

CBE	chemical beam epitaxy	N_A	number of acceptors cm^{-3}
R	alkyl group	PL	photoluminescence
Me	CH_3 , methyl	CARS	coherent anti-Stokes Raman Spectroscopy
Et	CH_2CH_3 , ethyl	TMG	trimethylgallium, $\text{Ga}(\text{CH}_3)_3$
Bu ⁱ	$\text{CH}(\text{CH}_3)(\text{C}_2\text{H}_5)$, isobutyl	TEG	triethylgallium, $\text{Ga}(\text{C}_2\text{H}_5)_3$
Bu ^t	$\text{C}(\text{CH}_3)_3$, <i>tert</i> -butyl	TMA	trimethylaluminum, $\text{Al}(\text{CH}_3)_3$
Neop	$\text{CH}_2\text{C}(\text{CH}_3)_3$, neopentyl	TEA	triethylaluminum, $\text{Al}(\text{C}_2\text{H}_5)_3$
Cp ^{Me}	$\text{C}_5\text{H}_4\text{CH}_3$, methylcyclopentadienyl	TMIn	trimethylindium, $\text{In}(\text{CH}_3)_3$
Ph	C_6H_5 , phenyl	TEIn	triethylindium, $\text{In}(\text{C}_2\text{H}_5)_3$
ERD	elastic recoil detection	T_G	temperature at which the material is grown
ICPAES	inductively coupled plasma atomic emission spectroscopy	T_{50}	temperature corresponding to 50% decomposition of a particular precursor
ICP	inductively coupled plasma	XPS	X-ray photoelectron spectroscopy
μ	electron mobility	SHG	second harmonic generation
SIMS	secondary ion mass spectrometry	EELS	electron energy loss spectroscopy
N_D	number of donors cm^{-3}	RDS	reflectance difference spectroscopy

α' -Sialon Ceramics: A Review

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α' -Sialons are a relatively new class of ceramics that promise excellent high-temperature mechanical properties and thermal shock resistance. This report reviews the current status of research on α' -sialons, including phase equilibria, formation, sintering, and properties.

Introduction

Silicon nitride and oxynitride ceramics have attracted interest for high-temperature engineering applications for nearly 40 years,¹⁻⁴ because of their excellent properties: (1) high strength; (2) wear resistance; (3) high decomposition temperature; (4) oxidation resistance; (5) thermal shock resistance; (6) low coefficient of friction; (7) resistance to corrosive environments.

The formation of silicon nitride (Si_3N_4) was reported about a century ago.⁵⁻⁷ However, fully dense silicon nitride ceramics were obtained by hot-pressing only in 1961.⁸ Huge efforts on the investigation of silicon nitride ceramics have been made in the past three decades, resulting in a tremendous progress.^{9,10}

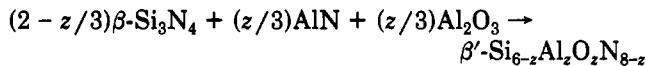
Good mechanical properties of silicon nitride ceramics are achieved only in fully dense materials. But as a highly covalent compound, silicon nitride exhibits a very low diffusivity¹¹⁻¹⁵ and therefore cannot be densified by using

conventional solid-state sintering methods. Instead densification has been achieved by means of liquid-phase sintering. To this end sintering additives are used, for instance, metal oxides, such as MgO , Al_2O_3 , Y_2O_3 , and Ln_2O_3 ,¹⁶⁻²³ but some metals, carbides, and nitrides have been tried as well.²⁴⁻²⁷ At high temperatures these additives react with both the oxygen-rich layer, which is always present at the surface of each silicon nitride particle,^{28,29} and a small fraction of silicon nitride to form an

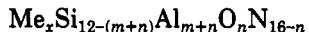
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oxynitride liquid phase, which allows densification by the mechanism of liquid-phase sintering. A problem with this method is, however, that the liquid phase upon cooling forms glassy phases at the grain boundaries, of which only a part can be crystallized by carefully controlling the cooling process and/or by using a post-sintering heat treatment.³⁰⁻³² Thus these intergranular phases degrade the chemical and mechanical properties of the densified products at high temperatures.

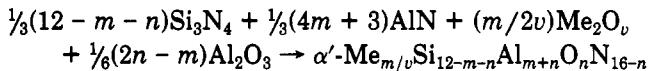
In the beginning of the 1970s, Oyama et al.³³⁻³⁵ and Jack et al.^{36,37} reported that Al^{3+} can enter the silicon nitride crystal lattice without changing the structure by replacing Si^{4+} if at the same time N^{3-} is replaced by O^{2-} as well. Such solid solutions have been named "sialon", the acronym of these four elements.³⁷ The solid solutions above are called β' -sialons since they are derived from the structure of β -silicon nitride:



As soon as β' -sialons were reported, the formation of α -silicon nitride solid solutions with an expanded α -structure by reaction of lithium silicon nitride with alumina³⁶ or of lithium aluminate with silicon nitride³⁸ was observed as well. So-called α' -sialons were found later not only in the Li-Si-Al-O-N system but also in Mg,Ca,Y-Si-Al-O-N systems.^{36,38-41} The general formula for a solid solution with the α -silicon nitride type structure is



where $x \leq 2$, and $m(\text{Al-N})$, $n(\text{Al-O})$ replace $(m+n)(\text{Si-N})$ in each unit cell. If the valency of Me is v , electroneutrality requires $x = m/v$. A possible chemical reaction leading to these solid solutions is



β' -Sialon ceramics have been widely investigated,⁴²⁻⁴⁵ and some commercial products are available now, mainly as wear parts, extrusion dies, and weld location pins. Composite materials of α' - β' sialons are commercially available as cutting tools. However, research of α' -sialon ceramics is still in the early stage. Recently they have attracted more attention,^{42,46-50} because they promise even better

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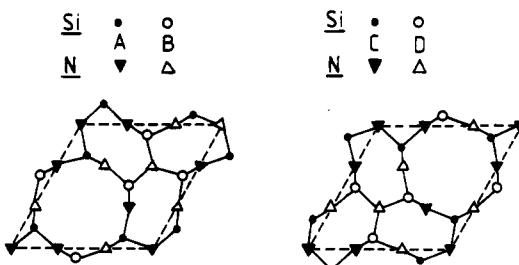


Figure 1. AB and CD Si-N layers in silicon nitride. The stacking sequence in the α -modification is ABCD... and in the β -modification ABAB...⁴⁶

mechanical properties and good thermal shock resistance. Furthermore, these materials offer possibilities to develop single-phase or composite ceramics without a grain boundary glassy phase, since the metal oxides present in the starting mixtures as either sintering additives or impurities can be incorporated into the structure of the final ceramics.

For a better understanding of α' -sialon ceramics, it is worthwhile to consider the structure of silicon nitride first and then discuss the crystal chemistry of α' -sialons.

Structure of α - and β - Si_3N_4

Silicon nitride occurs in two modifications, known as α and β . The structures of both α - and β - Si_3N_4 have been reported in a number of papers.⁵¹⁻⁶¹ The building units are SiN_4 tetrahedra forming a corner-shared three-dimensional structure. The tetrahedra are linked with one edge parallel and one edge perpendicular to the (0001) plane of the hexagonal structures. Although the tetrahedra are slightly distorted, the Si_3N groups perpendicular to the basal plane lie approximately in a plane. The β -structure as shown in Figure 1 is obtained from an ABAB... stacking of these planes. The resulting space group is $P6_3/m$, with $a = 0.759-0.761$ nm and $c = 0.271-0.292$ nm. In this structure there are continuous channels parallel to the c direction.

