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The Si–Al–O–N System at Temperatures of 1700–1775°C

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Abstract

Mixtures of Si_3N_4, SiO_2, Al_2O_3 and AlN have been used to prepare series of specimens heat treated at 1700, 1730, 1750 and 1775°C. The phase relations of the liquid-rich area of the Si–Al–O–N system were studied in detail by X-ray diffraction and scanning electron microscope analysis. Each specimen was chemically analysed after the heat treatment to determine any changes in the overall composition. Finally, the observations have been used to obtain a slightly revised phase diagram at a temperature range of 1700–1730°C for the system Si_3N_4–SiO_2–Al_2O_3–AlN.

Aus Si_3N_4, SiO_2, Al_2O_3 und AlN wurden Mischungen verschiedener Zusammensetzungen hergestellt und bei 1700, 1730, 1750 und 1775°C getempert. Im Bereich der flüssigen Phase im Si–Al–O–N System wurden die Phasenbeziehungen mittels der Röntgenbeugung und der Rasterelektronenmikroskopie genau untersucht. Zur Überprüfung der Zusammensetzung wurde jede Probe nach der Temperung chemisch analysiert. Die Ergebnisse konnten dazu benutzt werden, das Si_3N_4–SiO_2–Al_2O_3—AlN System im Temperaturbereich von 1700–1730°C zu verfeinern.

On a utilisé des mélanges de Si_3N_4, SiO_2, Al_2O_3 et AlN afin de préparer des séries d'échantillons destinés à subir des traitements thermiques à 1700, 1730, 1750 et 1775°C. On a étudié en détail les relations de phases du domaine riche en liquide du système Si–Al–O–N à l'aide de la diffraction X et de la microscopie à balayage. Chaque échantillon était analysé chimiquement après le traitement thermique dans le but de déterminer les changements de composition globale. Ces observations ont finalement été utilisées pour obtenir un diagramme de phase légèrement révisé du système Si_3N_4–SiO_2–Al_2O_3–AlN pour une température de 1700–1730°C.

1 Introduction

Silicon nitride (Si_3N_4) is not a naturally occurring compound, but it has for some time been considered as one of the candidates for engineering components where strength and wear resistance are required at high temperatures. There are, however, some difficulties associated with the sintering of silicon nitride into dense bodies, due to the highly covalent nature of the atomic bonding. The rate of intrinsic self-diffusion is very low at temperatures below that of decomposition.[1,2] One possible way to overcome this inertness is the introduction of metal oxide sintering aids, which form low-melting liquids with the SiO_2 present on the starting Si_3N_4 grains, and this facilitates diffusion of the atoms via the liquid phase at the sintering temperature. Typical examples of such sintering aids are MgO and Y_2O_3, but the use of high temperatures and high pressures, as in hot pressing, may still be needed to yield fully dense materials. It was observed, however, at the beginning of the 1970s, that addition of aluminium oxide together with the previously mentioned oxides was especially favourable and allowed pressureless sintering. In addition, the aluminium oxide reacted with Si_3N_4, forming a solid solution based on the β-Si_3N_4 type of structure.[3,4] The solid solution has the general formula $Si_{6-z}Al_zO_zN_{8-z}$, where $0 < z \lesssim 4$, and it is formed by simultaneous substitution of Al and O for Si and N, respectively. This phase has been named β-sialon, an acronym for Si–Al–O–N.

The part of the Si–Al–O–N system forming the quasi-ternary Si_3N_4–SiO_2–AlN–Al_2O_3 system was studied by Jack[5] and by Gauckler and co-workers.[6,7] It was recognized that this system could

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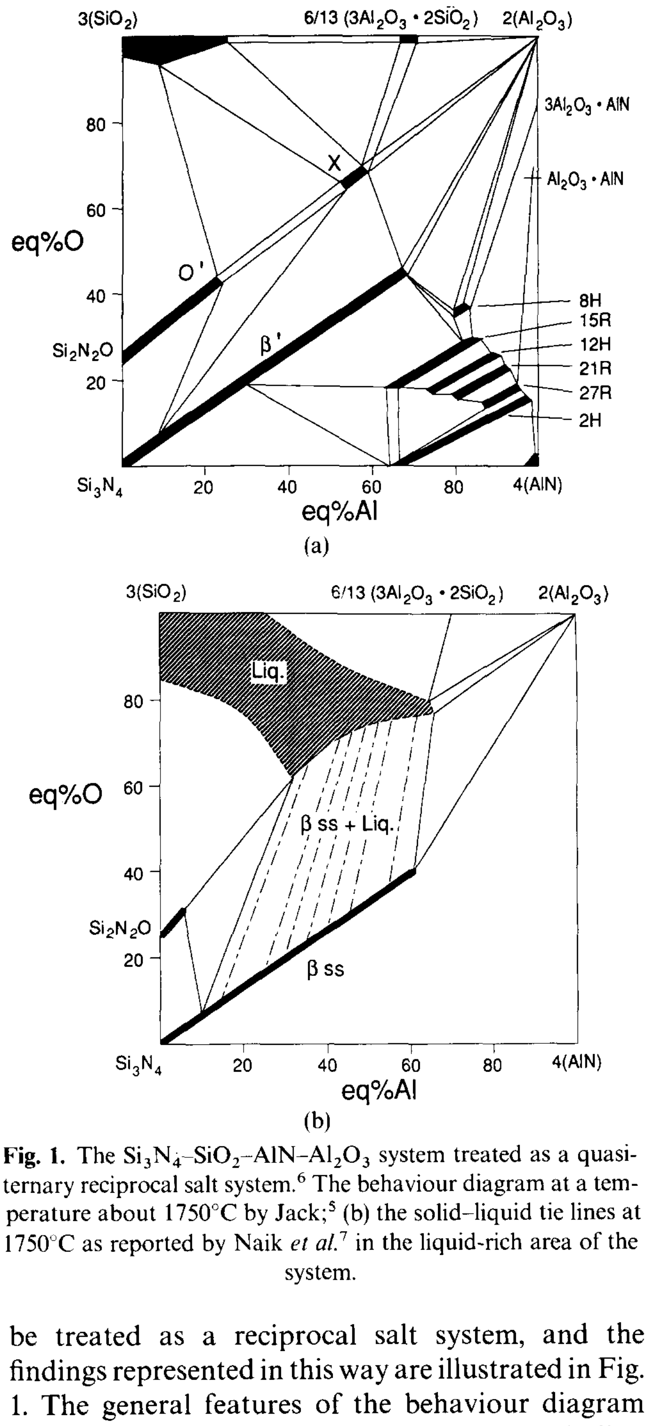


