**α’-Sialon Ceramics: A Review**

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α’-Sialons are 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 oxyxnitride 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 (Si3N4) was reported about a century ago.5 However, fully dense silicon nitride ceramics were obtained by hot-pressing only in 1961.6 Huge efforts on the investigation of silicon nitride ceramics have been made in the past three decades, resulting in a tremendous progress.7,8

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 diffusivity9-11 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, A12O3, Y2O3, Ln2O3,12-23 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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**Abbreviations**

CBE = chemical beam epitaxy  
R = alkyl group  
Me = CH3, methyl  
Et = CH2CH3, ethyl  
Bu = CH(CH3)2, isobutyl  
Bu' = C(CH3)3, tert-butyl  
Neop = C6H5C(CH3)3, neopentyl  
CpMe = C5H5CH3, methylcyclopentadienyl  
Ph = C6H5, phenyl  
ERD = elastic recoil detection  
ICP = inductively coupled plasma  
ICPAES = inductively coupled plasma atomic emission spectroscopy  
\( \mu \) = electron mobility  
SIMS = secondary ion mass spectrometry  
\( N_D \) = number of donors cm\(^{-3}\)  
\( N_A \) = number of acceptors cm\(^{-3}\)  
PL = photoluminescence  
CARS = coherent anti-Stokes Raman Spectroscopy  
TMG = trimethylgallium, Ga(CH3)3  
TEG = trimethylgallium, Ga(C2H5)3  
TMA = trimethylaluminum, Al(CH3)3  
TEA = triethylaluminum, Al(C2H5)3  
TMIn = trimethylindium, In(CH3)3  
TEIn = triethylindium, In(C2H5)3  
TG = temperature at which the material is grown  
\( T_{50} \) = temperature corresponding to 50% decomposition

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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.\(^{39,30}\) 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.\(^{38,35}\) and Jack et al.\(^{32,37}\) 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 \(\beta\)'-sialons since they are derived from the structure of \(\beta\)-silicon nitride:

\[
(2 - z/3)\beta\text{-Si}_3\text{N}_4 + (z/3)\text{AlN} + (z/3)\text{Al}_2\text{O}_3 \rightarrow \beta\text{-Si}_{3-x}\text{Al}_x\text{O}_y\text{N}_{2y-x}
\]

As soon as \(\beta\)'-sialons were reported, the formation of \(\alpha\)-silicon nitride solid solutions with an expanded \(\alpha\)-structure by reaction of lithium silicon nitride with alumina\(^{36}\) or of lithium aluminates with silicon nitride\(^{36}\) was observed as well. So-called \(\alpha\)'-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.\(^{36,39,41}\) The general formula for a solid solution with the \(\alpha\)-silicon nitride type structure is

\[
\text{Me}_8\text{Si}_{12(m+n)}\text{Al}_{m+n}\text{O}_{2n+6}N_{16-n}
\]

where \(z \leq 2\), 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 \(z = m/n\). A possible chemical reaction leading to these solid solutions is

\[
\frac{1}{2}(12 - 2m - 3n)\text{Si}_3\text{N}_4 + \frac{1}{3}(4m + 3)\text{AlN} + (m/2v)\text{Me}_2\text{O}_v + \frac{1}{2}(2n - m)\text{Al}_2\text{O}_3 \rightarrow \alpha\text{-Me}_{8m/3}\text{Si}_{12(m+n)}\text{Al}_{m+n}\text{O}_{2n+6}N_{16-n}
\]

\(\beta\)'-Sialon ceramics have been widely investigated.\(^{42,46}\) and some commercial products are available now, mainly as wear parts, extrusion dies, and weld location pins. Composites of \(\alpha\)'-\(\beta\)'-sialons are commercially available as cutting tools. However, recent studies have attracted more attention,\(^{42,46-50}\) because they promise even better 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 \(\alpha\)'-sialon ceramics, it is worthwhile to consider the structure of silicon nitride first and then discuss the crystal chemistry of \(\alpha\)'-sialons.