The α -structure is obtained from an ABCD stacking of the planes (Figure 1). The resulting structure has space group $P31c$, with $a = 0.775-0.777$ nm and $c = 0.516-0.569$ nm. Due to the c glide plane connecting the AB layers with the CD layers, the channels are closed. As a result there are, in each unit cell $\text{Si}_{12}\text{N}_{16}$, two large interstitial sites at $2/3, 1/3, 3/8$ and $1/3, 2/3, 7/8$. To form the α -structure, the

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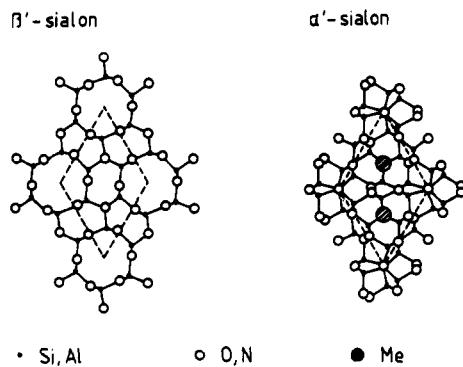


Figure 2. Projections of the α' - and β' -sialon crystal structure perpendicular to the c axis.⁹⁹

tetrahedra have to be distorted and tilted, producing some strain in the network.

The characteristics of α - and β -silicon nitride have been discussed widely, yet some uncertainties have remained in literature:

α -Silicon nitride was considered to be a silicon oxynitride with the formula $\text{Si}_{11.5}\text{N}_{15.5}\text{O}_{0.5}$ and with some special lattice sites for the oxygen atoms.^{54,55,62} However, later chemical analyses^{63,64} and refined structural analyses⁶⁵⁻⁶⁷ suggested that α -silicon nitride is a pure silicon nitride. Although this view has been generally accepted, some recent reports^{68,69} revealed that oxygen impurities in silicon nitride powders, which consist mainly of α -silicon nitride, exist not only in the surface layer but also in the bulk of the particles. So whether α -silicon nitride is an oxynitride or a pure nitride is still uncertain. There is no doubt that β -silicon nitride is a pure silicon nitride.^{54,55}

There is also some uncertainty about the stability of the two phases. According to refs 70 and 71 α -silicon nitride is a low-temperature modification and β -silicon nitride is a high-temperature modification. Thermodynamic data^{28,72-80} obtained so far are not sufficiently accurate to make a decision. Since the $\beta \rightarrow \alpha$ phase transformation is never observed, it is assumed that β -silicon nitride is more stable at all temperatures, whereas α -silicon nitride is formed only under special conditions for kinetics reasons during the nitridation of silicon. This would also be in accordance with what one would expect on basis of the higher strain in the α -structure.

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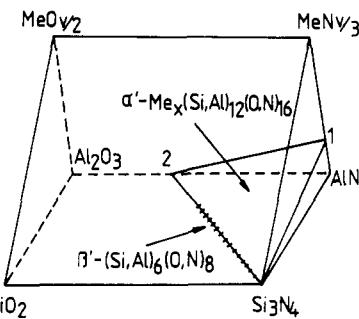


Figure 3. Schematic phase diagram of the α' - and β' -sialon stability regions; Me is a metal ion with valency $v:^{48}$ (1) $\text{Me}_{3/v}\text{Al}_3\text{N}_4$; (2) $\text{Al}_3\text{O}_3\text{N}$.

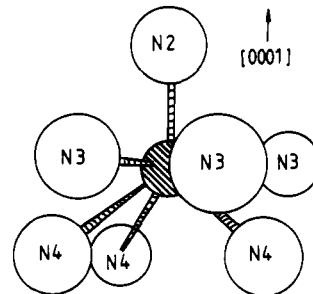


Figure 4. Coordination of the Y^{3+} cation in α' -sialon.^{101,102}

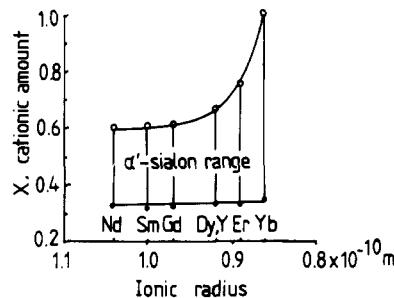


Figure 5. Solubility of some modifying cations in α' -sialon: $\text{Me}_x(\text{Si,Al})_{12}(\text{O,N})_6$.^{104,105}

The α to β phase transformation is a reconstructive transformation, which requires a considerable activation energy for the breaking of Si-N bonds.^{71,81-84} A solution precipitation mechanism is suggested: dissolution of α in a liquid phase and precipitation of β from the liquid at elevated temperatures.⁸⁵⁻⁸⁹ This $\alpha \rightarrow \beta$ phase transformation starts very slowly at about 1400 °C and completes close to 1800 °C only in the presence of a liquid phase. Earlier theories of transformation in the solid state as well as a reaction with deoxidation are no longer considered,^{90,91}

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and also a possible transformation via the gas phase is not observed.

Crystal Chemistry of α' -Sialon

Solid solutions with the β -type structure are formed only with aluminum and beryllium by a limited substitution of Si^{4+} by Al^{3+} or Be^{2+} and of N^{3-} by O^{2-} .^{39,42,46,47,92-96} The cation to anion ratio remains constant at 3:4, and no constitutional vacancies are formed. The aluminum substitution leads to $\text{Si}_{6-z}\text{Al}_z\text{O}_2\text{N}_{8-z}$ with $0 \leq z \leq 4.2$. In the case of beryllium the formula is $\text{Si}_{6-z}\text{Be}_z\text{O}_{2-z}\text{N}_{8-2z}$ with $0 \leq z \leq 2$. The β' -sialons can thus be described as solid solutions between Si_3N_4 and $\text{Al}_3\text{O}_3\text{N}$, and β' -sibeons between Si_3N_4 and Be_2SiO_4 . In contrast to the purely substitutional solubility in the β' -phase, in the α -silicon nitride structure there are two interstitial sites per unit cell that can be occupied by cations (see Figure 2). So the formation of solid solutions in the α -silicon nitride type structure occurs only in quinary $\text{Me}-\text{Si}-\text{Al}-\text{O}-\text{N}$ systems where $\text{Me} = \text{Li}, \text{Mg}, \text{Ca}, \text{Y}$, and rare-earth metals except La and Ce.^{38,39,41,42,46,47,51,97-100} Figure 3 shows a schematic phase diagram of the $\text{Me}-\text{Si}-\text{Al}-\text{O}-\text{N}$ system with the plane containing the α' -sialon stability region.⁴⁶

The α' -sialon crystal structure is derived from α - $\text{Si}_{12}\text{N}_{16}$ by partial replacement of Si^{4+} by Al^{3+} and stabilized by trapping "modifying" cations such as Li, Ca, and Y in the interstices of the $[\text{Si},\text{Al}]-[\text{O},\text{N}]$ network. In Y- α' -sialon, the coordination of the Y^{3+} cation is shown in Figure 4. This figure indicates that the Y^{3+} atom is surrounded by seven (N,O) atom sites with three different Y-(N,O) distances. A polar 3-fold rotation axis exists in the [0001] direction, which is also the direction of the shortest Y-(N,O) distance.^{101,102}

If α' -sialon is synthesized entirely from nitrides, the products should contain no oxygen, and thus valency compensation is due solely to the introduction of the modifier cations. Because there are only two sites per unit cell for these, the upper limiting compositions for α' -sialons with a v -valent metal ion are expected to be $\text{Me}_2\text{Si}_{12-2v}\text{Al}_{2v}\text{N}_{16}$, e.g., $\text{Li}_2\text{Si}_{10}\text{Al}_2\text{N}_{16}$, $\text{Ca}_2\text{Si}_8\text{Al}_4\text{N}_{16}$, and $\text{Y}_2\text{Si}_6\text{Al}_6\text{N}_{16}$. These limits have not been achieved, which may be due to the presence of oxygen in the silicon nitride particles. The highest solubility has been reported to be 1.83 Ca^{2+} per cell in Ca- α' -sialon with a composition of $\text{Ca}_{1.83}\text{Si}_{8.34}\text{Al}_{3.66}\text{N}_{16}$,⁴⁶ and 1.5 Li^+ in Li- α' -sialon on the line $\text{Si}_3\text{N}_4-\text{Li}_2\text{O}:3\text{AlN}$,¹⁰³ respectively. The upper limits of the solubility in α' -sialons generally decrease as the size of the modifying cations becomes larger; cf. Figure 5.^{104,105}

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 (103) Kuang, S. F.; Huang, Z. K.; Sun, W. Y.; Yan, D. S. *J. Mater. Sci. Lett.* 1990, 9, 72.