Fig. 1. The Si_3N_4–SiO_2–AlN–Al_2O_3 system treated as a quasi-ternary reciprocal salt system.[6] The behaviour diagram at a temperature about 1750°C by Jack;[5] (b) the solid–liquid tie lines at 1750°C as reported by Naik *et al.*[7] in the liquid-rich area of the system.

be treated as a reciprocal salt system, and the findings represented in this way are illustrated in Fig. 1. The general features of the behaviour diagram found by the two research groups are similar. However, there are some disagreements regarding the composition of the so-called X-phase and its melting temperature, and regarding the so-called sialon polytypoid phases at the AlN-rich corner.[8,9] The X-phase was reported by Gauckler *et al.*[6] to melt at about 1720°C, but is indicated still to be present at about 1750°C in the behaviour diagram by Jack.[5] Somewhat different opinions have also been voiced about the composition of the X-phase, which is reported as $Si_{12}Al_{18}O_{39}N_8$ by Naik *et al.*,[7] as $Si_3Al_6O_{12}N_2$ by Thompson & Korgul[10] and at a position corresponding to 55 equiv.% Al and 65 equiv.% O by Jack.[5] The structures of the sialon polytpoid phases have also been studied in detail by Thompson *et al.*[11] The substructures of the sialon polytypoid phases are based on the parent AlN (wurtzite structure), where the stacking of MeX layers along the c-axis in the unit cell is interrupted in a regular manner by MeX_2 layers, and these phases have been assigned names according to the Ramsdell notation.[9,11]

The formation of silicon oxynitride, Si_2N_2O, from silicon nitride and silicon dioxide is greatly enhanced by the presence of a liquid phase, e.g. by addition of small amounts of oxides like Y_2O_3 and Al_2O_3. Complete conversion to Si_2N_2O has been obtained within 1 h at 1500°C by Y_2O_3 additions.[12] Thus Si_2N_2O-based ceramics form readily at 1600–1700°C by simultaneous addition of these oxides.[13] The silicon oxynitride also has an extended solid solubility range in the Si–Al–O–N system, and it can be represented by $Si_{2-x}Al_xO_{1+x}N_{2-x}$. This aluminium-substituted phase was named 'O′-sialon' in early work[14] and the maximum extension is limited to $x \lesssim 0{\cdot}20$.[15]

The phase relations in the liquid-rich area of the Si_3N_4–SiO_2–AlN–Al_2O_3 system have been studied in this investigation, and the observations have resulted in a slightly modified phase diagram related to that of Jack,[5] which is presented in Section 4.

2 Experimental

The selected compositions in this study were based on Si_3N_4 as parent material with additions of SiO_2, Al_2O_3 or AlN. The overall compositions of three different series, A1–A8, B1–B5 and C1–C10, are illustrated in Fig. 2, where the equivalents are defined by the formula:

$$\text{equiv.\% Al} = \frac{3 \times (\text{at.\% Al})}{3 \times (\text{at.\% Al}) + 4 \times (\text{at.\% Si})} \times 100$$

$$\text{equiv.\% Si} = 100 - \text{equiv.\% Al}$$

$$\text{equiv.\% O} = \frac{2 \times (\text{at.\% O})}{2 \times (\text{at.\% O}) + 3 \times (\text{at.\% N})} \times 100$$

$$\text{equiv.\% N} = 100 - \text{equiv.\% O}$$

A first series of samples, A1–A8, was prepared at 1775°C to verify the overall phase relations as reported previously. The second series, B1–B5, prepared at 1730 and 1750°C established the melting temperature and composition of the X-phase and, finally, a third series of samples, C1–C10, was prepared at 1700°C to map out the extension of the liquid phase.

The raw materials were silicon nitride (H. C.

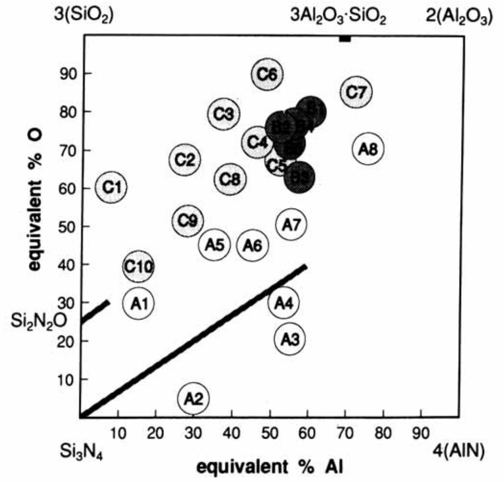


Fig. 2. Overall compositions of the prepared samples in this study. The series A1–A8 was heated at 1775°C; the series B1–B5 at 1730–1750°C and series C1–C10 at 1700°C.

Starck, Berlin, grade LC1), aluminium oxide (Alcoa, Pittsburgh, PA, USA, grade A16SG), aluminium nitride (H. C. Starck, Berlin, grade D) and silicon dioxide (99·9%). The analysed oxygen contents of the silicon nitride and aluminium nitride correspond to 2·9 wt% SiO_2 and 1·9 wt% Al_2O_3, respectively. This excess oxygen present in the starting materials was compensated for in the preparations. The starting powders were carefully weighed (the total batch size was 500 g for each composition), mixed in water-free propanol and milled in a vibratory mill for 17 h with a silicon nitride milling medium. After drying and agglomeration, the powder mixtures were dry-pressed (125 MPa) into compacts of size 16 × 16 × 6 mm. The first two series of samples were pressurelessly sintered at 1700–1775°C in a nitrogen atmosphere for 1–2 h. To avoid changes in the overall composition the samples were covered by micron-sized BN powder and placed in a BN crucible with a lid. The third series was glass-encapsulated and hot isostatically pressed at 1700°C (2 h) with 200 MPa of argon. Before encapsulation, the samples were coated with a BN layer in order to prevent direct contact with the SiO_2-rich glass.

