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STATE-OF-THE-ART OF SIAION MATERIALS

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STATE-OF-THE-ART OF SIAlON MATERIALS

by

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SUMMARY

Concurrent with the recent engineering efforts in developing advanced ceramics such as Si3N4 and SiC for structural components of high temperature heat engines, "SiAlON" ceramics have also become candidates for consideration. The acronym "SiAlON" was originally given to new compositions derived from silicon nitrides and oxynitrides by simultaneous replacement of silicon and nitrogen by aluminum and oxygen. Other metal atoms M such as Be, Mg, Li, and Ga can be incorporated, and the term has become a generic one applied to Si3N4 based materials. In this review, the state-of-the-art of "SiAlONS" is examined. The review includes work on phase relations, crystal structure, syntheses, and properties of various SiAlONS. The essential features of compositions, fabrication methods, and microstructure are reviewed. High temperature flexure strength, creep, fracture toughness, oxidation, and thermal shock resistance are discussed. These data are compared to those for some currently produced silicon nitride ceramics to assess the potential of SiAlON materials for use in advanced gas turbine engines.

INTRODUCTION

Materials currently being evaluated for structural components of high temperature heat engines include Si3N4, SiC, and a class of materials called SIAIONS. The term "SiAlON" was adopted to designate any composition containing the elements Si-Al-O-N as major constituents e.g. $\beta$-SiAlON (ref. 1,2), $\Omega$-SiAlON (ref. 4), 15R-SiAlON (ref. 3) etc. However, most frequently, the term SIAION refers to $\beta$-Si3N4 solid solution called $\beta$-SiAlON. SIAON compounds can be made by a high temperature reaction between silicon nitride or oxynitride and alumina in which simultaneous replacement of silicon and nitrogen by aluminum and oxygen occurs. Other metal atoms M such as Be, Mg, Li (ref. 5) and Ga (ref. 6) can also be incorporated and the term has thus become a generic one applied to Si-M-O-N based materials. Among various SiAlON materials, $\beta$-SiAlON has been of great interest because it was claimed to have a low thermal expansion (ref. 2,6), good high temperature modulus of rupture and good oxidation resistance (ref. 7). It was also reported that the $\beta$-SiAlON could be fabricated to high density by conventional sintering techniques (ref. 2). These reported properties indicate that $\beta$-SiAlON ceramics might be candidates for high temperature applications, and therefore, have generated considerable interest. In this paper, the state-of-the-art of SiAlON is examined. The paper reviews work on phase equilibria, structure, fabrication and properties. Based on this review, the potential of SiAlON materials for use in advanced gas turbines will be examined.

PHASE EQUILIBRIA AND STRUCTURE

The existence of $\beta$-SiAlON in the system Si3N4 - Al2O3 was first reported by Oyama and Kemiagoto (ref. 1) in Japan and by Jack and Wilson (ref. 2) in England. Subsequent studies by the same workers reported a solid solution ($\beta$-SiAlON) forming region in the systems Si3N4 - SiO2 - Al2O3 (refs. 5 and 6) and Si3N4 - AlN - Al2O3 (ref. 3). Detailed compatibility and phase equilibria studies were reported by Gauckler et. al (ref. 8) and Jack (ref. 4) in the system Si3N4 - AlN - SiO2 - Al2O3 and their diagrams are shown in Figs. 1 and 2. Jack (ref. 4) refers to his diagram (Fig. 2) as an "Idealized Behavior Diagram" rather than an equilibrium diagram since it combines data obtained from specimens hot pressed at temperatures ranging from 1550 to 2000 C. Most of the data, however, were obtained at 1775 C. On the other hand, the diagram by Gauckler et. al (ref. 8) is an isothermal section at 1760 C (Fig. 1). According to both Jack and Gauckler, the $\beta$-SiAlON region extends from the Si3N4 corner in the direction of AlN, Al2O3 along a line representing a constant metal/non-metal (M/X) ratio of 1:4 and can therefore be described by the empirical formula $Si_{4-x} Al_{x} O_{4} N_{4-x}$ with x=0 to 4.2. In the oxygen rich part of the diagram, mullite and X-phase SiAlON (formula $SiAlO_{4}(N_x)$) were observed. In the AlN-rich part of the system, five new phases were identified (ref. 8) in the region between $\beta$-SiAlON and AlN. The phases called X2, X4, X5, X6, and X7 are shown in Fig. 1 and are located along lines of constant metal:non-metal ratios. These were later identified by Jack (Fig. 2) as AlN polytypes (ref. 4). The diagrams proposed by Jack and Gauckler et. al. are quite similar except that the locations of AlN polytypes are slightly different. Work by Layden (ref. 9) established the liquidus isotherms (Fig. 3) in part of the system lying between SiO2-AlN corner of the diagram and X-phase.