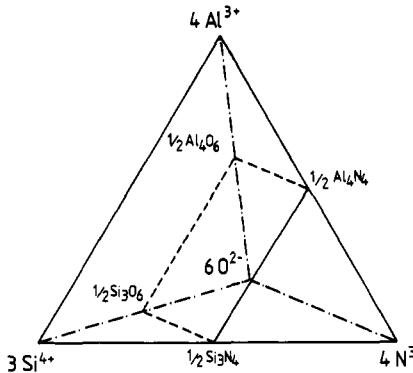


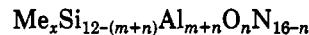
Figure 6. Regular tetrahedron representation of the Si-Al-O-N system; each corner represents 12 equivalent charges. The $\text{Si}_3\text{N}_4-\text{AlN}-\text{SiO}_2-\text{Al}_2\text{O}_3$ subsystem forms a two-dimensional square plane in this representation (see Figure 7).

Earlier work on α' -sialon suggested a miscibility gap between α -silicon nitride and the α' -phase, the α' -sialon compositions closest to Si_3N_4 being



Here RE can be all rare-earth elements except La and Ce. To stabilize the structure, the equivalent of not less than half a cationic valency ($\text{Ca}_{0.25}$ or $\text{RE}_{0.16}$) was considered necessary in each of the two interstices.^{46,51,104,105} However, later experimental results reveal some exceptions. In the Li- α' -sialon system the α' -phase composition closest to α -silicon nitride is $\text{Li}_{0.25}(\text{Si},\text{Al})_{12}(\text{O},\text{N})_{16}$, which indicates that only 0.125 cationic valency for each of the two interstices is sufficient to stabilize the α' -structure.¹⁰³ Similar results have been observed in the $\text{Si}_3\text{N}_4-\text{AlN}-\text{CaO}$ system as well.¹⁰⁶

Unlike the β' -sialon, $\text{Si}_{6-z}\text{Al}_z\text{O}_2\text{N}_{8-z}$, where the replacement without structure change is Si-N by Al-O, the replacement in α' -sialon is largely Si-N by Al-N. With bond lengths Si-N 0.174 nm, Al-O 0.175 nm, and Al-N 0.187 nm, the relative increases in unit cell dimensions for $\alpha \rightarrow \alpha'$ are much larger than for $\beta \rightarrow \beta'$. For a general composition



$m(\text{Al-N})$ replaces $m(\text{Si-N})$ and $n(\text{Al-O})$ replaces $n(\text{Si-O})$. The change of the cell dimensions fit reasonably with the relationships^{46,51}

$$\Delta a \text{ (pm)} = 4.5m + 0.9n \quad \Delta c \text{ (pm)} = 4.0m + 0.8n$$

This suggests that the dimensional increase upon replacement of (Si-N) by (Al-N) is about 5 times that for replacement by (Al-O). The size and solubility of the modifying cations does not influence the dimension expansion of α' -sialon. Possibly the interstitial holes are large enough to accommodate those cations.

Representation of Sialon Systems

Most sialons are quaternary or quinary systems due to the addition of oxides for both liquid-phase sintering and structure modification. The study of phase relationships is very important to understand the reactions. Before we consider these, we will first discuss the representation of sialon systems, which was introduced first by Gauckler et al.^{94,107} for the representation of the $\text{Si}_3\text{N}_4-\text{AlN}-\text{SiO}_2-\text{Al}_2\text{O}_3$

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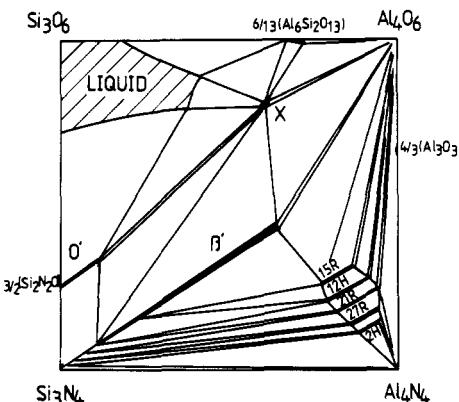


Figure 7. Phase diagram of the Si_3N_4 - SiO_2 - AlN - Al_2O_3 system at 1700 °C.¹²⁴

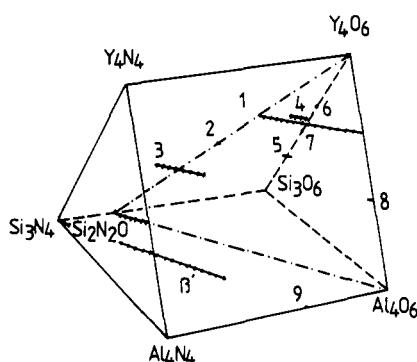


Figure 8. Jänecke prism for the Y - Si - Al - O - N system:⁴⁷ (1) $2\text{Y}_2\text{O}_3\text{·Si}_2\text{N}_2\text{O}$; (2) $\text{Y}_2\text{O}_3\text{·Si}_2\text{N}_2\text{O}$; (3) $\text{Y}_2\text{O}_3\text{·Si}_3\text{N}_4$; (4) $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$; (5) $\text{Y}_2\text{SiAlO}_6\text{N}$; (6) Y_2SiO_5 ; (7) $\text{Y}_2\text{Si}_2\text{O}_7$; (8) $3\text{Y}_2\text{O}_3\text{·5Al}_2\text{O}_3$; (9) $\text{Al}_3\text{O}_3\text{N}$.

system and Huseby et al.⁹² for the Si_3N_4 - SiO_2 - Be_3N_2 - BeO system. A detailed discussion is given by Jack.³⁹

The Si - Al - O - N system is an essential one for sialon systems. As a four-component system it might be represented by a regular tetrahedron, each corner representing one atom of the elements. Although the bonding in the sialons is predominantly covalent, there is a great advantage in assuming normal charges for the elements and using charge equivalents. With the tetrahedral representation as shown in Figure 6, there are 12 charge equivalents along each side of the tetrahedron. The requirement of charge neutrality is obeyed only at the midpoints of each side of the tetrahedron. These four points, with composition Si_3O_6 , Al_4O_6 , Al_4N_4 , and Si_3N_4 , therefore lie at the corners of a square. All compositions of four-valent silicon, three-valent aluminum and nitrogen, and two-valent oxygen lie on this plane. Figure 7 shows the phase diagram of the Si_3N_4 - SiO_2 - AlN - Al_2O_3 system at 1700 °C.¹²⁴ The β' -sialon compositions, which extend from the Si_3N_4 corner, are indicated in this diagram.