The density of the samples was measured using Archimedes principle and the materials were prepared for physical characterization with standard techniques. Phase analysis was based on X-ray diffraction patterns obtained either from polished cross-sections of the specimens, using a Rigaku diffractometer equipped with a graphite monochromator and a rotating Cu anode working at 10 kW, or from crushed powder samples by a Guinier–Hägg X-ray camera with strictly monochromatic Cu-radiation. The z-values of the β-sialon phase $Si_{6-z}Al_zO_zN_{8-z}$ or the x-values of the oxynitride phase $Si_{2-x}Al_xN_{2-x}O_{1+x}$ were evaluated from the lattice parameters.[15,16] For a quantitative estimate of the amounts of the different phases present, integrated intensities of the major peaks were used.

Specimens for scanning electron microscopy (JEOL JSM 840 and JSM 880 equipped with a Link AN 10 000 EDS analyser) were studied on polished surfaces after vapour application of a gold or carbon coating to reduce specimen charging in the electron beam. As standards for the elemental analysis fully dense single-phase β-sialon ceramics with $z = 0{\cdot}75$, 1·50 and 3·00 were used.[16] It is often quite difficult to distinguish by SEM between different phases in the sialon system. For example, the small difference in molecular weight between the phases often makes it difficult to use back-scattered imaging only. However, the microstructure can often be studied in a light-optical microscope (LOM), by using relief polishing which takes advantage of hardness differences between the phases. Regularly, specimens have been studied in a LOM before the SEM work. The relief polishing is useful also for SEM work in case the microstructure is too fine to be well resolved in an LOM. It is also of importance to check each specimen at different accelerating voltages in the SEM, because structural details may not be detected otherwise. In this study both 10 and 25 kV were used in SEI (secondary electron image) and BSEI (back-scattered electron image).

A thermodynamic assessment of the Si–Al–O–N system, based upon the obtained experimental information and a literature survey, will be published separately.[17] The assessment technique is based on the CALPHAD method, and the computer program PARROT[18] was applied for optimizing the model parameters needed.

3 Results from Heat Treatments

3.1 Overview of the Si–Al–O–N system

The overall compositions of sample series A1–A8 were placed in different phase fields of the Si–Al–O–N system according to Refs 5 and 7 (compare Figs 1 and 2). Visual inspection of specimens sintered at 1775°C gave clear evidence that samples A5–A8 had been partly melted. The X-ray diffraction results of the specimens after cooling to room temperature are given in Table 1. The cooling rate from the sintering temperature to 1000°C was about 100°C/min and somewhat lower thereafter. The presence of some small amounts of 'X-phase' in samples A1 and A5–A7 is believed to be caused by a quick formation

Table 1. Summary of the X-ray diffraction analysis of samples A1–A8 heated for 1 h at 1775°C and rapidly cooled to room temperature

Sample	*Phases observed by XRD*[a]	*Δ-Sialon z-value*
A1	55% β, 40% Si_2N_2O, 5% X-phase	0·9
A2	93% β, 7% 12H	1·5
A3	60% β, 40% 15R	2·0
A4	92% β, 8% 15R	2·9
A5	97% β, 3% X-phase	1·8
A6	93% β, 7% X-phase	2·5
A7	90% β, 10% X-phase	3·6
A8	40% β, 60% Al_2O_3	4·1

[a] β, 12H and 15R denote the β-sialon phase, the 12H-and 15R-sialon polytypoid phases, respectively.

from the liquid phase during cooling, despite the rapid cooling. The samples A2–A4 contained β-sialon together with a sialon polytypoid member, but the presence of the sialon polytypoid 2H[δ] could not be identified in any sample.

3.2 The existence of the X-phase

The samples B1, B2, B3, B4 and B5 correspond to the compositions $Si_3Al_6O_{12}N_2$, $Si_{12}Al_{18}O_{39}N_8$, $Si_{16}Al_{24}O_{45\cdot 5}N_{15}$, $Si_{7\cdot 5}Al_{12}O_{25\cdot 5}N_5$ and $Si_{31}Al_{48}O_{96\cdot 5}N_{25}$, respectively. B1 is the composition given by Thompson & Korgul[10] for the X-phase, B2 the composition given by Naik *et al.*[7] and B3 the composition indicated by Jack.[5] The sample B4 has a composition that is an average of B1 and B2, and sample B5 is an average of B1, B2 and B3. These compositions were heat treated for 2 h both at 1730°C and at 1750°C, and to establish any changes in the overall compositions by this heat treatment the samples were chemically analysed and the results are summarized in Table 2. The heat treatment causes a slight loss of Si and a subsequent enrichment of Al, which is more pronounced at the higher temperature. At the same time a slight loss of nitrogen can be seen. It can further be seen that the Si loss is highest for the B1 and B3 compositions.

The results of the X-ray diffraction phase analysis of the heat-treated specimens are summarized in Table 3. The major crystalline phase in all compositions and at both temperatures is the X-phase, the only crystalline phase present in samples B2, B4 and B5 heat treated at 1730°C. Finally, it can be noted that at the higher temperature, 1750°C, no single-phase sample is found and that β-sialon is present in small amounts in all samples. The SEM results obtained for the B-series specimens are in good overall agreement with the X-ray diffraction

Table 2. The weighed-in overall compositions and the results of a chemical analysis of the samples B1–B5 after heat-treatment at 1730°C and 1750°C for 2 h

Sample		*Composition (equiv.%)*			
		Si	*Al*	*O*	*N*
B1	Weighed-in	40·0	60·0	80·0	20·0
	1730°C	33·3	66·7	82·0	18·0
	1750°C	31·1	68·9	82·4	17·6
B2	Weighed-in	47·0	53·0	76·4	23·6
	1730°C	42·7	57·3	78·0	22·0
	1750°C	40·1	59·9	78·4	21·6
B3	Weighed-in	47·1	52·9	67·0	33·0
	1730°C	41·5	58·5	68·1	31·9
	1750°C	32·7	67·3	69·6	30·4
B4	Weighed-in	45·4	54·6	77·3	22·7
	1730°C	40·9	59·1	79·4	20·6
	1750°C	39·1	60·9	79·6	20·4
B5	Weighed-in	46·2	53·8	72·1	27·9
	1730°C	43·0	57·0	74·1	25·9
	1750°C	42·0	58·0	73·2	26·8

