\( \alpha' \)-Sialon Ceramics: A Review

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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\(_3\)N\(_4\)) 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. \(^8,10 \)

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 diffusivity \(^{11-15} \) 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\(_2\)O\(_3\), Y\(_2\)O\(_3\), and Ln\(_2\)O\(_3\),\(^{16-23} \) 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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oxy nitride 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" can enter the silicon nitride crystal lattice without changing the structure by replacing Si" if at the same time N" is replaced by O" as well. Such solid solutions have been named "sialon", the acronym of these four elements.37 The solid solutions above are called s'-sialons since they are derived from the structure of a-sialon nitride:

\[(2 - z/3)3\alpha\beta\text{Si}_3\text{N}_4 + (z/3)\alpha\text{AlN} + (z/3)\alpha\text{Al}_2\text{O}_3 \rightarrow \beta\text{Si}_3\text{Al}_2\text{O}_3\text{N}_6\]

As soon as s'-sialons were reported, the formation of a'-sialon solid solutions with an expanded a'-structure by reaction of lithium silicon nitride with aluminum36 or of lithium aluminate with silicon nitride35 was observed as well. So-called a'-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.30,36-39 The general formula for a solid solution with the a'-silicon nitride type structure is

\[\text{Me}_x\text{Si}_{12-m+n}\text{Al}_{m+n}\text{O}_{n+2}\text{N}_{16-n}\]

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

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

S'-Sialon ceramics have been widely investigated.40-46 and some commercial products are available now, mainly as wear parts, extrusion dies, and weld location pins. Composite materials of a'-sialons are commercially available as cutting tools. However, research of a'-sialon ceramics is still in the early stage. Recently they have attracted great interest 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 a'-sialon ceramics, it is worthwhile to consider the structure of silicon nitride first and then discuss the crystal chemistry of a'-sialons.

Structure of a'- and \(\beta\text{Si}_3\text{N}_4\)

Silicon nitride occurs in two modifications, known as \(\alpha\) and \(\beta\). The structures of both a'- and \(\beta\text{Si}_3\text{N}_4\) have been reported in a number of papers.31-41 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 SiN\(_4\) groups perpendicular to the basal plane lie approximately in a plane. The \(\beta\text{-}\)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 a'-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 \(\alpha\) glide plane connecting the AB layers with the CD layers, the channels are closed. As a result there are, in each unit cell Si\(_2\)N\(_6\) two large interstitial sites at \(2/3, 1/3, 3/8\) and \(1/2, 3/4, 1/8\). To form the \(a\)-structure, the

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(1) Reviewers.
(8) Oyama, Y.; Yogo-Kyokai-Shi 1974, 82, 351.
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 Si11.1 N18.8 O9.4 and with some special lattice sites for the oxygen atoms. However, later chemical analyses and refined structural analyses suggested that α-silicon nitride is a pure silicon nitride. Although this view has been generally accepted, some recent reports revealed that oxygen impurities in silicon nitride powders, which consist mainly of α-silicon nitride, are present. Since the α-silicon nitride is never observed, it is assumed that 0-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.

α-Silicon nitride is a high-temperature modification. Thermodynamic data obtained so far are not sufficiently accurate to make a decision. Since the α → β 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 no longer considered.

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

Figure 3. Schematic phase diagram of the α'- and β'-sialon stability regions; Me is a metal ion with valency υ:65 (1) Me8/2Al3Nυ; (2) Al2O3N.

Figure 4. Coordination of the Yυ+ cation in α'-sialon.101,105

Figure 5. Solubility of some modifying cations in α'-sialon: Me2(SiAl)12(O,N)19.64,65

![Diagram of α'- and β'-sialon crystal structure](image1)

![Schematic phase diagram of α'- and β'-sialon](image2)

![Coordination of Yυ+ cation in α'-sialon](image3)

![Solubility of modifying cations in α'-sialon](image4)
and also a possible transformation via the gas phase is not observed.