Let us next look at the α' -sialon diagrams, i.e., in the Me - Si - Al - O - N quinary systems. A simple representation is again obtained by using atom equivalents. This leads to the so-called Jänecke triangular prism,¹⁰⁸⁻¹¹⁰ in which all edges, expressed in equivalent units, are equal. Figure 8 shows the prism of the Si_3N_4 - SiO_2 - AlN - Al_2O_3 - Y - Y_2O_3 system. It is based on the usual square diagram of the

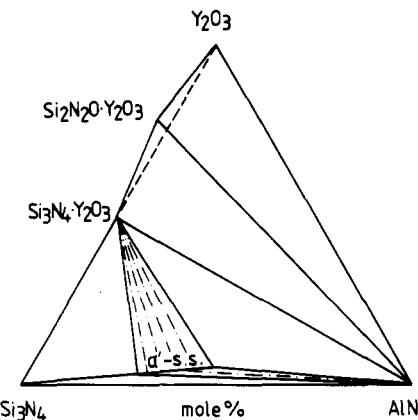


Figure 9. Subsolidus diagram of the Si_3N_4 - AlN - Y_2O_3 system.¹¹⁴

Si_3N_4 - SiO_2 - AlN - Al_2O_3 system extending to the third dimension by the addition of yttrium. This forms two more squares of the AlN - Al_2O_3 - Y - Y_2O_3 and Si_3N_4 - SiO_2 - Y - Y_2O_3 systems. The triangular face at the left-hand side is the nitride system and at the right-hand side the oxide system.

Although the representation mentioned above has led to much better understanding and easier interpretation of experimental observations, phase relationships in Me - Si - Al - O - N quinary systems are very complicated, and so most reports deal only with some triangular planes by cutting of the Jänecke prism, e.g., $\text{Si}_2\text{N}_2\text{O}$ - Al_2O_3 - Y_2O_3 , Si_3N_4 - SiO_2 - Y_2O_3 planes.¹¹¹⁻¹¹³

Phase Relationships Concerning α' -Sialon

When phase diagrams are used for nitride and oxynitride systems, some points should be kept in mind. In the first place, one should be aware that most phase diagrams of nitride and oxynitride systems do not represent thermodynamical equilibrium phase relationships. Due to the low self-diffusivity in silicon nitride, a small fraction of glassy grain boundary phase is always present but is not considered in the phase diagrams. Furthermore, only major solid phases are considered, while the presence and influence of vapor phases and a small amount of impurities are normally ignored. Also an accurate determination of the composition is difficult due to the light elements oxygen and nitrogen.

In spite of these limitations knowledge of these diagrams is an essential basis for the fabrication of nitride and oxynitride ceramics. This is the more so since the presence of secondary phases influences the microstructure and the resulting properties of the final products.

However, the number of phase equilibrium studies on α' -sialon systems is very limited. Some important diagrams will be discussed here. Several studies discuss the formation of α' -sialons along the $\text{Si}_3\text{N}_4\text{-M}_x\text{O}_y\text{-}m\text{AlN}$ join. However, as early as the appearance of the phase diagram of the Si_3N_4 - AlN - Y_2O_3 system,¹¹⁴ the existence of a two-dimensional region of α' -sialon stability was proposed (see Figure 3) and a tentative Ca - α' -sialon phase diagram was reported by Jack in the Ca - Si - Al - O - N system.⁴⁶

We will first discuss the phase relationships in the Y - Si - Al - O - N system, which is one of the most detailed α' -

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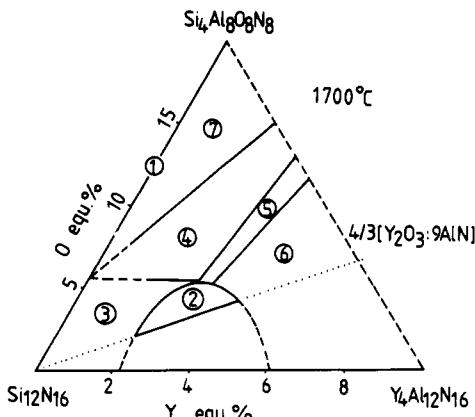
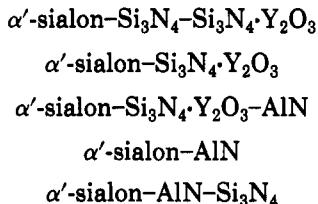


Figure 10. Phase relations in the concentration plane $\text{Si}_{12}\text{N}_{16}$ – $\text{Y}_4\text{Al}_{12}\text{N}_{16}$ – $\text{Si}_4\text{Al}_8\text{O}_8\text{N}_8$ at 1700 °C.^{99,102} (1) β' -sialon; (2) α' -sialon; (3) $\alpha' + \beta'$ -sialon; (4) $\alpha' + \beta'$ -sialon + 12H; (5) α' -sialon + 12H; (6) α' -sialon + 21R; (7) β' -sialon + 12H.

sialon system known so far.^{99,102,114–117} The general formula for the Y - α' -sialons is $\text{Y}_x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$, where $x = m/3$, and m and n are independent parameters. The phase diagram of the Si_3N_4 – AlN – Y_2O_3 system is the first complete α' -sialon diagram studied (see Figure 9),¹¹⁴ in which α' -silicon nitride forms a limited solid solution with a mixture of Y_2O_3 –9AlN. The solubility limits along this line are represented by $0.33 \leq x \leq 0.67$. Silicon nitride also reacts with Y_2O_3 to form Si_3N_4 – Y_2O_3 and $\text{Si}_2\text{N}_2\text{O}$ –2 Y_2O_3 , the latter of which does not lie on the plane of Si_3N_4 – AlN – Y_2O_3 . Five compatibility triangles containing α' -sialon were observed:



More detailed phase relationships in the system were studied on the $\text{Si}_{12}\text{N}_{16}$ – $\text{Y}_4\text{Al}_{12}\text{N}_{16}$ – $\text{Si}_4\text{Al}_8\text{O}_8\text{N}_8$ concentration plane at 1700 °C, and the diagrams are shown in Figures 10 and 11.^{99,102,115–117} According to the diagrams the boundaries of the single-phase α' -sialon region are $0.33 \leq x \leq 1$ (Y) and $0.5 \leq n \leq 1.5$ (O). A discussion is given in ref 117.

The Si_3N_4 – AlN – RE_2O_3 systems exhibit phase diagrams similar to those shown in Figure 9 when $\text{RE} = \text{Gd, Dy, Er}$, and Yb .^{104,105} The phase diagrams of the Si_3N_4 – AlN – Nd_2O_3 and Sm_2O_3 systems are slightly different, since AlN reacts with Nd_2O_3 and Sm_2O_3 to form $\text{Nd}_2\text{AlO}_3\text{N}$ and $\text{Sm}_2\text{AlO}_3\text{N}$, respectively (see Figure 12). The solubility limits of α' -sialon in these systems have been plotted in Figure 5. The lower limits are the same as for yttrium, and the upper limits increase when the size of the modifier cations decreases.

Two-dimensional phase relationships on the $\text{Si}_{12}\text{N}_{16}$ – $(\text{Nd}/\text{Sm})_4\text{Al}_{12}\text{N}_{16}$ – $\text{Si}_4\text{Al}_8\text{O}_8\text{N}_8$ concentration plane were also studied.¹¹⁸ Approximately the same phase relation-

ships were reported as in Figure 11.