$\beta$-SiAlON has a $\beta$-silicon nitride structure which extends along the 3M/4X line but the sizes of the tetrahedra and hence also the unit cell dimensions, increase as aluminum and oxygen replace silicon and nitrogen (ref. 8). Silicon oxynitride $\Omega$-SiAlON
Pressureless sintering when compared to hot pressing has the advantage of shape capability and high volume production of small as well as large components. The expense of machining prevents hot pressing from being a cost effective process for many applications. As a result, much effort has been devoted to fabrication by pressureless sintering. Table II shows a list of pressureless sintering studies conducted with various material combinations with and without additives. Sintering was conducted at about one atmosphere of nitrogen to produce bodies with densities as high as 98% theoretical. However, other work (ref. 11) indicated that the resulting SiAlON contained other phases. Morgan (ref. 24) predicted in a presentation cited by Layden (ref. 9) that single phase \( \beta' \)-SiAlON compositions having stoichiometries given by the formula \( Si_{3-x}Al_{x}O_{x}N_{4-x} \) would not sinter. Layden (ref. 9) also reported that as a pure phase \( \beta' \)-SiAlON could not be sintered to high final density. For example, Layden introduced the term "transient liquid phase sintering" or TLP. In

FABRICATION

A. Hot Pressing

Hot pressing has been found to be the easiest technique for fabricating theoretically dense, fine-grained bodies with high strength in covalent materials such as \( Si_{3}N_{4} \) and \( SiC \). Consequently, most early work on phase equilibria, structure, and property evaluation was conducted on \( \beta' \)-SiAlONs fabricated by hot pressing. Table I lists starting materials for various \( \beta' \)-SiAlON formulations and their hot pressing parameters. In most of the investigations, various material combinations listed in Table I were hot pressed at temperatures where simultaneous chemical reaction and densification were taking place under applied pressure. MgO was commonly used as an additive to promote densification. The most effective hot pressing temperature range was 1650-1750 C. Time at temperature varied in these investigations, but generally ranged from 30 minutes to 2 hours. Heating the compacts was accomplished by induction or resistance heating of graphite or SiC. The reaction of carbon with the compact was minimized by using a BN liner or container.

The experimental studies shown in Table I illustrate the varied nature of investigations in hot pressed \( \beta' \)-SiAlONs. Characterization of the hot pressed materials has included phase equilibria, structure, and chemistry which have been discussed in the preceding sections. Strength, creep, thermal and oxidation behavior will be discussed in following sections.

B. Pressureless Sintering

Pressureless sintering when compared to hot pressing has the advantage of shape capability and high volume production of small as well as large components. The expense of machining prevents hot pressing from being a cost effective process for many applications. As a result, much effort has been devoted to fabrication by pressureless sintering. Table II shows a list of pressureless sintering studies conducted with various material combinations with and without additives. Sintering was conducted at about one atmosphere of nitrogen to produce bodies with densities as high as 98% theoretical. The most effective sintering temperature regime and time period were 1700-1760 C for 2-4 hours respectively, although a much broader range of temperature and time was used by different investigators.

Jack (ref. 2) reported that a \( Si_{3}N_{4} \) and \( Al_{2}O_{3} \) mixture could be fabricated to dense single phase \( \beta' \)-SiAlON bodies by pressureless sintering. However, other work (ref. 11) indicated that the resulting SiAlON contained other phases. Morgan (ref. 24) predicted in a presentation cited by Layden (ref. 9) that single phase \( \beta' \)-SiAlON compositions having stoichiometries given by the formula \( Si_{3-x}Al_{x}O_{x}N_{4-x} \) would not sinter. Layden (ref. 9) also reported that as a pure phase \( \beta' \)-SiAlON could not be sintered to high final density. For example, Layden introduced the term "transient liquid phase sintering" or TLP. In
in contrast to sintering by forming liquid within the system itself, additives which
\[ 0.3 \] It is
\[ \frac{\text{of } 0'-\text{SiAlON and } N}{\text{of } 0'-\text{SiAlON}} \]
\[ \frac{\text{im}}{\text{mo''}} \]
\[ 3 \]
\[ \frac{\text{y varied from 0.57 to 1.92}}{\text{y varied from 0.57 to 1.92}} \]
\[ \frac{\text{utilizing starting materials } \text{Si}, \text{Al}, \text{O}, \text{N}}{\text{utilizing starting materials } \text{Si}, \text{Al}, \text{O}, \text{N}} \]
\[ \text{recently, Arias} \]
\[ \text{Arias} \]
\[ \frac{\text{ref. 26}}{\text{ref. 26}} \]
\[ \frac{\text{effect of oxygen to nitrogen ratio (O/N) on}}{\text{effect of oxygen to nitrogen ratio (O/N) on}} \]
\[ \frac{\text{on the pressureless sinterability of } \text{SiAlONs of formula } \text{Si}_{2.55} \text{Al}_{0.6} \text{O}_{3} \text{N}_{4} - 0.667 y}{\text{on the pressureless sinterability of } \text{SiAlONs of formula } \text{Si}_{2.55} \text{Al}_{0.6} \text{O}_{3} \text{N}_{4} - 0.667 y} \]
\[ \frac{\text{starting materials used were } \text{Si}, \text{Al}, \text{O}, \text{N}}{\text{starting materials used were } \text{Si}, \text{Al}, \text{O}, \text{N}} \]
\[ \frac{\text{with } x \text{ and } y \text{ molar ratio constant at } 0.2}{\text{with } x \text{ and } y \text{ molar ratio constant at } 0.2} \]
\[ \text{sintering was promoted by a liquid formed by an initial reaction between } yz \frac{2}{3} \text{SiO}_{2} \text{and } yz \frac{2}{3} \text{Al}_{2} \text{O}_{3}. \text{in any case whether a liquid formed by the foreign additives or during}}{\text{sintering was promoted by a liquid formed by an initial reaction between } yz \frac{2}{3} \text{SiO}_{2} \text{and } yz \frac{2}{3} \text{Al}_{2} \text{O}_{3}. \text{in any case whether a liquid formed by the foreign additives or during}} \]
\[ \frac{\text{sintering of bodies formulated with major constituents such that some liquid is formed}}{\text{sintering of bodies formulated with major constituents such that some liquid is formed}} \]
\[ \frac{\text{at the sintering temperature, a grain boundary glassy phase is retained in the sintered}}{\text{at the sintering temperature, a grain boundary glassy phase is retained in the sintered}} \]
\[ \frac{\text{body, it will be seen soon that this glassy phase has a controlling influence on the}}{\text{body, it will be seen soon that this glassy phase has a controlling influence on the}} \]
\[ \frac{\text{high temperature properties of the sintered body (ref. 9).}}{\text{high temperature properties of the sintered body (ref. 9).}} \]