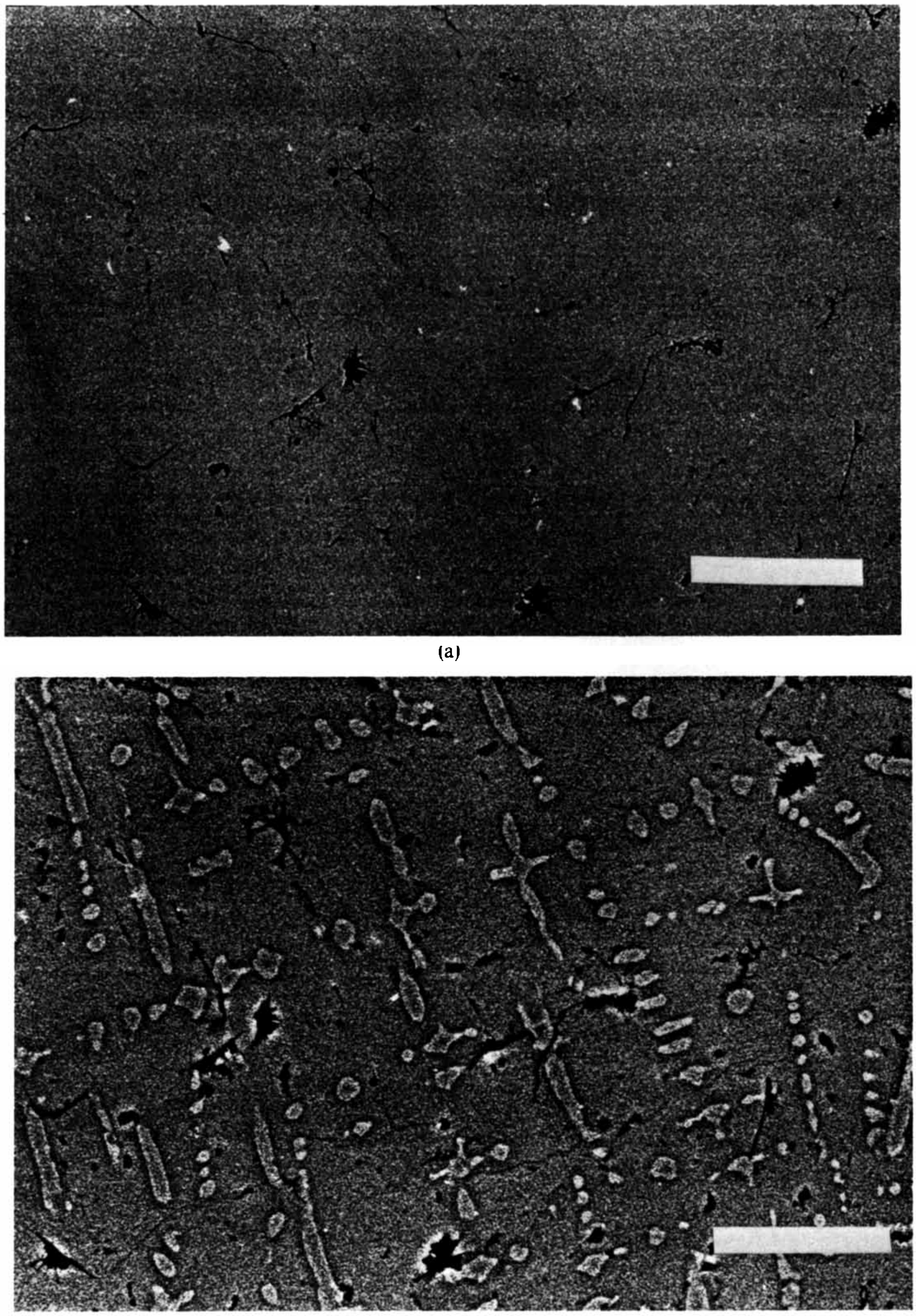
Table 3. Results of the phase analysis by XRD of the samples B1–B5 heat-treated for 2 h at 1730 and 1750°C

Sample		*Phases observed by XRD*[a]
B1	1730°C	60% X-phase, 25% mullite, 15% Al_2O_3
	1750°C	95% X-phase, 5% β, (15R)
B2	1730°C	100% X-phase
	1750°C	95% X-phase, 5% β, (15R)
B3	1730°C	70% X-phase, 25% β, 5% Al_2O_3
	1750°C	90% X-phase, 10% β, (12H)
B4	1730°C	100% X-phase
	1750°C	100% X-phase, (β), (15R)
B5	1730°C	100% X-phase
	1750°C	100% X-phase, (β)

[a] β, 12H and 15R denote the β-sialon phase, the 12H and the 15R-sialon polytypoid phases, respectively. Mullite has the composition $3Al_2O_3 . 2SiO_2$. Parentheses indicate very small or trace amounts.

Table 4. Results of an estimate of the volume fraction of the observed phases by SEM on the samples B1–B5 heat-treated for 2 h at 1730 and 1750°C

Sample		*Phases observed by SEM*
B1	1730°C	55% X-phase, 45% Al_2O_3 dendrites
	1750°C	85% X-phase, 15% Al_2O_3 dendrites
B2	1730°C	90% X-phase, 10% glass
	1750°C	85% X-phase, 5% Al_2O_3, 5% β-Si_3N_4, 5% glass
B3	1730°C	80% X-phase, 20% β-Si_3N_4
	1750°C	90% X-phase, 10% β-Si_3N_4
B4	1730°C	90% X-phase, 10% glass
	1750°C	90% X-phase, 5% β-Si_3N_4, 5% glass
B5	1730°C	90% X-phase, 10% β-Si_3N_4
	1750°C	95% X-phase, 5% β-Si_3N_4