The phase diagram of the Si_3N_4 – AlN – CaO system, shown in Figure 13,¹⁰⁶ is very similar to that of the Si_3N_4 – AlN – Y_2O_3 system. Silicon nitride reacts with the mixture of CaO :3AlN to form solid solutions with compositions in the range 0.3–1.4 Ca per unit cell of α' -sialon. Silicon nitride also reacts with CaO , resulting in the formation of $2\text{CaO}\cdot\text{Si}_3\text{N}_4$ and $3\text{CaO}\cdot\text{Si}_2\text{N}_2\text{O}$. Besides, at 1450 °C a metastable phase of $2\text{CaO}\cdot\text{Si}_3\text{N}_4\cdot\text{AlN}$ was found as well.

The phase relationships of the Si_3N_4 – AlN – Li_2O system have also been reported recently.¹⁰³ So far single-phase $\text{Li}\cdot\alpha'$ -sialon has been found only on the line Si_3N_4 – Li_2O :3AlN (Figure 14). $\text{Li}\cdot\alpha'$ -sialon exhibits a large solubility range, viz., from 0.25 to 1.50 Li per unit cell. The discrepancy here with previous work in the literature has been discussed before. The composition $10\text{Li}_2\text{O}\cdot\text{Si}_3\text{N}_4\cdot\text{AlN}$ has a liquidus temperature of only about 900 °C. Some more detailed work is still required in this system.

The phase diagram of the Si_3N_4 – AlN – MgO system is another studied recently.¹¹⁹ However, in this system single-phase $\text{Mg}\cdot\alpha'$ -sialon has not been obtained on the line Si_3N_4 – MgO :3AlN. The phase compositions along this line with increasing amount of MgO :3AlN are mixtures of the phases $\beta' + \alpha'$, $\alpha' + 12\text{H}$ (AlN polytypoid), and $\alpha' + 12\text{H} + \text{AlN}$, respectively. It is suggested that the small $\text{Mg}\cdot\alpha'$ -sialon region is located only at the nitrogen-rich side,¹¹⁹ thus preparation of single-phase $\text{Mg}\cdot\alpha'$ -sialon might be possible by using Mg_3N_2 .

The compatibility between α' - and β' -sialon indicates the possibilities for developing composite ($\alpha' + \beta'$)-sialon ceramics with tailored properties by varying the α'/β' ratio.

Preparation and Formation of α' -Sialon

Several preparation routes are possible. The most widely used method is the direct formation from α - Si_3N_4 , AlN, and the metal oxide(s). We will discuss the reaction sequence in more detail below. A second route is the carbothermal reduction of the appropriate oxides. For instance, Mitomo et al.¹²⁰ start with a solution of the metal alkoxides in isobutyl alcohol. After dispersion of carbon black the metal hydroxides are precipitated on the carbon particles, and then the dried powder is converted into α' -sialon at temperatures around 1500–1600 °C under nitrogen.

Finally, direct nitridation is also possible. Using amorphous silicon nitride, obtained via a diimide process, with metallic Al and metal oxide, Kohtoku prepared α' -sialons.¹²¹

The research on the formation of α' -sialons was mostly conducted in the Y – Si – Al – O – N system.^{99,115,116,122–124} Figure 15 gives, as an example, the reaction sequence of the formation of $\text{Y}\cdot\alpha'$ -sialon with a composition of $\text{Y}_{0.5}\text{Si}_{9.75}\text{Al}_{2.25}\text{O}_{0.75}\text{N}_{15.25}$ ¹²² from a starting mixture consisting of silicon nitride, aluminum nitride, and yttria. Since the surfaces of nitride particles are always covered with an oxygen-rich layer,^{28,29,125} an oxide subsystem SiO_2 –

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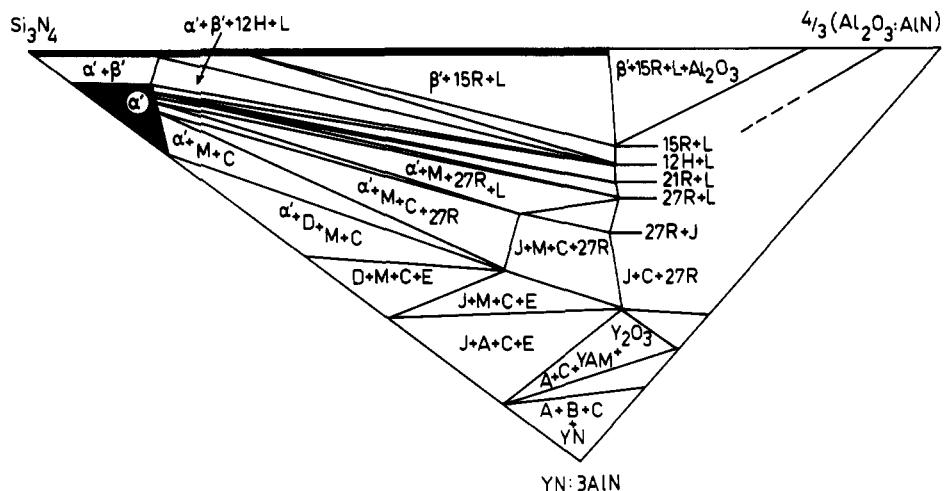


Figure 11. Phase relations in the Y- α' -sialon plane at 1705 °C.^{116,117} (A) $\text{Y}_6\text{Si}_3\text{N}_{10}$; (C) AlN; (D) YSi_3N_5 ; (E) $\text{Y}_2\text{Si}_3\text{N}_6$; (J) $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2\text{-Y}_4\text{Al}_2\text{O}_8\text{ss}$; (L) liquid; (M) $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$.

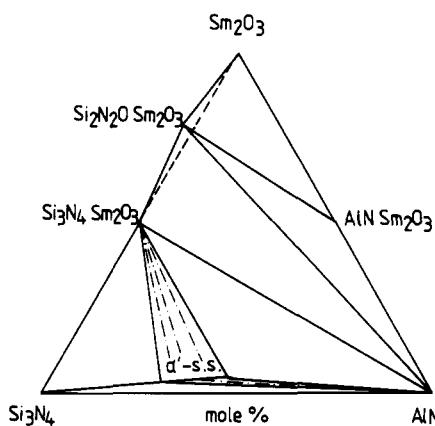


Figure 12. Subsolidus diagram of the $\text{Si}_3\text{N}_4\text{-AlN-Sm}_2\text{O}_3$ system.^{104,105}

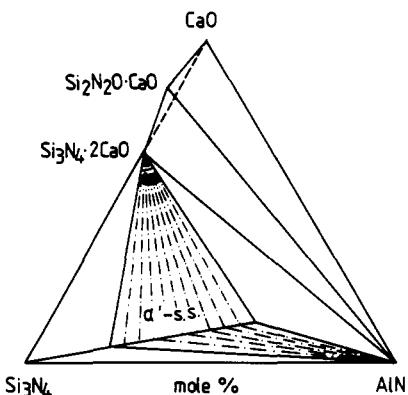


Figure 13. Subsolidus diagram of the $\text{Si}_3\text{N}_4\text{-AlN-CaO}$ system.¹⁰⁸

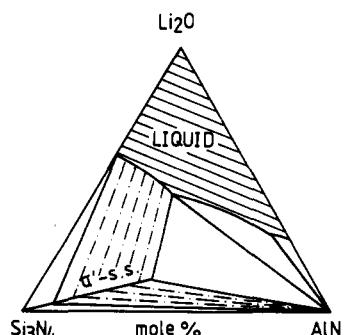


Figure 14. Isothermal section at 1750 °C of the $\text{Si}_3\text{N}_4\text{-AlN-Li}_2\text{O}$ system.¹⁰³

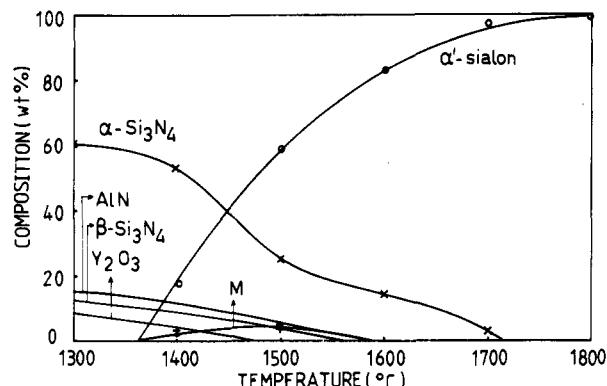


Figure 15. Reaction sequence of the formation of α' -sialon, heating rate 10 °C/min; M, $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$.¹²²

$\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ is supposed to be present in the mixture. As the temperature increases, the oxides react to form a eutectic liquid phase at about 1350 °C.^{126,127} Moreover, the presence of nitrogen as well as some other impurities will further lower this temperature.^{128,129} Therefore, this eutectic oxide liquid phase appears already at temperatures below 1350 °C.