**Structure of \(\alpha\)- and \(\beta\)-Si\(_3\)N\(_4\)**

Silicon nitride occurs in two modifications, known as \(\alpha\) and \(\beta\). The structures of both \(\alpha\)- and \(\beta\)-Si\(_3\)N\(_4\) have been reported in a number of papers.\(^{42,41}\) The building units are Si\(_3\)N\(_4\) 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\(_3\)N groups perpendicular to the basal plane lie approximately in a plane. The \(\beta\)-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 \(\alpha\)-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 Si\(_3\)N\(_4\), two large interstitial sites at \(2\text{/}3,1\text{/}3,0\text{/}3\), \(1\text{/}3,2\text{/}3,0\text{/}3\) and \(1\text{/}3,2\text{/}3,1\text{/}3\) for the \(\alpha\)-structure, the

![Figure 1. AB and CD Si-N layers in silicon nitride. The stacking sequence in the \(\alpha\)-modification is ABCD... and in the \(\beta\)-modification ABAB...](image-url)
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 Si_{11-x}N_{15+x}O_{x} and with some special lattice sites for the oxygen atoms. However, later chemical analyses revealed that α-silicon nitride is a pure silicon nitride. The α-silicon nitride is 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 silicon nitride.

There is 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 obtained so far are not sufficiently accurate to make a decision. Since the β → α 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.

The α to β phase transformation is a reconstructive transformation, which requires a considerable activation energy for the breaking of Si–N bonds. A solution precipitation mechanism is suggested: dissolution of α in a liquid phase and precipitation of β from the liquid at elevated temperatures. This α → β 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 not considered.

The schematic phase diagram of the α'- and β'-sialon stability regions; Me is a metal ion with valency +4; (1) Me_{2}(Si,Al)_{3}O_{4}N_{5}; (2) Al_{2}O_{3}N.

The solubility of some modifying cations in α'-sialon: Me_{x}(Si,Al)_{12}O_{15}N_{15}.0.10

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Crystal Chemistry of $\alpha'$-Sialon

Solid solutions with the $\beta$-type structure are formed only with aluminum and beryllium by a limited substitution of $\text{Si}^{4+}$ by $\text{Al}^{3+}$ or $\text{Be}^{2+}$ and of $\text{N}^{3-}$ by $\text{O}^{2-}$. The cation to anion ratio remains constant at 3:4, and no constitutional vacancies are formed. The aluminum substitution leads to $\text{Si}_x\text{Al}_y\text{O}_z\text{N}_{16}$, with $0 \leq x \leq 4.2$. In the case of beryllium the formula is $\text{Si}_{1-y}\text{Be}_y\text{O}_z\text{N}_{16}$, with $0 \leq y \leq 2$. The $\beta'$-sialons can thus be described as solid solutions between $\text{Si}_3\text{N}_4$ and $\text{Al}_2\text{O}_3$, and also a possible transformation via the gas phase is not observed.

Solid solutions between $\text{Si}_3\text{N}_4$ and $\text{Al}_2\text{O}_3$, and $\beta'$-sialons between $\text{Si}_3\text{N}_4$ and $\text{Be}_2\text{SiO}_4$. In contrast to the purely substitutional solubility in the $\beta'$-phase, in the $\alpha$-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 $\alpha$-silicon nitride type structure occurs only in quinary $\text{Me-Si-Al-O-N}$ systems where $\text{Me} = \text{Li, Mg, Ca, Y, and rare-earth metals except La and Ce}$. For a general composition of the $\text{Me}_m\text{Si}_{12-n}\text{Al}_n\text{O}_{16}$ system with the plane containing the $\alpha'$-sialon stability region.