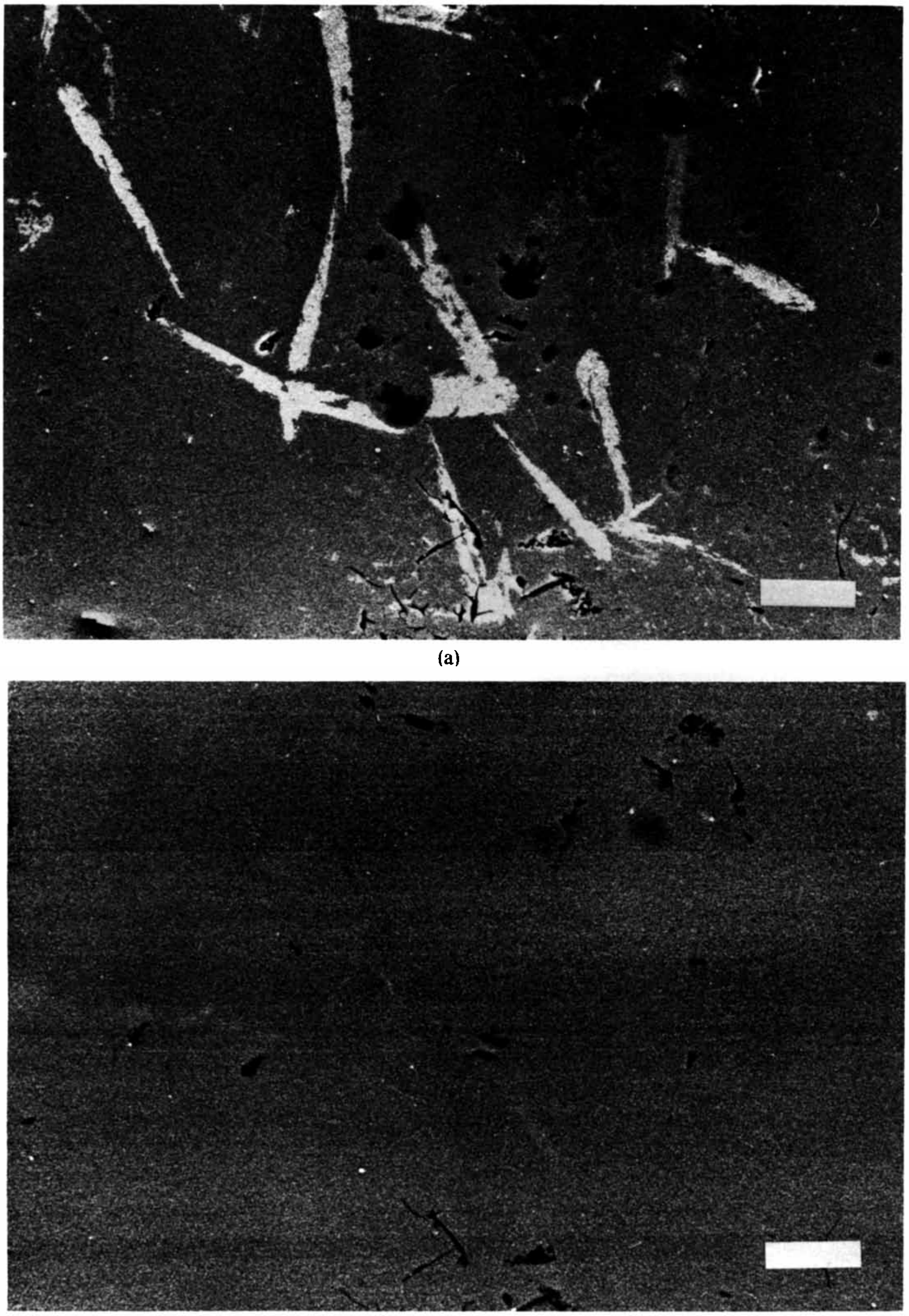

(a)

(b)

Fig. 3. Back-scattered electron images of specimen B1 heat-treated at 1750°C. Acceleration voltage (a) 10 kV and (b) 25 kV. The images are from the same area, but the Al_2O_3 dendrites are only seen at the higher voltage. The bar length is 50 μm.

results. In Table 4 rough estimates of the volume fractions of the different phases as observed by SEM are shown.

In Fig. 3(a) and (b) back-scattered electron images are shown of B1 (1750°C) at 10 and 25 kV, respectively. Interestingly, the Al_2O_3 dendrites can only be observed at the higher voltage. Similar difficulties with B3 (1750°C) are illustrated in Fig. 4(a) and (b) at an accelerating voltage of 10 kV and by using the SEI and BSEI detectors, respectively. The β-Si_3N_4 crystals are clearly seen only in the SEI mode.


(a)

(b)

Fig. 4. SEM images of specimen B3 heat-treated at 1750°C. The acceleration voltage is 10 kV. A secondary electron image is seen in (a) and a back scattered electron image in (b). The images are from the same area, but β-Si_3N_4 crystals are only seen in (a). The bar length is 10 μm.

3.3 The liquid-rich area of the Si–Al–O–N system

The samples C1–C10 (see Fig. 1) were hot isostatically pressed (HIPed) at 1700°C for 2 h. All samples were chemically analysed after HIPing and these results are compared with the weighed-in compositions in Table 5. As seen, there is only negligible, if any, loss of silicon or nitrogen during HIPing. In Table 6 the X-ray diffraction results are shown. The cooling rate after HIPing is very high, from 1700 to 1200°C in about 5 min, and this means

Table 5. The weighed-in overall compositions and the results of a chemical analysis of the samples C1–C10 after heat-treatment at 1700°C for 2 h

Sample		*Composition (equiv.%)*			
		Si	*Al*	*O*	*N*
C1	Weighed-in	92·3	7·7	60·2	39·8
	1700°C	92·0	8·0	63·7	36·3
C2	Weighed-in	72·7	27·3	67·5	32·5
	1700°C	72·9	27·1	68·1	31·9
C3	Weighed-in	62·9	37·1	80·3	19·7
	1700°C	63·7	36·3	80·1	19·9
C4	Weighed-in	53·6	46·4	72·4	27·6
	1700°C	53·7	46·3	72·5	27·5
C5	Weighed-in	47·6	52·4	67·9	32·1
	1700°C	47·0	53·0	69·8	30·2
C6	Weighed-in	51·9	48·1	90·0	10·0
	1700°C	52·5	47·5	90·3	9·7
C7	Weighed-in	28·5	71·5	86·3	13·7
	1700°C	27·0	73·0	86·0	14·0
C8	Weighed-in	60·7	39·3	63·3	36·7
	1700°C	60·3	39·7	65·1	34·9
C9	Weighed-in	71·8	28·2	52·3	47·7
	1700°C	71·2	28·8	52·6	47·4
C10	Weighed-in	85·3	14·7	40·2	59·8
	1700°C	84·9	15·1	39·9	60·1

that the high-temperature state is most probably frozen.

According to X-ray diffraction, specimens C1 and C2 only contain O′-sialon, and Fig. 5 shows sample C1 with its O′-sialon rods in a glass matrix. Due to the fineness of the microstructure it could be thought that these crystals had precipitated during cooling from the HIPing temperature. However, the fast cooling should probably rule out this possibility.