**Density and Microstructure**

\[ \text{Si} \text{AlON compositions have been fabricated to essentially theoretical density by} \]
\[ \text{hot pressing, while pressureless sintering has resulted in maximum densities close to} \]
\[ \text{95% of theoretical, (ref. 30, 31). The density values of hot pressed } \text{Si} \text{AlON have} \]
\[ \text{ared from 1.05 to 1.15 g/cc (ref. 17). Utilizing starting materials } \text{Si}, \text{Al}, \text{O}, \text{N} \]
\[ \text{and } \text{SiO}_{2} \text{plus a small amount of } \text{Al}_{2} \text{O}_{3} \text{from the grinding media but no additive, a maximum} \]
\[ \text{density of about 98% of theoretical occurred in the } \text{O:N ratio range between 0.2 and} \]
\[ \text{0.3. it is very likely, that liquid formed in various phase fields according to the behavior diagram shown in} \]
\[ \text{Fig. 2 and promoted densification in all compositions by varying from 0.37 to 1.92.} \]

In contrast to sintering by forming liquid within the system itself, additives which
\[ \text{provide a liquid phase at the sintering temperatures are commonly used for densifying} \]
\[ \text{SiAlON based ceramics. For example, Fig. 7 shows typical densification behavior of} \]
\[ \text{Si} \text{AlON compositions as a function of temperature (ref. 31). The starting materials used were } \text{Si}, \text{Al}, \text{O}, \text{N} \]
\[ \text{and } \text{SiO}_{2} \text{with } x \text{ and } y \text{ molar ratio constant at 0.2. Sinter-} \]
\[ \text{ing was promoted by a liquid formed by an initial reaction between } yz \frac{2}{3} \text{SiO}_{2} \text{and } yz \frac{2}{3} \text{Al}_{2} \text{O}_{3}. \text{In any case whether a liquid formed by the foreign additives or during}} \]
\[ \text{sintering of bodies formulated with major constituents such that some liquid is formed} \]
\[ \text{at the sintering temperature, a grain boundary glassy phase is retained in the sintered}} \]
\[ \text{body, it will be seen soon that this glassy phase has a controlling influence on the}} \]
\[ \text{high temperature properties of the sintered body (ref. 9).} \]

**Properties**

Host of the mechanical properties reported in the literature are for \( \text{Si} \text{AlON in the system } \text{Si}, \text{Al}, \text{O} \]
\[ \text{SiAlON compositions in the system } \text{Si}, \text{Al}, \text{O} \]
\[ \text{are similar. In this review, the properties of various } \text{Si} \text{AlON compositions in the system } \text{Si}, \text{Al}, \text{O} \]
\[ \text{are discussed.} \]

**Modulus of Rupture**

Arrol (ref. 7) reported the room temperature modulus of rupture (3-point MOR) of a
\[ \text{hot pressed } \text{Si} \text{AlON to be as high as 825 MPa. He also reported the strength of sintered} \]
\[ \text{SiAlON compositions or formulations as in Table II. In Table II, average values at room temperature} \]
\[ \text{and at } 1370 \text{C are given for various } \text{Si} \text{AlONs made from different starting materials. The highest} \]
\[ \text{room temperature strength of hot pressed } \text{Si} \text{AlON bodies was found to be 648 MPa (ref. 17), while the highest strength obtained in pressureless sintered bodies was} \]
\[ \text{483 MPa (ref. 31).} \]