We have studied the reaction both by dilatometric studies and by X-ray powder diffraction.¹²² After the formation of the oxide liquid phase, silicon nitride starts to dissolve into the liquid and forms an oxynitride liquid phase approximately at 1380 °C, and the precipitation of α' -sialon follows immediately. The dissolution-precipitation proceeds as the temperature rises and is nearly completed approximately at 1800 °C. Further investigation reveals that the formation of α' -sialon proceeds independent of the amount and composition of the liquid phase and is therefore proposed to be a reaction-controlled process. The precipitation of the intermediate compound $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$ starts concurrently with that of α' -sialon; its content increases with the temperature until 1500 °C and then decreases by redissolution into the liquid. No sig-

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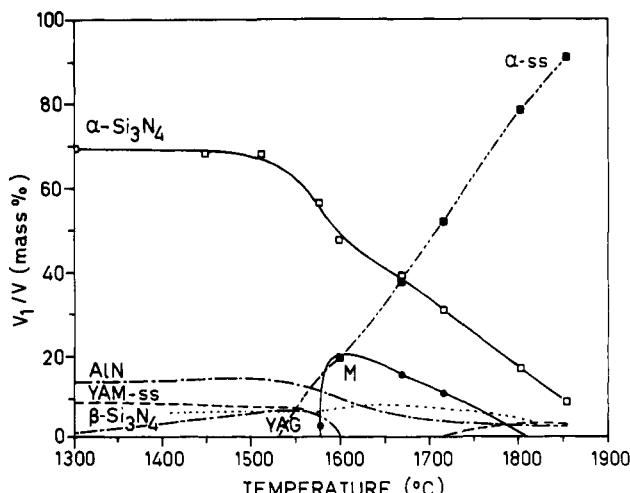


Figure 16. Reaction sequence of the formation of α' -sialon, with heating rate $14\text{ }^{\circ}\text{C}/\text{min}$.¹²³ M, $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$; YAG, $3\text{Y}_2\text{O}_3\text{-5Al}_2\text{O}_3$; YAM-ss, $\text{YAl}_2\text{O}_9\text{-Si}_2\text{Y}_4\text{O}_7\text{N}_2\text{ss}$.

nificant influence on the formation of α' -sialon has been observed.¹²² If the composition of the starting mixture is changed slightly, other intermediate compounds such as $\text{Si}_2\text{N}_2\text{O}\text{-Y}_2\text{O}_3$, $3\text{Y}_2\text{O}_3\text{-5Al}_2\text{O}_3$, 12H, and $\text{Y}_2\text{SiAlO}_5\text{N}$ may occur as well.^{99,116,116,122-124,130,131} Figure 16 shows another reaction sequence for the formation of α' -sialon with a composition of $\text{Y}_{0.53}\text{Si}_{9.6}\text{Al}_{2.4}\text{O}_{0.8}\text{N}_{15.2}$.¹²³ According to these measurements the dissolution of α -sialon nitride into the liquid and the precipitation of α' -sialon start approximately at $1550\text{ }^{\circ}\text{C}$ instead of $1380\text{ }^{\circ}\text{C}$. The formation of the intermediate compound N-melilite, $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$ does not start simultaneously with that of the α' -phase but $100\text{ }^{\circ}\text{C}$ higher and remains until $1800\text{ }^{\circ}\text{C}$ with a continuously decreasing quantity.

Research on the formation of α' -phases was also conducted in Ca,Nd,Sm-containing systems.^{116,118,130,131} The reaction sequence in these systems is similar to that of Y- α' -sialons. As an exception, the reaction sequence of the formation of Li- α' -sialon exhibits some differences.¹⁰³ The dissolution of silicon nitride into the liquid results in the precipitation of O'-sialon instead of the α' -phase in the early stage, but as the temperature increases to $1600\text{ }^{\circ}\text{C}$ the O'-sialon dissolves into the liquid and the precipitation of Li- α' -sialon occurs.

Note that whether α - and β -silicon nitride is used as starting material does not make any difference in the formation of α' -sialon.^{46,122}

The α' -sialon structure is stabilized to high temperatures by trapping metal cations in its interstitial sites, and no α to β phase transformation occurs. However, the transformation between α' - and β' -sialons by chemical reactions might be expected:^{42,46,47,51,97}



The transformation of $\alpha' \rightarrow \beta'$ has been observed in the Ca- α' -sialon and Y- α' -sialon systems.^{42,46,47,51,124,130,132} In the case of the presence of secondary phases with a composition suitably adjusted, this phase transformation proceeds very easily.

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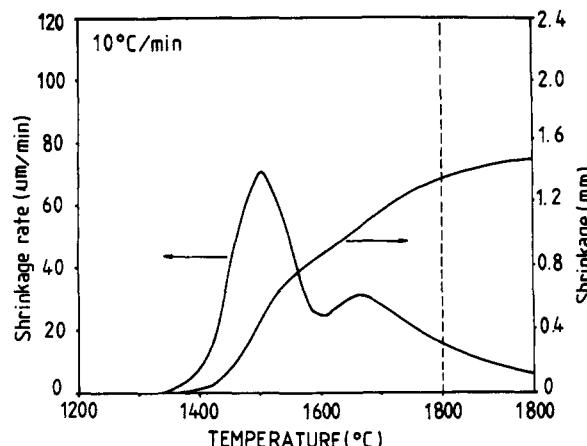


Figure 17. Shrinkage and shrinkage rate curves for α' -sialon, $\text{Y}_{0.5}\text{Si}_{9.6}\text{Al}_{2.4}\text{O}_{0.8}\text{N}_{15.2}$, heating rate $10\text{ }^{\circ}\text{C}/\text{min}$.¹²²

The mechanism of the phase transformation $\alpha \rightarrow \alpha'$ has not yet been studied systematically; however, the similarity in the formation of α' - and β' -sialons suggests that it could be a reconstructive phase transformation, just as that of $\beta \rightarrow \beta'$, similar to the $\alpha \rightarrow \beta$ phase transformation.^{128,129,133} This phase transformation requires a liquid phase, which allows the dissolution of silicon nitride and precipitation of β' -sialon.

Densification of α' -Sialon Ceramics

The densification of silicon nitride or oxynitride ceramics with oxide additives occurs via a liquid-phase sintering process.⁹⁰ Liquid-phase sintering is generally described to proceed in three (partly overlapping) stages:¹³⁴⁻¹⁴²

Stage I: primary particle rearrangement, immediately following the formation of the liquid phase, is brought about by the remaining solid particles sliding over each other under the action of capillary forces. The rate and extent of shrinkage will depend upon the viscosity and quantity of the liquid and its wetting properties.