Table 6. Results of the X-ray phase analysis of samples C1–C10 HIPed at 1700°C for 2 h

Sample	*Phases observed by XRD*	*Unit cell of O′-sialon*		
		a (nm)	*b (nm)*	*c (nm)*
C1	O′-sialon	05501	0·8892	0·4861
C2	O′-sialon	0·5499	0·8887	0·4861
C3	X-phase, (O′-sialon)			
C4	X-phase, (O′-sialon)			
C5	X-phase, (β-sialon)			
C6	X-phase, mullite			
C7	X-phase, Al_2O_3			
C8	O′-sialon, X-phase	0·5495	0·8890	0·4856
C9	O′-sialon, X-phase	0·5496	0·8906	0·485·8
C10	O′-sialon, (X-phase)	0·5498	0·890·8	0·4859

The error in the lattice parameters of O′-sialon, refined by computer on a large number of the diffraction peaks, is 0·0002. Parentheses indicate that only small or trace amounts have been observed of the phase concerned.

In specimens C3–C7 the major crystalline phase is the X-phase. The microstructure of C3 is seen in Fig. 6. Coarse elongated X-phase crystals with a hexagonal cross-section of 2 μm are seen. The matrix is a glass phase, and according to the X-ray diffraction results it should also contain O′-sialon crystals.

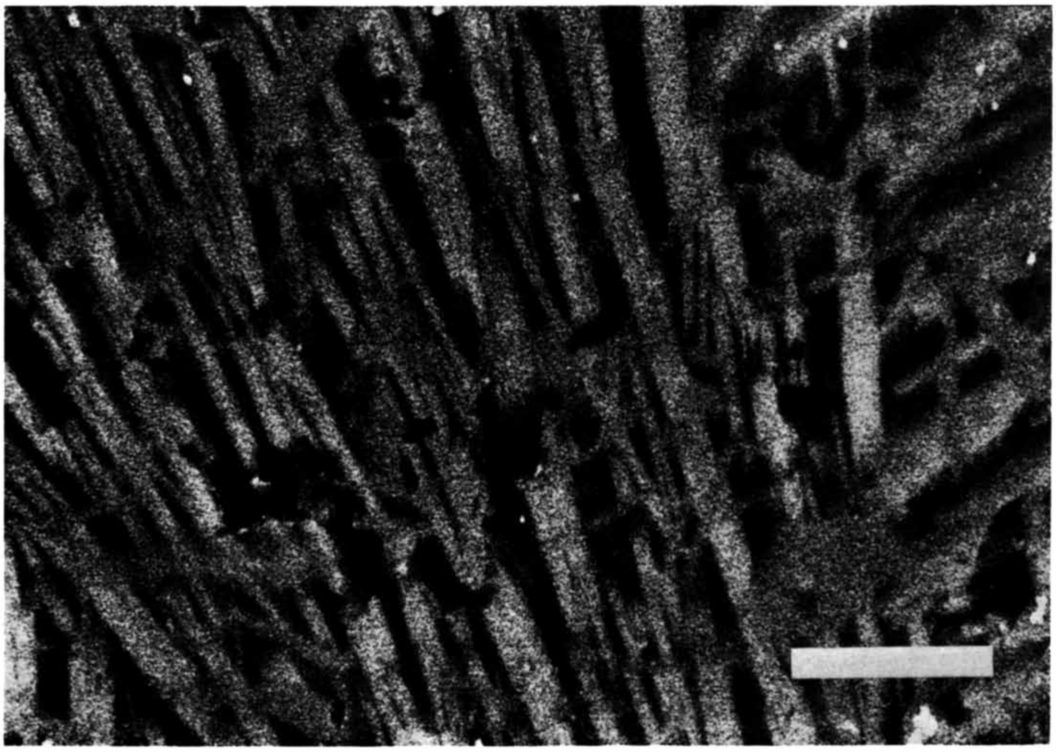


Fig. 5. Back-scattered electron image of specimen C1. The acceleration voltage is 20 keV. Fine rods of O′-sialon are seen. The bar length is 5 μm.

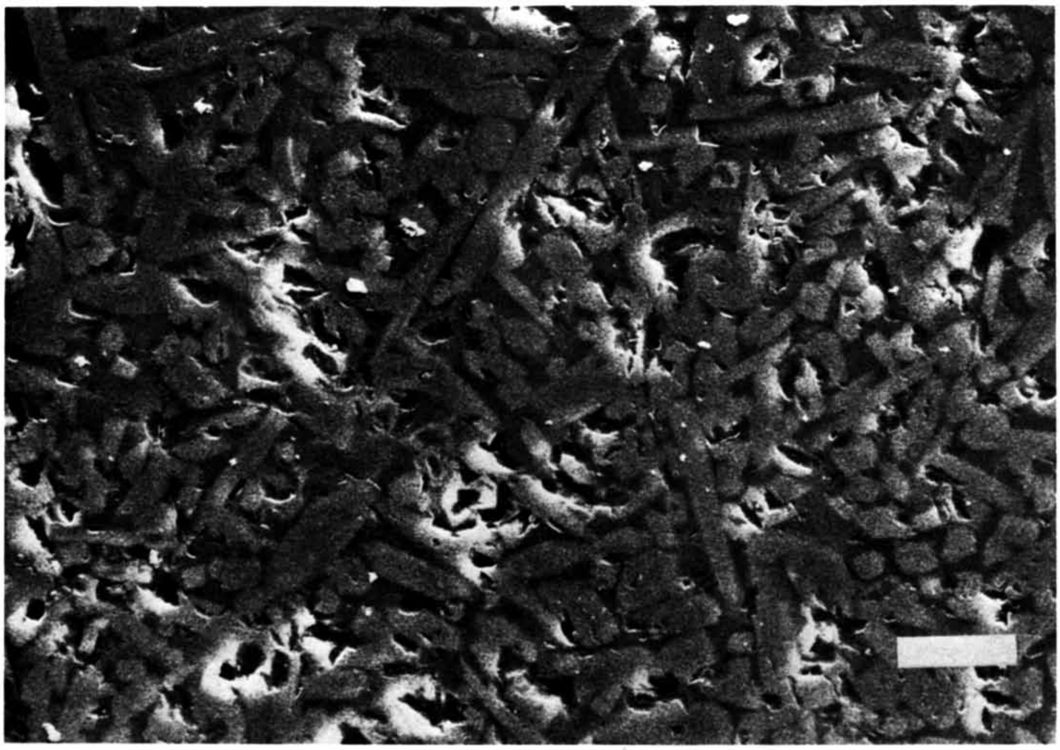


Fig. 6. Secondary electron image of specimen C3. The acceleration voltage is 20 keV. Coarse elongated X-phase crystals of hexagonal cross-section are seen embedded in a glassy phase. The bar length is 10 μm.