Crystal Chemistry of $\alpha'$-Sialon

Solid solutions with the $\beta$-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$^{2-}$. The cation to anion ratio remains constant at 3:4, and no constitutional vacancies are formed. The aluminum substitution leads to Si$_{25}$Al$_{12}$O$_{25}$N$_{16}$ with 0 ≤ z ≤ 4.2. In the case of beryllium the formula is Si$_{25}$Be$_{6}$O$_{25}$N$_{16}$ with 0 ≤ z ≤ 2. The $\beta'$-sialons can thus be described as solid solutions between Si$_N$ and Al$_2$O$_N$, and $\beta'$-sibons between Si$_N$ and Be$_2$SiO$_4$. In contrast to the purely substitutional solubility in the $\alpha$-phase, the $\alpha'$-sialons can be occupied by cations (see Figure 2). So the formation of solid solutions in the $\alpha$-silicon nitride structure occurs only in quaternary Me-Si-Al-O systems where Me = Li, Mg, Ca, Y, and rare-earth metals except La and Ce. In these systems, the $\alpha'$-sialon crystal structure is derived from a-Si$_{12}$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 [Si,Al]$_2$O$_x$N$_{y}$ network. In Y-$\alpha'$-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 $\alpha'$-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 $\alpha'$-sialons with a v-ivalent metal ion are expected to be Me$_2$Si$_{12}$Al$_{2}$N$_{16}$, e.g., Li$_2$Si$_{12}$Al$_{2}$N$_{16}$, Ca$_2$Si$_{12}$Al$_{2}$N$_{16}$, and Y$_2$Si$_{12}$Al$_{2}$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-$\alpha'$-sialon with a composition of Ca$_{12}$Si$_{12}$Al$_{2}$O$_{25}$N$_{16}$ and 1.5 Li$^+$ in Li-$\alpha'$-sialon on the line Si$_3$N$_4$-Li$_2$O-SiAlN.103 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-$\alpha'$-sialon with a composition of Ca$_{12}$Si$_{12}$Al$_{2}$O$_{25}$N$_{16}$ and 1.5 Li$^+$ in Li-$\alpha'$-sialon on the line Si$_3$N$_4$-Li$_2$O-SiAlN.103

$\Delta$(pm) = 4.5m + 0.9n
$\Delta$c (pm) = 4.0m + 0.8n
This suggests that the dimensional increase upon replacement of Si$^{4+}$ by Al$^{3+}$ is about 5 times that for replacement by Al$^3$. The size and solubility of the modifying cations does not influence the dimensional expansion of $\alpha'$-sialon. Possibly the interstitial holes are large enough to accommodate these 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.104,105 for the representation of the Si$_3$N$_4$-$\text{AlN-SiO}_2$-$\text{Al}_2\text{O}_3$ subsystem forms a two-dimensional square plane in this representation (see Figure 7).

Earlier work on $\alpha'$-sialon suggested a miscibility gap between $\alpha$-silicon nitride and the $\alpha'$-phase, the $\alpha'$-sialon compositions closest to Si$_3$N$_4$ being

Ca$_{10.5}$Si$_{10.5}$Al$_{1.5}$O$_{2.5}$N$_{15.5}$ RE$_{0.33}$Si$_{10.5}$Al$_{1.5}$O$_{2.5}$N$_{15.5}$

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 (Ca$_{25.5}$ or RE$_{25.5}$) is considered necessary in each of the two interstices.106 However, later experimental results reveal some exceptions. In the Li$\alpha'$-sialon system the $\alpha$-phase composition closest to $\alpha$-silicon nitride is Li$_{25.5}$(Si$_2$,Al)$_{12}$(O$_{25}$N$_{16}$), which indicates that only 0.125 cationic valency for each of the two interstices is sufficient to stabilize the $\alpha'$-structure.107 Similar results have been observed in the Si$_3$N$_4$-AlN-CaO system as well.108