Stage II: a solution-reprecipitation process will become operative if the solid particles have some solubility in the liquid phase. This can also lead to secondary rearrangement. Material transport away from the contact points causes a decrease in the center-to-center distance between particles. Besides this flattening mechanism, a shape accommodating Ostwald ripening plays an important role.

Stage III: coalescence and closed pore elimination require a solid-state sintering mechanism.

In the case of the densification of α' -sialon ceramics, the sintering mechanism is more complicated than that in the well-known hard metals, since during the heating cycle, some intermediate compounds form, phase transformations occur, and some liquid constituents are incorporated into the structure.^{42,46,47,51}

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Figure 17 shows shrinkage curves of α' -sialon ceramics with a composition $Y_{0.5}Si_{0.75}Al_{2.25}O_{0.75}N_{15.25}$. These curves were obtained by in situ dilatometry in a gas pressure sintering furnace.¹²² As the eutectic oxide liquid phase appears above 1300 °C, no evident shrinkage is observed, probably due to the minor amount of liquid. When the temperature rises further, the densification starts due to a combination of secondary rearrangement of the particles and a dissolution-precipitation process parallel to the formation of α' -sialon via the liquid phase. The shrinkage rate increases rapidly with temperature until 1550 °C and then gradually decreases. Above 1600 °C the densification is accelerated once again and then proceeds slowly to a final value. A comparison of the reaction sequence and the densification rate suggests that the precipitation and redissolution of the intermediate compound $Si_3N_4Y_2O_3$ has the following effect: The precipitation accelerates the dissolution of silicon nitride in the early stages. When more of this compound is formed, a solid skeleton, consisting of both sialon and the intermediate compound, is built up, resulting in a decrease of the shrinkage rate above 1500 °C. When the temperature rises further, $Si_3N_4Y_2O_3$ redissolves into the liquid, resulting in an increase of the amount of the liquid, and therefore the densification rate increases again.

If the composition of the starting mixtures is changed, the reaction sequence of the formation of α' -sialon changes and consequently the densification curve changes as well. Moreover, differences in starting powders and/or powder processing also result in a different sintering behavior, even if the composition of the starting mixtures remains unchanged; cf. refs 99, 115, and 123.

It should be noted here that although the emergence of intermediate compounds greatly changes the densification curves, hardly any influence has been observed on the final density values and the grain size.

Microstructures and Properties of α' -Sialon Ceramics

Microstructures. Theoretically, the metal oxides present in the starting mixtures as either sintering additives or impurities can be incorporated into the α' -structure of the final ceramics as described previously. In practice, it is very difficult to complete the formation and densification of α' -sialons, because the high nitrogen content results in a small amount of oxynitride liquid with a high viscosity.¹⁴³ Furthermore, as α' -sialon forms during the heating cycle, the amount of liquid gradually decreases until in the equilibrium situation all liquid is incorporated into the α' -sialon lattice.

Although some examples of α' -sialon and/or ($\alpha' + \beta'$)-sialon ceramic microstructures without intergranular glassy phases have been reported,¹⁴⁴ TEM studies reveal that most microstructures still contain a small amount of a residual glassy phase after sintering.^{99,102,115,122} In those cases where intergranular phases were indeed absent, glass-encapsulated hot isostatic pressing has been used for the densification.^{145,146}

Thermal Properties. The thermal conductivities of α' -sialons at room temperature are about 8 W/mK, which is only 12–15% of those of α -silicon nitride obtained by chemical vapor deposition.^{147,148} It was shown that the

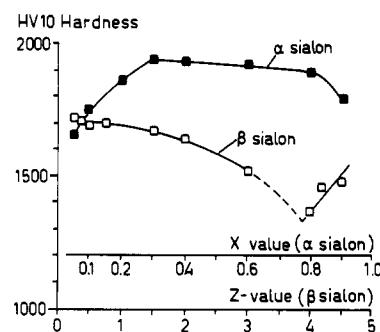


Figure 18. Vickers hardness (HV10) in kg/mm^2 for α' - and β' -sialon samples with different compositions.^{145,146}

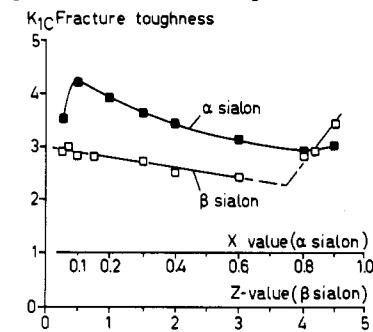


Figure 19. Fracture toughness K_{Ic} in $MPa/m^{1/2}$ for α' - and β' -sialon samples with different compositions.^{145,146}

dissolution of metal atoms into the interstitial sites of the α -silicon nitride structure decreases the thermal conductivity.

α' -Sialon ceramics have linear thermal expansion coefficients of about $(3.7-4.0) \times 10^{-6} K^{-1}$ in the range from room temperature to 1400 °C.^{46,97,149,150}

Mechanical Properties. Although the mechanical properties of α' -sialon ceramics have been studied more widely compared to other properties,^{99,115,116,145,146,150-161} only a very limited understanding of the mechanical properties has been obtained.

The literature data are widely scattered. This is in part due to differences in composition and microstructure but also to differences in measuring methods. Yet some general conclusions can be drawn. Especially the data from Ekström et al. do show systematic trends in mechanical properties. Figures 18 and 19 give a comparison of Vickers hardness (HV) and fracture toughness (K_{Ic}) of α' - and β' -sialon ceramics,^{145,146} respectively. It is seen that α' -sialon ceramics ($Y_x(Si,Al)_{12}(O,N)_{16}$, $0.33 \leq x \leq 0.8$) have both higher hardness and fracture toughness than β' -sialon ceramics ($Si_{6-z}Al_zO_zN_{8-z}$, $0 \leq z \leq 4.2$). Ekström^{156,157} also

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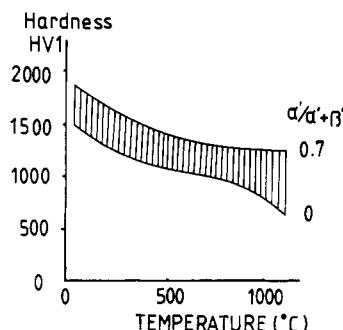


Figure 20. Vickers hardness HV1 in kg/mm^2 as a function of temperature for sialon composites with different α'/β' ratios.¹⁵⁶

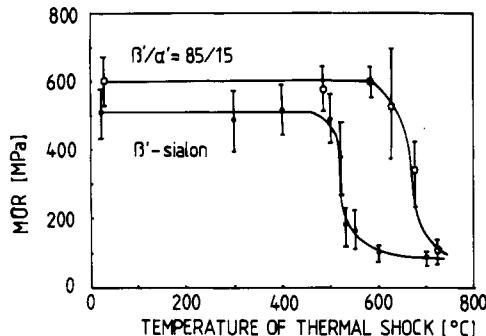


Figure 21. Thermal shock resistance of β' - and $(\alpha' + \beta')$ -sialon ceramics.⁹⁹

shows that the Vickers hardness HV10 increases linearly from 1500 kg/mm^2 for pure β' -phase to about 1850 kg/mm^2 for a composite $(\alpha' + \beta')$ -sialon with 75% α' content. At the same time the fracture toughness decreases linearly from 5.2 to 3.8 $\text{MPa}/\text{m}^{1/2}$. These changes are in part due to changes in phase composition and in part to the simultaneously occurring changes in microstructure. For instance, with increasing β' content the proportion of elongated grains increases, resulting in increasing K_{IC} values. It should be noted that the highest fracture toughness in Figure 19 was achieved at a composition of "α'-sialon" with $x = 0.1$, which is actually a composite $(\alpha' + \beta')$ -sialon. Also the increasing values at the right-hand side of Figures 18 and 19 for β' -sialon are obtained for z values > 4.2 , i.e., outside the single-phase sialon region. A second factor influencing the hardness is the intergranular phase. The glass phase has a hardness $\text{HV} < 1000 \text{ kg}/\text{mm}^2$, i.e., considerably lower than of the sialons. The glass phase has a clear influence on the high-temperature behavior. Figure 20 does illustrate this.¹⁵⁶ The drop in hardness of the pure β' -phase is due to the relatively large amount of glassy phase.