The $\alpha'$-sialon crystal structure is derived from $\alpha$-$\text{Si}_3\text{N}_4$ by partial replacement of $\text{Si}^{4+}$ by $\text{Al}^{3+}$ and stabilized by trapping "modifying" cations such as $\text{Li, Ca, and Y}$. The interstices of the $[\text{Si,Al}]-[\text{O,N}]$ network. In $\alpha'$-sialon, the coordination of the $\text{Y}^{3+}$ atom is shown in Figure 4. This figure indicates that the $\text{Y}^{3+}$ atom is surrounded by seven $(\text{N,O})$ atom sites with three different $\text{Y}-(\text{N,O})$ distances. A polar 3-fold rotation axis exists in the [0001] direction, which is also the direction of the shortest $Y\cdots(N,O)$ distance.

If $\alpha'$-sialon is synthesized entirely from nitrides, the products should contain no oxygen, and thus the phase relation is given by $\alpha$-$\text{Si}_3\text{N}_4-Li_2\text{O}$, $\text{Li}_2\text{Si}_12\cdots\text{Al}_2\cdots\text{O}_{16}$, e.g., $\text{Li}_2\text{Si}_12\cdots\text{Al}_2\cdots\text{O}_{16}$, $\text{Ca}_2\text{Si}_12\cdots\text{Al}_2\cdots\text{O}_{16}$, and $\text{Y}_2\text{Si}_12\cdots\text{Al}_2\cdots\text{O}_{16}$.

Not all $\alpha'$-sialons have a $\alpha$-$\beta$-transition, a phase change from the $\beta$- to the $\alpha$-phase, and the change of the cell dimensions fits reasonably to the $\text{Me}_m\text{Si}_{12-n}\text{Al}_n\text{O}_{16}$ system; each corner represents 12 equivalent charges. The plane in this representation (see Figure 5) is also the direction of the shortest $Y\cdots(N,O)$ distance.

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Unlike the $\beta'$-sialon, $\text{Si}_3\text{Al}_2\text{O}_4\cdots\text{N}_{16}$, where the replacement by (Al-0) is about 5 times larger than for (Si-N). With bond lengths $\text{Si-N}$ 0.174 nm, $\text{Al-O}$ 0.175 nm, and $\text{Al-N}$ 0.187 nm, the relative increases in unit cell dimensions for $\beta$ to $\alpha'$ are much larger than for $\beta$ to $\beta'$. For a general composition $\text{Me}_m\text{Si}_{12-n}\text{Al}_n\text{O}_{16}$, $\text{Me} = \text{Li, Mg, Ca, Y, and rare-earth metals except La and Ce}$.

Earlier work on $\alpha'$-sialon suggested a miscibility gap between $\alpha$-silicon nitride and the $\alpha'$-phase, the $\alpha'$-sialon compositions closest to $\text{Si}_3\text{N}_4$ being $\text{Ca}_{0.33}\text{Si}_{10.5}\text{Al}_{1.5}\text{O}_{5.5}\cdots\text{N}_{16.5}$. 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 was considered necessary in each of the two interstices. However, later experimental results reveal some exceptions. In the $\text{Li}_2\text{Si}_{12-n}\text{Al}_n\text{O}_{16}$ system the $\alpha'$-phase composition closest to $\alpha$-silicon nitride is $\text{Li}_2\text{Si}_{12-n}\text{Al}_n\text{O}_{16}$, which indicates that only 0.125 cationic valency for each of the two interstices is sufficient to stabilize the $\alpha'$-structure. Similar results have been observed in the $\text{Si}_3\text{N}_4\cdots\text{Al}_2\cdots\text{O}_{16}$ system as well.

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$\alpha'$-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. for the representation of the $\text{Si}_3\text{N}_4\cdots\text{Al}_2\cdots\text{O}_{16}$. The change of the cell dimensions fits reasonably to the $\text{Me}_m\text{Si}_{12-n}\text{Al}_n\text{O}_{16}$ system; each corner represents 12 equivalent charges. The $\text{Si}_3\text{N}_4\cdots\text{Al}_2\cdots\text{O}_{16}$ system forms a two-dimensional square plane in this representation (see Figure 7).
systems. As a four-component system it might be represented by a regular tetrahedron, each corner representing to the so-called Jänecke triangular prism, in which is again obtained by using atom equivalents. This leads and two-valent oxygen lie on this plane. Figure of four-valent silicon, three-valent aluminum and nitrogen, Me-Si-Al-O-N quinary systems. A simple 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$_2$O$_6$, Al$_2$O$_6$, Al$_2$N$_6$, and Si$_3$N$_6$, 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$_3$N$_4$-SiO$_2$-AlN-Al$_2$O$_3$ system at 1700 °C.\textsuperscript{124}