Unlike the $\beta'$-sialon, Si$_{25}$Al$_{12}$O$_{25}$N$_{16}$, where the replacement without structure change is Si$^{4+}$ by Al$^{3+}$, the replacement in $\alpha'$-sialon is largely Si$^{4+}$ by Al$^{3+}$. With bond lengths Si-N 0.174 nm, Al-O 0.175 nm, and Al-N 0.178 nm, the relative increases in unit cell dimensions for $\alpha \rightarrow \alpha'$ are much larger than for $\beta \rightarrow \beta'$. For a general composition

$$\text{Me}_2\text{Si}_{12-(m+n)}\text{Al}_m\text{N}_n\text{O}_m\text{N}_n$$

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

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

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

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

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systems. As a four-component system it might be represented by a regular tetrahedron, each corner representing 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 at 1700 °C.124

target in assuming normal charges for the elements and sialons is predominantly covalent, there is a great advan-
squares of the AlN-A12O3-Y2O3 and Si3N4-SiO2-Y2O3 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., Si3N4-Al2O3-Y2O3, Si3N4-SiO2-Y2O3 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 Si3N4-M2O3-MAIN join. However, as early as the appearance of the phase diagram of the Si3N4-Al2O3-Y2O3 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'-
A compatibility triangle containing the latter of which does not lie on the plane of Si$_3$N$_4$ which a-silicon nitride forms a limited solid solution with aialon; a mixture of Y$_2$O$_3$. The solubility limits along this studied on the phase diagram of the Si$_3$N$_4$-AlN-Y$_2$O$_3$ system is the first reacts with Y$_2$O$_3$ to form Si$_3$N$_4$-Y$_2$O$_3$ and Si$_2$N$_2$O, the latter of which does not lie on the plane of Si$_3$N$_4$-AlN-Y$_2$O$_3$. Five compatibility triangles containing $\alpha'$-sialon were observed:

$$\alpha'$-sialon - Si$_3$N$_4$ - Si$_3$N$_4$Y$_2$O$_3$$
$$\alpha'$-sialon - Si$_3$N$_4$-Y$_2$O$_3$$
$$\alpha'$-sialon - Si$_3$N$_4$-Y$_2$O$_3$-AlN
$$\alpha'$-sialon - AlN

More detailed phase relationships in the system were studied on the Si$_3$N$_4$-AlN-Re$_2$O$_3$ systems exhibit phase diagrams similar to those shown in Figure 9 when RE = Gd, Dy, Er, and Yb. The phase diagrams of the Si$_3$N$_4$-AlN-Nd$_2$O$_3$ and Sm$_2$O$_3$ systems are slightly different, since AlN reacts with Nd$_2$O$_3$ and Sm$_2$O$_3$ to form Nd$_3$AlO$_5$N and Sm$_2$AlO$_3$N, respectively (see Figure 12). The solubility limits of $\alpha'$-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 Si$_3$N$_4$-N$_2$O$_5$Al$_2$N$_{15}$-Si$_3$AlO$_6$N$_5$ concentration plane were also studied. Approximately the same phase reaction:

$$\beta'$-sialon + 12H; (6) $\alpha'$-sialon + 21R; (7) $\beta'$-sialon + 12H.

More detailed phase relationships in the system were studied on the Si$_3$N$_4$-AlN-Y$_2$O$_3$ systems 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 $\alpha'$-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$_3$N$_4$-AlN-Re$_2$O$_3$ systems exhibit phase diagrams similar to those shown in Figure 9 when RE = Gd, Dy, Er, and Yb. The phase diagrams of the Si$_3$N$_4$-AlN-Nd$_2$O$_3$ and Sm$_2$O$_3$ systems are slightly different, since AlN reacts with Nd$_2$O$_3$ and Sm$_2$O$_3$ to form Nd$_3$AlO$_5$N and Sm$_2$AlO$_3$N, respectively (see Figure 12). The solubility limits of $\alpha'$-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.