Also the thermal shock resistance is improved with increasing α' -sialon content (see Figure 21).^{99,115}

Although ceramics generally show brittle behavior at room temperature, several examples are known of superplastic behavior at high temperature. A prerequisite for superplasticity is a submicron grain size and a sufficiently slow dynamic grain growth. Although grain growth in single-phase β' -sialons is too fast, superplastic deformation has been demonstrated in β' -sialon/SiC composites.^{162,163} The SiC particles prevent grain growth. An advantage of α' -sialons is that the grains are equiaxed and that grain

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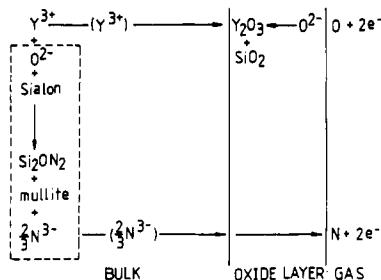
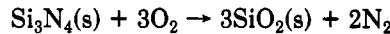


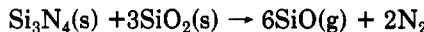
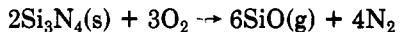
Figure 22. Schematic diagram of the proposed oxidation mechanism for β' -sialon.^{166,167}

growth is slower in comparison with the β' -sialons. Recently it has been demonstrated that single-phase α' -sialon does show superplastic behavior at 1500 °C with strain rates of the order of 10^{-4} s^{-1} .¹⁶⁴ It is assumed that the deformation takes place via the liquid phase. This offers very interesting possibilities for near net shaping of these materials.

Oxidation Resistance. Similar to silicon and silicon carbide,^{165,166} silicon nitride can undergo two distinctive types of chemical reactions.^{28,167,168} At high oxygen partial pressures so-called passive oxidation takes place:



and a dense silica layer is formed, which inhibits further oxidation, and thus provides excellent oxidation resistance. At 1600 K this layer is stable at oxygen partial pressures above 8×10^{-4} bar. At lower oxygen partial pressures so-called active oxidation occurs, and volatile SiO is formed according to the reactions



As opposed to passive oxidation, active oxidation causes a continuous loss of material from the surface due to the formation of SiO gas.

Extensive investigations of the oxidation of various types of silicon nitride ceramics have shown that passive oxidation follows a parabolic relationship of the form $X^2 = kt$, where X is the oxide layer thickness or the weight gain at time t and k is a temperature-dependent rate constant.¹⁶⁹⁻¹⁸¹ The rate of this reaction is controlled by the oxygen diffusion through the oxide layer and is greatly

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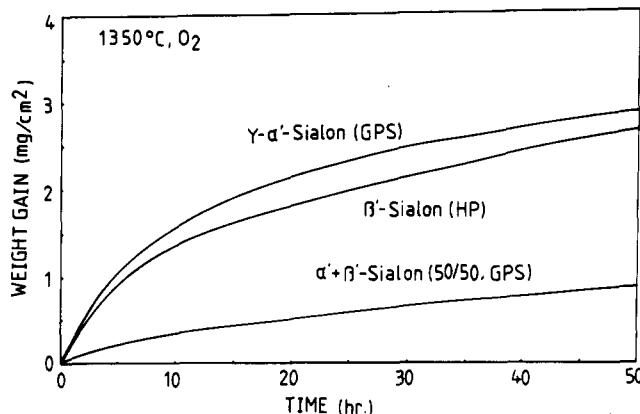


Figure 23. Weight gain during oxidation of sialons in oxygen at 1350 °C.¹⁸⁸ HP, hot-pressed; GPS, gas pressure sintered.

influenced by the composition, crystallinity, and quantity of the intergranular phase.

Investigations of β' -sialons¹⁸²⁻¹⁸⁷ also showed the occurrence of passive oxidation in air. For β' -sialon with yttria as a sintering aid, an oxidation mechanism has been proposed.^{186,187} This mechanism is shown schematically in Figure 22. Oxygen ions diffuse through the oxide layer, mainly amorphous. Yttrium ions diffuse to the surface and can form different phases in the Y-Si-Al-O-N system, but eventually yttria precipitates are formed. Sialon decomposes and forms mullite and silicon oxynitride. The resulting nitrogen ions diffuse to the surface. The escaping nitrogen gas often leads to the formation of craters in the oxide layer.

For α' -sialon ceramics we have observed a parabolic relationship as well (see Figure 23). The composite (α' + β')-sialon with a composition $Y_{0.25}Si_{10.89}Al_{1.11}O_{0.37}N_{15.63}$ shows an excellent oxidation resistance compared to that of both monolithic α' - and β' -sialon ceramics, with compositions of $Y_{0.5}Si_{9.75}Al_{2.25}O_{0.75}N_{15.25}$ and $Si_3Al_3O_3N_5$, respectively.¹⁸⁸ TEM microstructure analysis reveals that in the (α' + β')-sialon composites only a very minor amount of intergranular phase exists at the grain boundaries. As in the case of β' -sialon the oxide layer consists of α -crys-

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toballite, often together with mullite. Although detailed studies are still under way, the oxidation mechanisms seem quite similar for α' - and β' -sialon ceramics.

Electrical Conductivity. The electrical conductivity of the β' -sialons is very low.¹⁸⁹⁻¹⁹¹ DC conductivities are about 10^{-7} S/cm at 700 °C and vary exponentially with an activation energy of about 1.3 eV for higher temperatures. Charge transport may be due to Si^{4+} ions. The structure of α' -sialon on the other hand suggests that ionic electrical conductivity could be possible via the cations in the large interstitial sites. A relatively high conductivity has been found indeed in some hot-pressed Li- α' -sialons.¹⁹² At 700 °C the conductivity is of the order 10^{-4} - 10^{-5} S/cm, with activation energies of about 0.2 eV. For the larger ions, such as Y^{3+} , the mobility is low and the conductivity is comparable with that of β' -sialon. However, since complex impedance measurements are still lacking, it is uncertain whether the reported data represent bulk conductivity or are due to conduction via grain boundary phases.¹⁹³

Summary

α' -Sialon ceramics promise the possibility of a reduction of the amount of glassy grain boundary phases by incorporating the oxides, present in the starting mixture as either sintering additives or impurities, into its final lattice. It has been shown that techniques such as gas pressure sintering can be used successfully to obtain fully reacted and dense α' - or (α' + β')-sialons. By combination of suitable modifier cations and heat treatment the amount of grain boundary phases can be kept very low. This may lead to improved mechanical properties, especially at elevated temperatures. The equiaxed microstructure of α' -sialons, compared with the needlelike structure of β' -sialons, leads to specific differences in mechanical behavior. However, at this moment the complicated interrelationships between the formation sequence, fabrication conditions, properties, and microstructures are still insufficiently understood.

Yet, even with the present-day materials, wear resistance, high-temperature mechanical strength, thermal shock resistance, and oxidation resistance are such that further studies are worth-while.

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