Only one value 240 MPa (ref. 18) is listed for a hot pressed \( \text{Si} \text{AlON at } 1370 \text{C.} \)

Where data are available over a range of temperatures, the strength of sintered 
sp-SiAlON is compared with the strength of silicon nitride currently produced in USA. 
This is shown in Fig. 8. As can be seen, the room temperature strength of sintered 
sp-SiAlON compares favorably with room temperature strength of sintered Si3N4. On 
the other hand, the room temperature strengths of sintered sp-SiAlON are considerably 
lower than the room temperature strength of hot pressed Si3N4 (NC-132).

At high temperature (1370°C), the strength of sintered sp-SiAlON is equivalent to or
higher than the strength of sintered Si3N4 but lower than the strength of hot press-
ed Si3N4 (NC-132).

The room temperature strength is controlled by residual porosity, surface flaws,
foreign inclusions etc., in the body, while the high temperature strength is controlled 
by the grain boundary phases retained in the body during cooling from the sintering tem-
perature. The grain boundary phase softens at high temperatures thus leading to slow 
creep and subsequent loss in strength. Fig. 9 shows an example of such typical slow 
creep growth failure (V-shaped area) in the fracture surfaces of a 1380°C MOR bar 
of sp-SiAlON sintered with 6 mol% Y2O3 - SiO2 additive. Since the intended use 
of SiAlON has largely been for high temperature, high performance applications similar 
to those being attempted with Si3N4 and SiC, improvement in strength at high temper-
ature is desirable.

Creep

Limited creep data are available on sp-SiAlONs as compared with modulus of rupture 
data. Arrol (Ref. 7) determined the creep behavior of several hot pressed SiAlONs, and 
compared the data with hot pressed Si3N4 (HS-110) and (HS-130), hot pressed SiC 
and reaction bonded Si3N4. These are shown in Table IV. As can be seen, creep in the 
SiAlONs can vary depending on composition from a high value similar to that of HS-110 to 
a value as low as that of hot pressed SiC. Lumby et al. (Ref. 33) compared the creep 
data of a pressureless sintered SiAlON with the data for various silicon based ceramics
which are shown in Fig. 10. The sintered SiAlON has a creep rate lower than that of 
hot pressed Si3N4 (HS-110), reaction bonded Si3N4 or Arrol SiC but slightly higher 
than that of hot pressed SiC. Lumby further observed a strong dependency of creep be-
avor on AlN content. Creep after 20 hours at 1227°C and 77 MN/m2 decreased from 
0.75% to 1.25% for a sp-SiAlON composition containing 4% AlN down to 0.64% 
strain for a composition which contained 11.25% AlN (Ref. 17).

According to Layden (Ref. 9), three point flexural creep tests in argon of TLP sinter-
ed SiAlON gave a steady state creep rate of 3.1 x 10^-4 hr^-1 at a stress level of 
82 MN/m2 at 1400°C. This value was below the compressional creep rate of hot pressed 
Si3N4 under those conditions which has been reported (Ref. 36) to be 5.4 x 10^-4 hr^-1. 
It was determined that the creep rate of the Y2O3 containing sp-SiAlON bodies was about 
6 x 10^-5 hr^-1 at 1370°C and a stress level of 69 MN/m2 which was comparable to that of commercial hot pressed Si3N4 (HS-130) at the same 
stress levels. Layden observed that creep behavior was controlled by the properties 
of the grain boundary phases. For example, sp-SiAlON compositions containing 
ZrO2 additives exhibited slow crack growth during testing due to rapid flow of the 
grain boundary phases at stresses as low as 69 MN/m2 at 1370°C. On the other hand, 
sp-SiAlONs containing 6 mol% Y2O3 exhibited higher refractoriness of the grain boundary 
phases. Therefore, no slow crack growth occurred during testing to 345 MN/m2 at 1370°C 
and the specimens failed by fast fracture.

Fracture Toughness

Fracture toughness (KIC) values reported in the literature for various SiAlON com-
mpositions are listed in Table IV. Generally, the values are lower than those of hot 
pressed Si3N4. For example, Wills et al. (Ref. 37) found the fracture toughness values 
varying between 1.32 and 2.65 MN/m^1/2 as compared with 6 MN/m^1/2 for 
(HS-130) hot pressed Si3N4. Wills also suggested that the presence of X - phase 
should be kept at very low levels and preferably be eliminated completely to improve 
the fracture toughness in SiAlONs. Similarly, Gauckler et al. (Ref. 18) reported lower 
fracture toughness values (Table IV). However, Lumby et al. (Ref. 33) obtained high 
fracture toughness value (6.0 MN/m^1/2) for a pressureless sintered SiAlON similar to 
(HS-130) hot pressed Si3N4 as well as hot pressed SiAlON, measured by the same 
technique (Ref. 2). He also determined the variation of fracture toughness with tem-
perature for both hot pressed and sintered SiAlONs which is shown in Fig. 11. Lumby sug-
gested that the increase in fracture toughness at higher temperatures was associated 
with the viscous deformation of the grain boundary phase. The variation in KIC values 
shown in Table IV could probably be attributed to variation with SiAlON composition and 
fabrication techniques as well as variation with the fracture toughness measuring tech-
nique.