These crystals must be very small, as they are not visible in SEM.

In specimen C6 the crystalline phases are X-phase and mullite. The growth morphologies of these phases are similar, and it is therefore difficult to distinguish between them. A typical microstructure of this specimen is demonstrated in Fig. 7, and besides these crystalline phases a glass phase is seen. The amount of glassy phase in the C1–C10 specimens has been estimated, and the results are given in Table 7.

EDS analyses of the X-phase and glassy phase were made on specimens with large enough phase regions, i.e. greater than 1 μm. In Table 8 the obtained EDS results are shown. This analysis was performed by measuring the Al, Si and O contents, and the N content was calculated by using the electroneutrality condition. In addition, the EDS information obtained from large areas (10 000 μm^2) was compared with the chemical analysis given in Table 5. The equiv.% Al and equiv.% O obtained in this way were found to be about 4% higher than the values given by the chemical analysis. By adjusting the EDS values according to this constant difference, the corrected values shown in Table 8 were obtained. The composition of the glassy 'matrix' from Table 8 is $Si_{0{\cdot}28}Al_{0{\cdot}067}O_{0{\cdot}53}N_{0{\cdot}021}$ and $Si_{0{\cdot}27}Al_{0{\cdot}082}O_{0{\cdot}60}N_{0{\cdot}044}$ in specimens C3 and C4, respectively, which should correspond to the composition of the

Table 7. Results from the SEM-EDS analysis of samples C1–C10 HIPed at 1700°C for 2 h

Sample	*Glassy phase (vol.%)*
C1	30
C2	25
C3	35
C4	10
C5	5
C6	40
C7	0
C8	5–10
C9	5–10
C10	5–10

Table 8. The results of an EDS analysis of the X-phase and the glass phase expressed as equiv.% in the specimens C3 and C6

Sample	*Element*	*X-Phase (equiv.%)*	*Glass phase (equiv.%)*
C3	Si	47·2	84·9
	Al	52·8	15·1
	O	80·4	95·2
	N	19·6	4·8
C4	Si	43·1	80·8
	Al	56·9	19·2
	O	81·7	90·2
	N	18·3	9·8

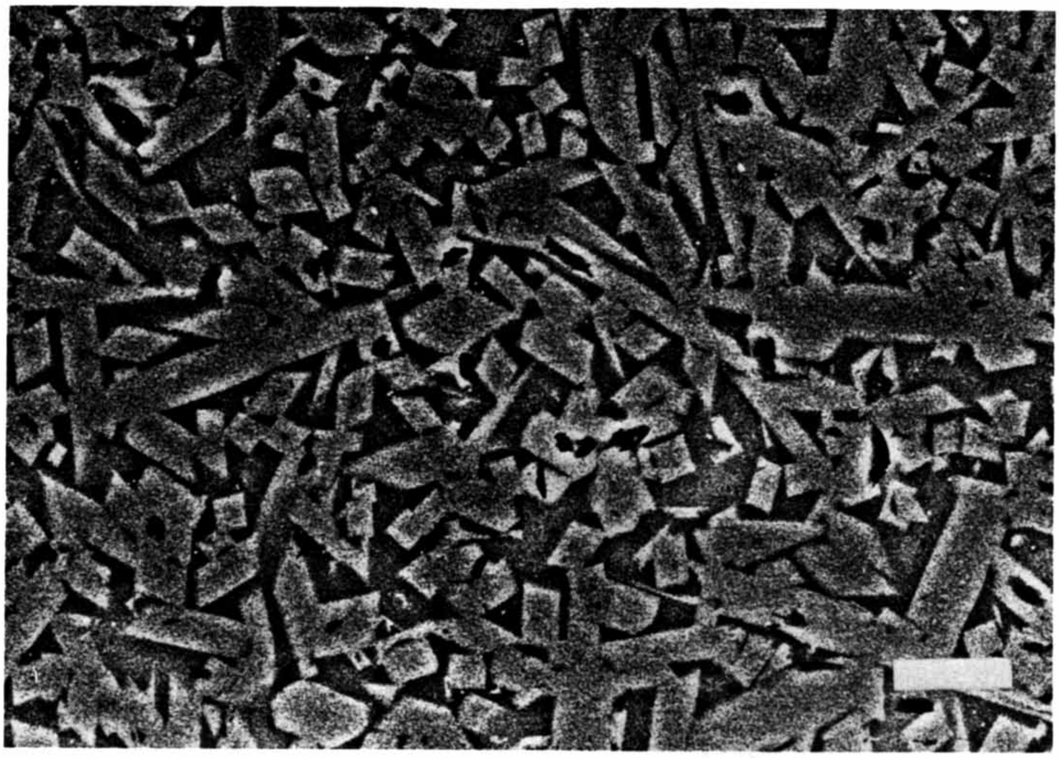


Fig. 7. Back-scattered electron image of specimen C6. The acceleration voltage is 20 keV. X-Phase and mullite crystals in a glassy phase are seen. The bar length is 10 μm.

glassy phase in equilibrium with the X-phase at 1700°C. Similarly, the composition of the X-phase should be about $Si_{12}Al_{17\cdot9}O_{40\cdot9}N_{6\cdot7}$ and $Si_{12}Al_{21\cdot1}O_{45\cdot8}N_{6\cdot8}$ in specimens C3 and C4, respectively.

4 Discussion

The experimental findings from series A1–A8 confirm the general appearance of the behaviour diagrams given previously by Jack[5] and Naik *et al.*[7] They also show that the X-phase is not stable at 1750°C or higher (cf. Fig. 1). The X-phase is, however, formed very rapidly from the liquid in samples close to its composition, as seen from the sample series B1–B5. The combined use of X-ray diffraction and microscopy techniques on the samples heat treated at 1730 and 1750°C showed that the X-phase was only stable at 1730°C or lower (cf. Tables 3 and 4).