Figure 7. Phase diagram of the Si$_3$N$_4$-SiO$_2$-AlN-Al$_2$O$_3$ system at 1700 °C.\textsuperscript{124}

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$_2$O$_6$, Al$_2$O$_6$, Al$_2$N$_6$, and Si$_3$N$_6$, 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$_3$N$_4$-SiO$_2$-AlN-Al$_2$O$_3$ system at 1700 °C.\textsuperscript{124}

Figure 8. Jänecke prism for the Y-Si-Al-O-N system: (1) 2Y$_2$O$_3$Si$_2$N$_4$O$_6$; (2) Y$_2$O$_3$Si$_3$N$_4$O$_3$; (3) Y$_2$O$_3$Si$_4$N$_4$; (4) Y$_3$SiO$_6$N$_6$; (5) Y$_2$SiO$_2$N$_{2}$; (6) Y$_2$SiO$_4$N$_{2}$; (7) Y$_2$Si$_2$O$_6$N$_{2}$; (8) 2Y$_2$O$_3$Si$_3$AlO$_6$; (9) Al$_2$O$_3$N.

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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,\textsuperscript{108-110} in which all edges, expressed in equivalent units, are equal. Figure 8 shows the prism of the Si$_3$N$_4$-SiO$_2$-AlN-Al$_2$O$_3$ system. It is based on the usual square diagram of the

Figure 8. Jänecke prism for the Y-Si-Al-O-N system:

Figure 9. Subsolidus diagram of the Si$_3$N$_4$-AlN-Y$_2$O$_3$ system.\textsuperscript{114}

Si$_3$N$_4$-SiO$_2$-AlN-Al$_2$O$_3$ system extending to the third dimension by the addition of yttrium. This forms two more squares of the AlN-Al$_2$O$_3$-YN-Y$_2$O$_3$ and Si$_3$N$_4$-SiO$_2$-YN-Y$_2$O$_3$ 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., Si$_2$N$_2$O-Al$_2$O$_3$-Y$_2$O$_3$, Si$_3$N$_4$-SiO$_2$-YN-Y$_2$O$_3$ planes.\textsuperscript{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 Si$_3$N$_4$-M$_2$O$_3$Al$_2$N join. However, as early as the appearance of the phase diagram of the Si$_3$N$_4$-AlN-Y$_2$O$_3$ system,\textsuperscript{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.\textsuperscript{46}

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


\textsuperscript{(109)} Lowenherz, R. Z. *Phys. Chem.* 1894, 13, 469.

\textsuperscript{(110)} Jänecke, E. Z. *Phys. Chem.* 1908, 51, 132.


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The latter of which does not lie on the plane of Si₃N₄— which a-silicon nitride forms a limited solid solution with sialon system aialon; a mixture of Y₂0₃:AlN. The solubility limits along this studied on the phase diagram of the Si₃N₄-AlN-Y₂O₃ system is the first line are represented by 0.33 reacts with Y₂O₃ to form Si₃N₄-Y₂O₃ and Si₃N₂0.2Y₂O₃, the latter of which does not lie on the plane of Si₃N₄—AlN-Y₂O₃. Five compatibility triangles containing α′- sialon were observed:

\[ \alpha'-\text{sialon-Si₃N₄-Si₃N₄} \times \text{Y₂O₃} \]

\[ \alpha'-\text{sialon-Si₃N₄-Y₂O₃} \]

\[ \alpha'-\text{sialon-Si₃N₄} \times \text{AlN} \]

More detailed phase relationships in the system were studied on the Si₃N₄—Y₂O₃—Si₃AlO₂N₃ concentration plane at 1700 °C, and the diagrams are shown in Figures 10 and 11. According to the diagrams the boundaries of the single-phase α′-sialon region are 0.33 ≤ x ≤ 1 (Y) and 0.5 ≤ n ≤ 1.5 (O). A discussion is given in ref 117.