Oxidation

Oxidation resistance is one of the key properties that must be satisfied by a mater-
ial in order to be candidate for high temperature applications. Jack (Ref. 2) and Acrol 
(Ref. 7) reported that the oxidation resistance of sp-SiAlONs is better than that of 
hot pressed Si3N4 (HS-130). Layden (Ref. 9) later confirmed this in his evaluation 
of the material of TLP sintered SiAlON compositions. He observed that the oxida-
tion rate of TLP Si3AlN4 (60% SiN2) was an order of magnitude less than that 
of (HS-130) hot pressed Si3N4 at 1400°C (Ref. 39). Layden (Ref. 29) also made an ex-
tensive study on the oxidation behavior of $\beta'$-SiAlON compositions pressureless sintered with various additions such as CeO$_2$, Y$_2$O$_3$, ZrO$_2$, Y$_2$O$_3$-ZrO$_2$. These are shown in parabolic plots in Fig. 13 (ref. 29, 39). CeO 2 doped material had the highest weight gain while TLP material (without any additive) had the lowest weight gain followed by ZrO$_2$ doped SiAlON (Fig. 13). Both TLP and ZrO$_2$ doped SiAlONs had much higher oxidation resistance than that of hot pressed SiN$_4$ (HS-130). Similarly, Dutta (ref. 31) and Arias (ref. 30) reported a higher oxidation resistance in $\beta'$-SiAlON doped with Y$_2$O$_3$-SiO$_2$ and ZrO$_2$ respectively, as compared with HS-130. Very recently, Arias (ref. 29) determined the oxidation resistance of SiAlON-C (Si$_{14.9}$Al$_{26.7}$O$_{6.7}$N$_{4.9}$) to be lower than that of TLP and ZrO$_2$ doped SiAlONs. This is shown in Fig. 14. The oxidation behavior of several SiAlONs is compared with those of hot pressed silicon nitride (HS-130) produced commercially. All the sintered SiAlONs showed better oxidation resistance than hot pressed HS-130. This hot pressed SiN$_4$ had the highest weight gain, while SiAlON - C (ref. 32) had the lowest weight gain followed by TLP SiAlON (ref. 9). The oxidation rate constant for SiAlON - C is $2.5 \times 10^{-10}$ g/cm$^2$ hr$^{-1}$ as compared with $2.67 \times 10^{-8}$ g/cm$^2$ hr$^{-1}$ for hot pressed SiN$_4$ and $1.96 \times 10^{-9}$ g/cm$^2$ hr$^{-1}$ for TLP SiAlON, indicating that SiAlON compositions can be produced with excellent oxidation resistance as compared with these sintered SiAlONs. However, these sintered SiAlONs such as SiAlON-C and TLP SiAlON have poor room temperature strength as compared with hot pressed SiN$_4$. For these materials to be accepted for turbine applications, further composition development is necessary to combine good oxidation behavior and good mechanical properties.

**Thermal Expansion**

Jack (ref. 2) reported the linear thermal coefficient of expansion of $\beta'$-SiAlON (Si$_{14.9}$Al$_{26.7}$O$_{6.7}$N$_{4.9}$) to be $2.7 \times 10^{-6} \text{C}^{-1}$ which was less than that of $\beta$-SiN$_4$ ($3.5 \times 10^{-6} \text{C}^{-1}$). On the other hand, Gauckler et. al (ref. 10) reported an average value of $3.4 \times 10^{-6} \text{C}^{-1}$ which was in good agreement with the value for pure $\beta$-SiN$_4$. Gauckler observed an almost linear decrease of the thermal expansion coefficient with increasing Al concentration for the Si$_{14.9}$Al$_{26.7}$O$_{6.7}$N$_{4.9}$-x SiAlON which is shown in Fig. 15.

Wills et. al (ref. 37) reported linear thermal expansion of three sintered SiAlON compositions. The expansion of the two compositions Si$_{14.9}$Al$_{26.7}$O$_{6.7}$N$_{4.9}$ and Si$_{15.5}$Al$_{26.7}$O$_{6.7}$N$_{4.9}$ was identical ($3.3 \times 10^{-6} \text{C}^{-1}$) but the third composition Si$_{14.9}$Al$_{26.7}$O$_{6.7}$N$_{4.9}$-x showed greater expansion ($3.3 \times 10^{-6} \text{C}^{-1}$) because of X - phase (ref. 37). Collectively, data clearly indicated that the thermal expansion coefficients of $\beta'$-SiAlON compositions and of $\beta$-SiN$_4$ are quite similar.