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Figure 10. Phase relations in the concentration plane Si$_3$N$_4$-N$_2$O$_5$Al$_2$N$_{15}$-Si$_3$AlO$_6$N$_5$ at 1700 °C. (1) $\beta'$-sialon; (2) $\alpha'$-sialon; (3) $\alpha'$ + $\beta'$-sialon; (4) $\alpha'$ + $\beta'$-sialon + 12H; (5) $\alpha'$-sialon + 12H; (6) $\alpha'$-sialon + 21R; (7) $\beta'$-sialon + 12H.

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

Preparation and Formation of $\alpha'$-Sialon
Several preparation routes are possible. The most widely used method is the direct formation from $\alpha$-Si$_3$N$_4$, 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. start with a solution of the metal alkoxides in isobutanol alcohol. After dispersion of carbon black the metal hydroxides are precipitated on the carbon particles, and then the dried powder is converted into $\alpha'$-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 $\alpha'$-sialons.

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Figure 15 gives, as an example, the reaction sequence of the formation of $\alpha'$-sialon with a composition of Y$_{58}$Nd$_{38}$Al$_{28}$O$_{75}$N$_{15.56}$ 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, an oxide subsystem SiO$_2$-
Figure 11. Phase relations in the Y-α'-sialon plane at 1705 °C:116,117 (A) \( Y_6Si_3N_{16} \); (C) AlN; (D) YSi_3N_5; (E) Y_2Si_3N_6; (J) \( Y_4Si_2O_7N_2-Y_4Al_2O_3 \); (L) liquid; (M) \( Y_2Si_3O_3N_4 \).

Figure 12. Subsolidus diagram of the \( Si_3N_4-AlN-Sm_2O_3 \) system.104,105

Figure 13. Subsolidus diagram of the \( Si_3N_4-AlN-CaO \) system.106

Figure 14. Isothermal section at 1750 °C of the \( Si_3N_4-AlN-Li_2O \) system.108

Figure 15. Reaction sequence of the formation of α'-sialon, heating rate 10 °C/min; M, \( Si_3N_4-Y_2O_3 \) 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.128,129 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 \( Si_3N_4-Y_2O_3 \) 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-

116 O'Meara, C.; Dunlop, G. L.; Pompe, R. High-Technology Ceramics; Viceczinni, F., Ed.; Elsevier Science Publisher B.V.: Amsterdam, 1987; p 265.
117 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.\(^\text{(122)}\) If the composition of the starting mixture is changed slightly, other intermediate compounds such as Si2N2O.Y2O3, 3YzO3-5Al2O3, 12H, and Y2SiAl05N may occur as well.\(^{96,116,118,122-124,130,131}\) Figure 16 shows another reaction sequence for the formation of α'-sialon with a composition of YzSi0.65A10.15N.\(^{125}\) 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-mellite, Si3N4-Y2O3 does not start simultaneously with that of the α'-phase but 100 °C higher and remains until 1800 °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 α'-sialon.\(^{100}\) The rate and extent of shrinkage will depend upon the viscosity and quantity of the liquid and its wetting properties.

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–precipitation 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.

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

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: \(^{136-142}\)

The transformation of α' to β' 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.\(^{125,129,133}\) 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: \(^{136-142}\)

- **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–precipitation 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.
- **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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**References**


Figure 17 shows shrinkage curves of α'-sialon ceramics with a composition Y₃₋₀.₅Si₉₋₇.₅Al₂₀.₂₅O₅₋₀.₇₅N₉₋₁.₂₅. These curves were obtained by in situ dilatometry in a gas pressure sintering furnace.ⁱ²² 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 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 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.⁴¹³ 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,⁴¹⁴ TEM studies reveal that most microstructures still contain a small amount of a residual glassy phase after sintering.⁴⁹,¹⁰⁶,¹¹⁶,¹²² In those cases where intergranular phases were indeed absent, glass-encapsulated hot isostatic pressing has been used for the densification.⁴⁶⁴,¹⁴⁶