The Si₃N₄—AlN—RE₂O₃ systems exhibit phase diagrams similar to those shown in Figure 9 when RE = Gd, Dy, Er, and Yb. The phase diagrams of the Si₃N₄—AlN—Nd₂O₃ and Sm₂O₃ systems are slightly different, since AlN reacts with Nd₂O₃ and Sm₂O₃ to form Nd₃AlO₂N₄ and Sm₃AlO₂N₄, respectively (see Figure 12). The solubility limits of α′-sialon in these systems have been plotted in Figure 5. The lower limits are as same as for yttrium, and the upper limits increase when the size of the modifier cations decreases.

Two-dimensional phase relationships on the Si₃N₄—(Nd/Sm)₀.₅Al₃N₁₆—Si₃AlO₂N₃ concentration plane were also studied. Approximately the same phase relation-

![Figure 10. Phase relations in the concentration plane Si₁₉⁻
N₄₋₁₀Y₂₀₀₃₋₁₀Si₃₀₆N₄₋₁₀ at 1700 °C. (1) β'-sialon; (2) α’-
 sialon; (3) α’ + β'-sialon; (4) α’ + β-sialon + 12H; (5) α’-sialon + 12H; (6) α’-sialon + 21R; (7) β'-sialon + 12H.](image-url)

ships were reported as in Figure 11.

The phase diagram of the Si₃N₄—AlN—CaO system, shown in Figure 13, is very similar to that of the Si₃N₄—AlN—Y₂O₃ 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 2CaO·Si₃N₄ and 3CaO·Si₃N₂O. Besides, at 1450 °C a metastable phase of 2CaO·Si₃N₄·AlN was found as well.

The phase relationships of the Si₃N₄—AlN—Li₂O system have also been reported recently. So far single-phase Li-α′-sialon has been found only on the line Si₃N₄—Li₂O—AlN (Figure 14). Li-α′-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 10Li₂O·Si₃N₄·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 Si₃N₄—AlN—MgO system is another studied recently. However, in this system single-phase Mg-α′-sialon has not been obtained on the line Si₃N₄—MgO:3AlN. The phase compositions along this line with increasing amount of MgO:3AlN are mixtures of the phases β’ + α’, α’ + 12H (AlN polytypoid), and α’ + 12H + AlN, respectively. It is suggested that the small Mg-α′-sialon region is located only at the nitrogen-rich side; thus preparation of single-phase Mg-α′-sialon might be possible by using Mg₃N₂.

The compatibility between α′- and β′-sialon indicates the possibilities for developing composite (α′ + β′)-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-Si₃N₄, 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. start with a solution of the metal alkoxides in isobutanyl 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.

The research on the formation of α′-sialons was mostly conducted in the Y-Si-Al-O-N system. The reaction sequence of the formation of Y-α′-sialon with a composition of Y₀.₅Si₅₋₅Al₂O₃₋₅N₀.₅₋₅₋₅ from a starting mixture consisting of silicon nitride, aluminum nitride, and yttrium. Since the surfaces of nitride particles are always covered with an oxygen-rich layer, an oxide subsystem SiO₂–

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(120) Mitomo, M.; Takeuchi, M.; Ohmae, M. Ceramic Int. 1988, 14, 43.


Figure 11. Phase relations in the Y-α'-sialon plane at 1705 °C. (A) Y$_3$Si$_3$N$_6$; (C) AlN; (D) Y$_3$Si$_3$N$_6$; (E) Y$_2$Si$_3$N$_6$; (J) Y$_2$SiO$_7$N$_2$-Y$_4$Al$_2$O$_9$; (L) liquid; (M) Y$_2$Si$_3$O$_4$N$_4$.