**Thermal Shock**

Water quench thermal shock resistance ($\Delta T_c$) of several SiAlONs determined by various investigators are listed in Table V along with data for other silicon based ceramics for comparison. The collective $\Delta T_c$ values for $\beta'$-SiAlONs are comparable to those of hot pressed silicon nitride and reaction bonded silicon nitride. However, the values are considerably lower than that of hot pressed silicon nitride (Table V). Gauckler suggested that the poor thermal shock behavior of the $\beta'$-SiAlON despite its lower coefficient of thermal expansion was caused by the low thermal conductivity and poor fracture toughness of the material.

**CONCLUDING REMARKS**

The present review has shown that since the discovery of SiAlONs, a number of investigations have been made of their phase equilibria, structure, fabrication and properties. SiAlONs can be prepared by several chemical routes. Fully dense bodies can be produced by hot pressing, while a final density ~98% of theoretical can be achieved by pressureless sintering. Both room temperature and high temperature strength of sintered $\beta'$-SiAlONs are equivalent to or higher than the strengths of sintered silicon nitrides but lower than the strength of hot pressed silicon nitride (HS-130). On the other hand, many SiAlON compositions have higher oxidation resistance than those of hot pressed silicon nitrides, and therefore, have a better chance of longer survival in an oxidizing environment. However, the most significant lack in the current state of the art of SiAlON is that no SiAlON composition has yet been developed which exhibits good low temperature strength as well as good oxidation resistance. Indeed some of the SiAlONs that have exhibited the best oxidation resistance have also had low strength at high temperature. Only a few of the SiAlONs identified to date hold promise for high temperature use in gas turbines. Because of their low strength at lower temperature, it is not likely that sintered SiAlONs nor sintered silicon nitride will be used for integrally bladed turbine wheels. Such wheels are highly stressed in the lower temperature region of the hot pressed SiN$_4$. However, SiAlON materials have the advantage of pressureless sintering to high density and thereby have the potential for providing low cost net shape components to intricate geometry without expensive machining.

*\(\Delta T_c\) - critical quenching-temperature difference required to initiate thermal stress fracture (see ref. 41 for more detailed explanation).
At present, a more likely use for sintered SiAlONs in the turbine is for stator vanes which run hotter, and at lower stresses than turbine blades or disks. For these SiAlONs that have potential for use in gas turbines, much work remains to be done to characterize them in the depth required for such an application.

It is to be hoped that improvement in mechanical properties can be achieved in combination with good oxidation resistance by choosing proper chemical formulations. Work to date indicates that such a combination can be best achieved at low Al2O3 concentrations. However, to select an optimum composition, a clear understanding of the phase equilibria of the particular system is essential.