**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.⁴⁷⁴,¹⁴⁶ It was shown that the 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) × 10⁻⁶ K⁻¹ in the range from room temperature to 1400 °C.⁴⁶⁹,⁹⁷,¹⁴⁸,¹⁵⁰

**Mechanical Properties.** Although the mechanical properties of α'-sialon ceramics have been studied more widely compared to other properties,⁹⁶,¹¹⁵,¹⁴⁶,¹⁵⁰,¹⁵¹ 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.⁴¹⁴,¹⁴⁶ respectively. It is seen that α'-sialon ceramics (Y₃₋₀.₅Si₉₋₀.₅Al₂₀.₂₅O₅₋₀.₇₅N₉₋₀.₇₅) have both higher hardness and fracture toughness than β'-sialon ceramics (Si₌₋₀.₅Al₂₀.₂₅O₅₋₀.₇₅N₉₋₀.₇₅). Ekström's data also suggest that the mechanical properties are strongly influenced by the presence of intermediate compounds.

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from 5.2 to 3.8 MPa/m. These changes are in part due to simultaneous changes in microstructure. For elongated grains increases, resulting in increasing temperature for sialon composites with different to changes in phase composition and in part to the s-

At the same time the fracture toughness decreases linearly in Figure 19 was achieved at a composition of values >4.2, i.e., outside the single-phase sialon region. A 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. The rate of this reaction is controlled by the oxygen diffusion through the oxide layer and is greatly

**Figure 22.** Schematic diagram of the proposed oxidation mechanism for β'-sialon.

**Table 1.** Hardness and fracture toughness of β'-sialon.

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

Investigations of \( \beta' \)-sialons\(^{182-187} \) also showed the occurrence of passive oxidation in air. For \( \beta' \)-sialon with yttria as a sintering aid, an oxidation mechanism has been proposed.\(^{188,187} \) 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 \( \alpha' \)-sialon ceramics we have observed a parabolic relationship as well (see Figure 23). The composite \((\alpha' + \beta')\)-sialon with a composition \( Y_{0.25}Si_{10.88}Al_{1.11}O_{3.37}N_{16.82} \) shows an excellent oxidation resistance compared to that of the monolithic \( \alpha' \)- and \( \beta' \)-sialon ceramics, with compositions of \( Y_{0.80}Si_{16.76}Al_{25.60}O_{7.76}N_{15.25} \) and \( Si_9Al_5O_{20}N_5 \), respectively.\(^{188} \) TEM microstructure analysis reveals that in the \((\alpha' + \beta')\)-sialon composites only a very minor amount of intergranular phase exists at the grain boundaries. As in the case of \( \beta' \)-sialon the oxide layer consists of \( \alpha' \)-crystallites, often together with mullite. Although detailed studies are still under way, the oxidation mechanisms seem quite similar for \( \alpha' \)- and \( \beta' \)-sialon ceramics.

**Electrical Conductivity.** The electrical conductivity of the \( \beta' \)-sialons is very low.\(^{189-191} \) DC conductivities are about \( 10^{-7} \text{ S/cm} \) 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 \( \alpha' \)-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-\( \alpha' \)-sialons.\(^{192} \) At 700 °C the conductivity is of the order \( 10^{-4} \text{ to } 10^{-5} \text{ S/cm} \), 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 \( \beta' \)-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**

\( \alpha' \)-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 \( \alpha' \)- or \((\alpha' + \beta')\)-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 \( \alpha' \)-sialons, compared with the needlelike structure of \( \beta' \)-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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(183) Deleted in Proof.


(188) Cao, G. Z.; Metselaar, R.; Ziegler, G., to be published.