The samples B1, B2 and B3 had starting compositions corresponding to previously reported compositions of the X-phase. The change in overall composition caused by the heat treatment, however, makes it important to compare the obtained results with the analysed overall compositions. The samples B2, B4 and B5 heat treated at 1730°C are very close to the X-phase according to the XRD and SEM observations. The samples B2 and B4 at 1730°C consisted mainly of X-phase and some glassy phase, and an analysed overall composition of these two specimens is about $Si_{0\cdot42}Al_{0\cdot58}O_{0\cdot79}N_{0\cdot21}$ (see Table 2). As the glass phase present is rich in Si and O, this implies an X-phase composition with Si and O contents slightly lower than those of the analysed overall composition. On the other hand, sample B5 at 1730°C with an analysed composition of $Si_{0\cdot43}Al_{0\cdot57}O_{0\cdot74}N_{0\cdot26}$ contains traces of β-Si_3N_4, indicating an X-phase composition slightly lower in Si and N than the overall composition. Hence this implies that a good approximation to the X-phase composition is $Si_{0\cdot40}Al_{0\cdot60}O_{0\cdot76}N_{0\cdot24}$ or $Si_{12}Al_{18}O_{36}N_{10}$ after balancing for the charges. This should be compared with the composition of the X-phase reported as $Si_{12}Al_{18}O_{39}N_8$ by Naik *et al.*[7] and as $Si_{12}Al_{24}O_{48}N_8$ by Thompson & Korgul.[10] The X-phase formed in the B-series samples at 1730°C is thus in good agreement with the value given by Naik *et al.*[7]

It should be stressed, however, that the EDS analyses of the X-phase in samples C3 and C4 indicated compositions of $Si_{12}Al_{17\cdot9}O_{40\cdot9}N_{6\cdot7}$ and $Si_{12}Al_{21\cdot1}O_{45\cdot8}N_{6\cdot8}$, respectively. This indicates a narrow solid solubility range of X-phase, and the two slightly different values previously given by Naik *et al.* and by Thompson & Korgul might well represent the two endpoints of the solid solubility range.

The chemical analysis of the samples heat treated

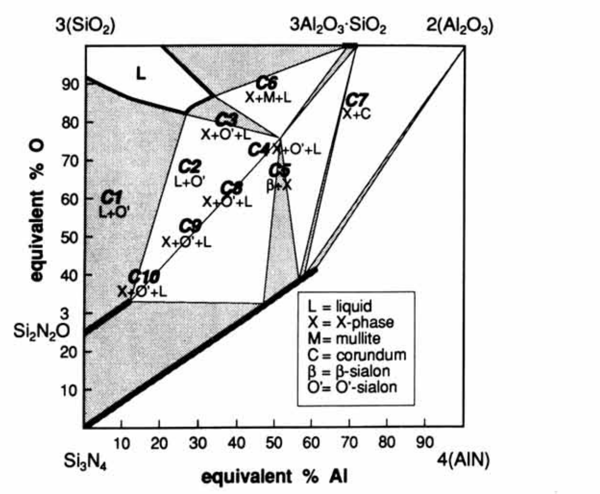


Fig. 8. The preliminary assessed Si–Al–O–N phase diagram for a temperature of 1700°C, by thermodynamic calculations,[17] with the experimental findings from the C-series, prepared at 1700°C superimposed for comparison.

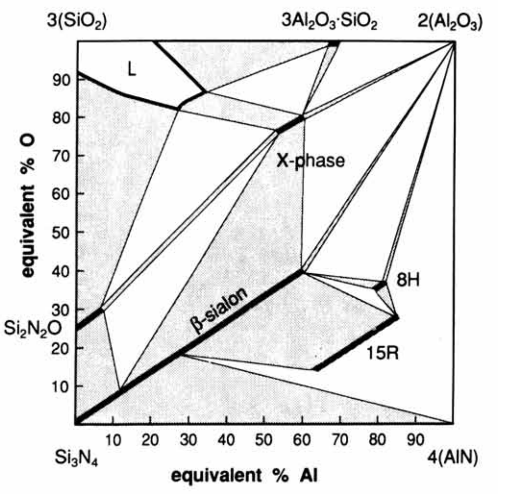


Fig. 9. A summary of the findings in this study represented as an Si_3N_4–SiO_2–Al_2O_3–AlN phase diagram for the temperatures of 1700–1730°C, where the X-phase is still stable.

by glass-encapsulated HIPing at 1700°C showed only slight deviations from the weighed-in compositions (see Table 5). This is believed to be a result of the locally formed system around every powder compact with a very small gas volume in equilibrium with the sample. The results summarized in Tables 6 and 7 are therefore representative of the phase relationships in the liquid-rich area of the Si–Al–O–N system at 1700°C.

The maximum substitution of (Al + O) into the O′-sialon, $Si_{2-x}Al_xN_{2-x}O_{1+x}$, has been reported to be $x = 0{\cdot}20$, and at this composition the orthorhombic unit cell has the dimensions $a = 0{\cdot}5500$ nm, $b = 0{\cdot}8905$ nm and $c = 0{\cdot}4861$ nm.[15] The observed O′-sialon in this study has a composition at this higher end of the solid solubility range, as can be seen from the calculated lattice parameters shown in Table 6. The specimens C1 and C2 are in a two-phase area between the O′-sialon and the glassy phase, whereas specimens C3, C4, C8, C9 and C10 are in a three-phase region also including the X-phase. Sample C5 is close to the X-phase and contains only small amounts of β-sialon and a glassy phase. It is also interesting to note that specimen C7 contains only two major phases and no glassy phase, and will therefore fall on the tie-line between X-phase and Al_2O_3.

A study by one of us using high-resolution electron microscopy on samples prepared in the sialon polytypoid area of the phase diagram has shown that a two-phase equilibrium occurs between the 27R-polytypoid structure and the wurtzite structure of AlN.[19] The structure of the 27R-phase can be considered to be an ordered intergrowth of the AlN (wurtzite) and the Al_2O_3 (corundum) structure. The evidence found in the high-resolution electron microscopy study confirmed that there is a two-phase region and this is in accordance with the X-ray diffraction findings in this study, where no diffraction lines corresponding to the sialon polytypoid $2H^{\delta}$ could be seen.

The Si–Al–O–N phase diagram is currently being assessed by thermodynamic calculations.[17] From the ongoing work it can be concluded that there is good agreement between the calculated diagram at 1700°C and the experimental findings in the C-series (see Fig. 8). This assessment is, however, preliminary, and a number of constraints have been used to simplify the calculations. The results of the experimental findings and the thermodynamic calculations at 1700–1730°C are summarized in the refined Si–Al–O–N phase diagram given in Fig. 9. The overall features are very similar to those previously reported by Jack[5] and by Gauckler and co-workers.[6,7]

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