REFERENCES


32. A. Arias, "Modulus of Rupture and Oxidation Resistance of a Si_{2.55}Al_{0.60}N_{3.52} SiAlON," NASA TP-1490 1979.


<table>
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<tr>
<th>Starting materials</th>
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<th>Pressure, MN/m²</th>
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<td>Si₃N₄, Al₂O₃</td>
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<td>1700</td>
<td>30</td>
<td>(a)</td>
<td>Phase analysis</td>
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<td>Si₃N₄, Al₂O₃</td>
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<td>1765-1880</td>
<td>60-120</td>
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<td>Si₃N₄, Al₂O₃</td>
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<td>1650-1850</td>
<td>6-60</td>
<td>25</td>
<td>Sintering, grain growth</td>
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<td>Si₃N₄, Al₂O₃</td>
<td>MgO</td>
<td>1500-2000</td>
<td>1-1440</td>
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<td>Fabrication, modulus of</td>
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<td>Si₃N₄, Al₂O₃</td>
<td>MgO</td>
<td>1750</td>
<td>30-240</td>
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<td>Processing and properties</td>
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<td>Si₃N₄, Al₂O₃</td>
<td>Si, Al, MgO</td>
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<td>1-1440</td>
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<td>Fabrication, modulus of</td>
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<td>1750</td>
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<td>(a)</td>
<td>(a)</td>
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<td>Si₃N₄, Al₂O₃</td>
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<td>1800</td>
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<td>Formation, microstructure</td>
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<td>Si₃N₄, Al₂O₃</td>
<td>MgO</td>
<td>1500-1700</td>
<td>120</td>
<td>5.5-27.5</td>
<td>Characterization</td>
<td>16</td>
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<td>Si₃N₄, Al₂O₃</td>
<td>MgO</td>
<td>1600-1800</td>
<td>5-60</td>
<td>3.5-22</td>
<td>Physical, mechanical</td>
<td>17</td>
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<td>Si₃N₄, Al₂O₃</td>
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<td>1700-1870</td>
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<td>13.8-34.5</td>
<td>Electrical resistivity</td>
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<td>Si₃N₄, Al₂O₃</td>
<td>MgO</td>
<td>1200-1700</td>
<td>120</td>
<td>27.6</td>
<td>Hot pressing and micro-structure characterization</td>
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*aNot reported.*
<table>
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<tr>
<th>Starting materials</th>
<th>Additives</th>
<th>Temperature, °C</th>
<th>Time, min</th>
<th>Nature of investigation</th>
<th>Reference</th>
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<td>Si₃N₄, Al₂O₃</td>
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<td>60</td>
<td>Fabrication (slip casting) and sintering</td>
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<td>Si₃N₄, Al₂O₃</td>
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<td>1600-1850</td>
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<td>Fabrication, modulus of rupture, creep, impact oxidation</td>
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<td>Si₃N₄, Al₂O₃</td>
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<td>1600-1800</td>
<td>60</td>
<td>Microstructure analysis</td>
<td>10</td>
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<tr>
<td>Si₃N₄, Al₂O₃</td>
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<td>1600-2000</td>
<td>0-180</td>
<td>Liquid phase sintering</td>
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<td>Si₃N₄, Al₂O₃, AIN</td>
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<td>1670-1830</td>
<td>240</td>
<td>Effect of oxygen to nitrogen ratio on densification</td>
<td>26</td>
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<tr>
<td>Si₃N₄, Al₂O₃</td>
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<td>1775-1800</td>
<td>60</td>
<td>Fabrication and modulus of rupture</td>
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<td>Si₃N₄, Al₂O₃</td>
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<td>1740</td>
<td>60</td>
<td>Fabrication and modulus of rupture, creep and oxidation</td>
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<tr>
<td>β⁺-SIALON</td>
<td>CeO₂, Y₂O₃, ZrO₂, AI₂O₃, Gap₃O₈, ZrC, La₂O₃, Er₂O₃, Nd₂O₃ (Sm,Gd)O₃</td>
<td>1700-1800</td>
<td>60-180</td>
<td>Fabrication, modulus of rupture and oxidation</td>
<td>29</td>
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<tr>
<td>Si₃N₄, SiO₂, AIN</td>
<td>Y₂O₃</td>
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<td>240</td>
<td>Fabrication, modulus of rupture and oxidation</td>
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<tr>
<td>Si₃N₄, AIN, Al₂O₃</td>
<td>Y₂O₃-SiO₂</td>
<td>1450-1750</td>
<td>60-120</td>
<td>Fabrication, modulus of rupture and oxidation</td>
<td>31</td>
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<tr>
<td>Si₃N₄, AIN, Al₂O₃</td>
<td>Y₂O₃, MgO-Y₂O₃, MgAl₂O₄</td>
<td>1750</td>
<td>240</td>
<td>Fabrication, modulus of rupture and oxidation</td>
<td>Current work by the author</td>
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TABLE III. - MODULUS OF RUPTURE OF HOT-PRESSED AND SINTERED SIAlONS

<table>
<thead>
<tr>
<th>Starting materials</th>
<th>Basic formula</th>
<th>Fabrication method</th>
<th>Average 4-point modulus of rupture, MPa</th>
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<tr>
<td></td>
<td></td>
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<td>25°C</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₃Al₂.67O₄N₄</td>
<td>Hot-pressed</td>
<td>310</td>
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<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>a</td>
<td></td>
<td>420</td>
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<tr>
<td>Si₃N₄, Al₂O₃, SiO₂ (NgO)</td>
<td>Si₂.67Al0.30O₁.43N₃.57</td>
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<td>6648</td>
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<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.25Al₁.75O₁.75N₃.25</td>
<td></td>
<td>3510</td>
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<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>a</td>
<td>Sintered</td>
<td>250</td>
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<td>Si₃N₄, Al₂O₃</td>
<td>Si₄Al₂.60O₂N₆</td>
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<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.64Al₁.60O₁.60N₂.4</td>
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<tr>
<td>Basic β'(Y₂O₃)</td>
<td>Si₂.45Al₁.55O₁.55N₃.45</td>
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<td>β'(Y₂O₃)</td>
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<td>β'(ZrO₂)</td>
<td>Si₂.45Al₁.55O₁.55N₃.45</td>
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<td>Si₃N₄, Al₂O₃, SiO₂ (Y₂O₃)</td>
<td>Si₂.64Al₀.39O₁.45N₁.36</td>
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<td>460</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃, SiO₂ (Y₂O₃)</td>
<td>Si₂.64Al₁.08O₁.60N₁.36</td>
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<td>483</td>
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<tr>
<td>Si₃N₄, Al₂O₃, SiO₂ (NgO)</td>
<td>Si₂.55Al₀.60O₁.72N₁.52</td>
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<td>404</td>
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<tr>
<td>Si₃N₄, Al₂O₃, SiO₂ (NgO)</td>
<td>Si₂.55Al₀.60O₁.72N₁.52</td>
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<td>410</td>
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<td>Si₂.07Al₁.24O₁.25N₁.32</td>
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<td>Current work by</td>
<td>the author</td>
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*aNot reported.
*bThe additive or sintering aid is enclosed in parentheses.
*c3-point NOR.
### Table IV. Fracture Toughness ($K_{IC}$) of Sialon Materials

