolidus phase relationships in the system Si_3N_4–AlN–Al_2O_3–Y_2O_3 containing α'-SiAlON. These compositions are on the tie lines connecting α'-SiAlON–melilite, α'-SiAlON–AlN and in the compatibility triangles α'-SiAlON–β'-SiAlON–12H, α'-SiAlON–β'-SiAlON–YAG, and α'-SiAlON–β'-SiAlON–melilite. These compositions were hot-pressed at 1650°C for 3 to 4 h. No unreacted α-Si_3N_4 was detected and the liquid phase was negligible. If any liquid phase is present, Jss will crystallize during cooling. These compositions were not used for the subsolidus determinations. The compositions listed in Table II confirmed the compatibility relationships. Compositions 4 and 5 are located on the tie lines of the alumina-rich composition of the α'-SiAlON and melilite, and α'-SiAlON and AlN, respectively. The terminal composition of α'-SiAlON on the alumina-rich side is m = 1 and n = 1.7. The results confirmed that the compatibility region of α'-SiAlON and melilite and α'-SiAlON and AlN do extend to the terminal points. The appearance of 2H[δ] and 27R in composition 5 is expected because all of the tie lines between α'-SiAlON and AlN-polytypoids are squeezed into the terminal point forming very narrow compatibility triangles. The observed unit-cell dimensions of α'-SiAlON in compositions 4 and 5 are a = 7.813 Å, c = 5.691 Å, and a = 7.816 Å, c = 5.699 Å, respectively. Considering the starting compositions and the phases present, the n value can be considered to be at the maximum at n = 1.7, thus giving the m value of 1.2, which is reasonably close to the limit of α'-SiAlON toward the alumina side. Composition 6 further confirms that the α'-SiAlON in equilibrium with 12H occurs at the alumina-rich terminal point. The β'-SiAlON composition, which is in equilibrium with 12H, is at the β_{10}, which is also the solubility limit in the α'-SiAlON and β'-SiAlON two-phase regions. These results agreed with the values obtained by Slasor,[7] who reported that the limiting composition of β'-SiAlON in equilibrium with α'-SiAlON occurs at an x value slightly less than unity ($Si_{6-x}Al_xO_xN_{8-x}$, x = 1 corresponds to β_{13}). Compositions 7 and 8 were designed for the determination of the tie lines between α'-SiAlON and β'-SiAlON. At higher temperatures, α'-SiAlON and β'-SiAlON coexist with a liquid phase. The

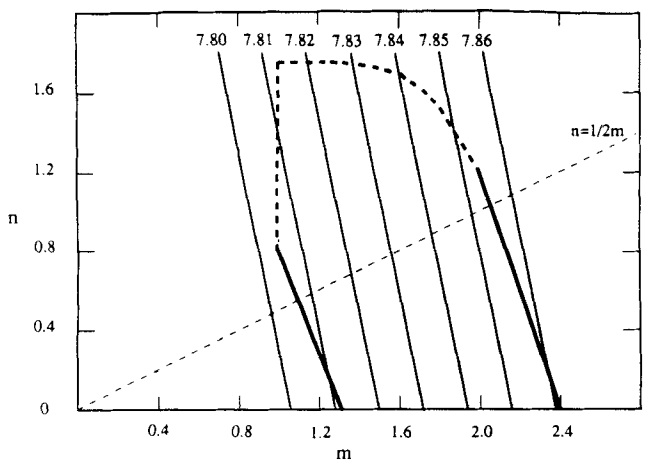

Fig. 2. Y–α'-sialon solubility region and its corresponding a-dimension values.

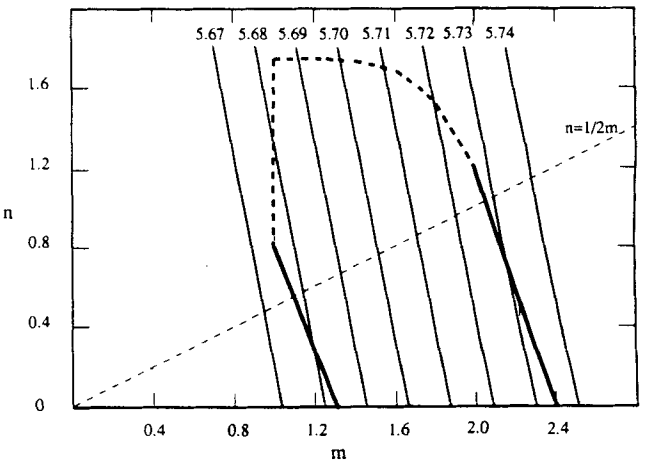

Fig. 3. Y–α'-sialon solubility region and its corresponding c-dimension values.

tie lines between α'-SiAlON and β'-SiAlON are likely to be parallel. Below subsolidus temperatures, melilite coexists with the entire α'-SiAlON region and β-Si_3N_4. YAG coexists with the entire β'-SiAlON and alumina-rich α'-SiAlON compositions. From these relationships, the following compatibility tetrahedra can be established:

β-Si_3N_4–α'-SiAlON (boundary facing to β')–melilite

β-Si_3N_4–α'-SiAlON ($m = 1$, $n = 1.7$)–melilite–YAG

β-Si_3N_4–β_{10}–α'-SiAlON ($m = 1$, $n = 1.7$)–YAG

The results obtained from compositions 7 and 8 confirmed the existence of the above relationships.

Based on the experimental data obtained in the present work and the subsolidus phase relationships involving α'-SiAlON in the system Si_3N_4–AlN–Al_2O_3–Y_2O_3,[1] the following compatibility tetrahedra have been established:

α'-SiAlON (entire region)–melilite

α'-SiAlON (entire region)–AlN

α'SiAlON (boundary facing β')–β_0–melilite

α'SiAlON (boundary facing β')–β_0–AlN

α'-SiAlON ($m = 1, n = 1.7$)–β_0–melilite–YAG

α'-SiAlON ($m = 1, n = 1.7$)–β_0–β_{10}–YAG

α'-SiAlON ($m = 1, n = 1.7$)–β_{10}–YAG–12H

α'-SiAlON ($m = 1, n = 1.7$)–β_{10}–12H–21R

α'-SiAlON ($m = 1, n = 1.7$)–β_8–β_{10}–21R

α'-SiAlON ($m = 1, n = 1.7$)–β_8–21R–27R

α'-SiAlON ($m = 1, n = 1.7$)–β_5–β_8–27R

α'-SiAlON ($m = 1, n = 1.7$)–β_5–27R–2H$^\delta$

α'-SiAlON ($m = 1, n = 1.7$)–β_5–β_2–2H^d

α'-SiAlON ($m = 1, n = 1.7$)–β_2–2H$^\delta$–AlN

α'-SiAlON ($m = 1, n = 1.7$)–β_0–β_2–AlN

α'-SiAlON ($m = 1, n = 1.7$)–12H–21R–YAG

α'-SiAlON ($m = 1, n = 1.7$)–21R–YAG–melilite

α'-SiAlON ($m = 1, n = 1.7$)–21R–27R–melilite

α'-SiAlON ($m = 1, n = 1.7$)–27R–2H$^\delta$–melilite

α'-SiAlON ($m = 1, n = 1.7$)–2H$^\delta$–AlN–melilite

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