Figure 12. Subsolidus diagram of the Si$_3$N$_4$-AlN-Sm$_2$O$_3$ system.°

Figure 13. Subsolidus diagram of the Si$_3$N$_4$-AlN-CaO system.°

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

Figure 15. Reaction sequence of the formation of α'-sialon, heating rate 10 °C/min; M, Si$_3$N$_4$.Y$_3$O$_3$. Al$_2$O$_3$.Y$_2$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. Moreover, the presence of nitrogen as well as some other impurities will further lower this temperature. 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. 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 Si$_3$N$_4$.Y$_2$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-


(127) Levin, E. M.; McMurdie, F. H. Phase Diagrams for Ceramists; American Ceramics Society: Columbus, OH, 1978; Figure 2586.


significant influence on the formation of α'-sialon has been observed.\textsuperscript{122} If the composition of the starting mixture is changed slightly, other intermediate compounds such as Si\textsubscript{2}N\textsubscript{2}O\textsubscript{3}, \textsubscript{3}Y\textsubscript{2}O\textsubscript{3}-5Al\textsubscript{2}O\textsubscript{3}, 12H, and \textsubscript{Y}2SiAl\textsubscript{10}N may occur as well.\textsuperscript{118,119,122-124,130,131} Figure 16 shows another reaction sequence for the formation of α'-sialon with a composition of Y\textsubscript{6.85}Si\textsubscript{2}Al\textsubscript{2}O\textsubscript{8}N\textsubscript{15.2}.\textsuperscript{123} According to these measurements, the dissolution of α-sialon nitride into the liquid and the precipitation of α'-sialon start approximately at 1550 °C instead of 1380 °C. The formation of the intermediate compound N-melilite, Si\textsubscript{4}N\textsubscript{4}Y\textsubscript{2}O\textsubscript{3} does not occur.

As an exception, the reaction sequence of the formation of Li-α'-sialon exhibits some differences.\textsuperscript{102} The dissolution of silicon nitride into the liquid results in the precipitation of O'-sialon instead of the α'-phase in the reaction sequence in these systems. As an exception, the reaction sequence of the formation of Li-α'-sialon exhibits some differences.\textsuperscript{102} The transformation of α'→β' has been observed in the Ca-α'-sialon and Y-α'-sialon systems.\textsuperscript{46,47,51,124,125,126} In the case of the presence of secondary phases with a composition suitably adjusted, this phase transformation proceeds very easily.

![Figure 16. Reaction sequence of the formation of α'-sialon, with heating rate 14 °C/min.\textsuperscript{122} M, Si\textsubscript{3}N\textsubscript{4}Y\textsubscript{2}O\textsubscript{3}; YAG, 3Y\textsubscript{2}O\textsubscript{5}-5Al\textsubscript{2}O\textsubscript{3}; YAM-ss, \textsubscript{Y}2Al\textsubscript{3}O\textsubscript{8}-Si\textsubscript{2}Y\textsubscript{2}O\textsubscript{5}N.](image)

The mechanism of the phase transformation α→α' 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 β→β', similar to the α→β phase transformation.\textsuperscript{128,129,130} 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.\textsuperscript{90} Liquid-phase sintering is generally described to proceed in three (partly overlapping) stages:\textsuperscript{134-142}

1. 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.
2. 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.
3. Stage III: coalescence and closed porosity 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.\textsuperscript{42,46,47,51}

Figure 17 shows shrinkage curves of α'-sialon ceramics with a composition Yo.5Si9.75Al2.25O1.75N1.25. These curves were obtained by in situ dilatometry in a gas pressure sintering furnace. 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 1500 °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 Si3N4-Y2O3 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, Si3N4-Y2O3 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. 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. 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 (α' + β')-sialon ceramic microstructures without intergranular glassy phases have been reported, TEM studies reveal that most microstructures still contain a small amount of a residual glassy phase after sintering. In those cases where intergranular phases were indeed absent, glass-encapsulated hot isostatic pressing has been used for the densification.