<table>
<thead>
<tr>
<th>Starting materials</th>
<th>Basic formula</th>
<th>Fabrication method</th>
<th>Fracture toughness ($K_{IC}$) [MN/m$^{3/2}$]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$, Al$_2$O$_3$</td>
<td>*</td>
<td>Hot-pressed</td>
<td>1.2</td>
<td>15</td>
</tr>
<tr>
<td>Si$_3$N$_4$, AlN, SiO$_2$</td>
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<td>Hot-pressed</td>
<td>0.4</td>
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<td>Hot-pressed</td>
<td>0.6</td>
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<td>Si$_3$N$_4$, AlN, SiO$_2$ (MgO)</td>
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<td>Sintered</td>
<td>0.6</td>
<td>33</td>
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<td>Si$_3$N$_4$, AlN, Al$_2$O$_3$</td>
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<td>Sintered</td>
<td>2.2</td>
<td>37</td>
</tr>
<tr>
<td>X</td>
<td>*</td>
<td>Sintered</td>
<td>1.3</td>
<td>37</td>
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</table>

*Not reported.

### Table V. Water Quench Thermal Shock Resistances ($T_s$) of Sialon, Si$_3$N$_4$, and Sic Ceramics

<table>
<thead>
<tr>
<th>Material</th>
<th>Basic formula</th>
<th>$T_s$ [°C]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot-pressed Sialon</td>
<td>Si$<em>2$O$<em>x$Al$</em>{2-x}$SiO$</em>{3-2x}$</td>
<td>320</td>
<td>18</td>
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<tr>
<td>Sintered Sialon</td>
<td>Si$_2$O$<em>x$Al$</em>{2-x}$</td>
<td>550</td>
<td>33</td>
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<tr>
<td>Sintered Sialon</td>
<td>SiC</td>
<td>510</td>
<td>33</td>
</tr>
<tr>
<td>Reaction sintered SIC</td>
<td>SiC</td>
<td>515</td>
<td>40</td>
</tr>
<tr>
<td>Reaction sintered Si$_3$N$_4$</td>
<td>Si$_3$N$_4$</td>
<td>510</td>
<td>40</td>
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<tr>
<td>Not pressed Si$_3$N$_4$</td>
<td>Si$_3$N$_4$</td>
<td>730</td>
<td>18</td>
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</tbody>
</table>

*Not reported.*
Figure 1. - Isothermal section $Si_3N_4$ - AlN - $Al_2O_3$ - SiO$_2$ of the system Si-Al-O-N at 1760°C (ref. 8).
Figure 2. - The Si$_3$N$_4$-AlN-Al$_2$O$_3$-SiO$_2$ system (ref. 4).
Figure 3. - The Si$_3$N$_4$-AlN-Al$_2$O$_3$-SiO$_2$ system showing liquidus isotherms (1650° - 1800° C) between the SiO$_2$ corner and X-phase (ref. 9).

Figure 4. - Isothermal section of the system Si$_3$N$_4$-SiO$_2$-BeO-Be$_3$N$_2$ at 1780° C (ref. 12).
Figure 5. Phase diagram of the quaternary system Si₃N₄ - Al₂O₃ - BeON - Be₂O₃ at 1700°C (ref. [13]).
Figure 6. - The systems Si-Al-Be-N at 1780°C (ref. 13).

Figure 7. - Density of sintered β' - SiAlON for 1 hour at different temperatures (ref. 31).
Figure 8. Comparison of strength behavior of $\beta'$ SiAlON and $\text{Si}_3\text{N}_4$ materials.
Figure 9. - Fracture surface (1380°C) of sintered B'-SIAION (Si₂₄Al₀·₈₀N₀·₆₂₃) bend bar. V-shaped area indicates slow crack growth (ref. 31).

Figure 10. - Creep of various ceramic materials. 1227°C, 77 MN/m².
(After Arrol⁷).

* Composition not defined.
Figure 11. - Comparison of creep (4-pt. bend) behavior of Si$_3$N$_4$, SiC, and SIAION (ref. 33).

*Composition not defined.

Figure 12. - Variation of fracture toughness with temperature for hot-pressed and sintered SIAIONs (ref. 33).

Figure 13. - Weight gain in air at 1400°C (2550°F) of various SIAION compositions (Si$_{3-x}$Al$_2$O$_3$N$_{4-x}$) after Layden (ref. 29) and Ashbrook (ref. 39).
Figure 14. - Parabolic plots of the oxidation of various Si$_3$N$_4$ ceramics at 1370° to 1400° C.
Figure 15. - Linear coefficient of thermal expansion between 25° and 1000° C for β'-
$\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}\text{SiAlON}$ (after Gauckler, ref. 18).