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 structure decreases the thermal conductivity.

α'-Sialon ceramics have linear thermal expansion coefficients of about (3.7–4.0) × 10^-6 K^-1 in the range from room temperature to 1400 °C.143,144

Mechanical Properties. Although the mechanical properties of α'-sialon ceramics have been studied more widely compared to other properties, 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 (KIC) of α'- and β'-sialon ceramics. It is seen that α'-sialon ceramics (Y2O3(SiAl)12(O,N)16; 0.33 ≤ x ≤ 0.8) have both higher hardness and fracture toughness than β'-sialon ceramics (Si6.3Al1.8O15N6.3; 0 ≤ z ≤ 4.2). Ekström also dissolution of metal atoms into the interstitial sites of the α-silicon nitride structure decreases the thermal conductivity.

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Reviews from 5.2 to 3.8 MPa/m². These changes are in part due to simultaneously occurring changes in microstructure. For elongated grains increases, resulting in increasing temperature for sialon composites with different α'/β' content. It should be noted that the highest fracture toughness decreases linearly for values >4.2, i.e., outside the single-phase sialon region. A second factor influencing the hardness is the intergranular amount of glassy phase.

Figure 20. Vickers hardness HV10 increases linearly from 1500 kg/mm² for pure β'-phase to about 1850 kg/mm² for a composite (α' + β')-sialon with 75% α' content. At the same time, the fracture toughness decreases linearly from 5.2 to 3.8 MPa/m². 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 KIC 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 (α' + β')-sialon. Also the increasing values at the right-hand side of Figures 18 and 19 for β'-sialon are obtained for x 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 HV < 1000 kg/mm², 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. 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). 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. The SiC particles prevent grain growth. An advantage of α'-sialons is that the grains are equiaxed and that grain 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. 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, silicon nitride can undergo two distinctive types of chemical reactions. At high oxygen partial pressures so-called passive oxidation takes place:

\[ \text{Si}_3\text{N}_4(s) + 3\text{O}_2 \rightarrow 3\text{SiO}_2(s) + 2\text{N}_2 \]

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 x 10⁴ bar. At lower oxygen partial pressures so-called active oxidation occurs, and volatile SiO is formed according to the reactions

\[ 2\text{Si}_3\text{N}_4(s) + 3\text{O}_2 \rightarrow 6\text{SiO(g)} + 4\text{N}_2 \]

\[ \text{Si}_3\text{N}_4(s) + 3\text{SiO}_2(s) \rightarrow 6\text{SiO}_2(g) + 2\text{N}_2 \]

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. The rate of this reaction is controlled by the oxygen diffusion through the oxide layer and is greatly

\[ \text{Si}_3\text{N}_4(s) + 3\text{O}_2 \rightarrow 3\text{SiO}_2(s) + 2\text{N}_2 \]

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shows an excellent oxidation resistance compared to that oxide layer. This mechanism is shown schematically 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 a'-sialon ceramics we have observed a parabolic relationship as well (see Figure 23). The composite (a' + b')-sialon with a composition \( Y_{0.25}Si_{10.96}Al_{1.11}O_{0.37}N_{15.63} \) shows an excellent oxidation resistance compared to that of both monolithic a'- and b'-sialon ceramics, with compositions of \( Y_{0.63}Si_{6.76}Al_{12.26}O_{0.75}N_{15.31} \) and \( Si_{2}Al_{2}O_{3}N_{5} \), respectively. TEM microstructure analysis reveals that in the (a' + b')-sialon composites only a very minor amount of intergranular phase exists at the grain boundaries. As in the case of b'-sialon the oxide layer consists of a-crys-

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

**Electrical Conductivity.** The electrical conductivity of the b'-sialons is very low. 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 a'-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-a'-sialons. 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 b'-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.

**Summary**

a'-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 a'- or (a' + b')-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 a'-sialons, compared with the needlelike structure of b'-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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