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STATE-OF-THE-ART OF SIALON MATERIALS

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STATE-OF-THE-ART OF SIAION MATERIALS

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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 oxyxynitrides 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, synthesis, fabrication, 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. β-SiAlON (ref. 1,2,3), Ω-SiAlON (ref. 4), 15R-SiAlON (ref. 5) etc. However, most frequently, the term SiAlON refers to β-Si3N4 solid solution called β-SiAlON. SiAlON compounds can be made by a high temperature reaction between silicon nitride or oxyxynitride 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 SiAlION materials, β-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 β-SiAlON could be fabricated to high density by conventional sintering techniques (ref. 2). These reported properties indicate that β-SiAlON ceramics might be candidates for high temperature applications, and therefore, have generated considerable interest. 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 turbine engines will be examined.

PHASE EQUILIBRIA AND STRUCTURE

The existence of β-SiAlON in the system Si3N4 - Al2O3 was first reported by Oyama and Nemigaito (ref. 1) in Japan and by Jack and Wilson (ref. 2) in England. Subsequent studies by the same workers reported a solid solution (β-SiAlON) forming region in the systems Si3N4 - SiO2 - Al2O3 (ref. 5) 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 1500 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 β-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 3:4 and can therefore, be described by the empirical formula Si6-x Alx Oy N3-x with x=0 to 4.2. In the oxygen rich part of the diagram, mullite and X-phase SiAlON (formula SiAlO2O2(N2)2) were observed. In the AlN-rich part of the system, five new phases were identified (ref. 8) in the region between β-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 and the SiAlON ceramic which extends along the 3M/4X line but the size of the tetrahedra and hence also the unit cell dimensions, increase as aluminum and oxygen replace silicon and nitrogen (ref. 8). Silicon oxyxynitride O*-SiAlON
(ref. 4) extends along the 2M/3X (metal/non-metal) line with the $\text{Si}_3\text{N}_4\text{O}$-type structure and larger unit-cell dimensions. The structure of $X$-phase, also designated as "Oyama-Phase" (ref. 4) and "J-phase" (ref. 4) has been interpreted in terms of several different unit cells (ref. 10) proposed a triclinic structure, while Gugel (ref. 11) proposed an orthorhombic lattice. Most recently, the unit cell has been determined to be monoclinic (ref. 4).

Single phase $\epsilon^\prime$-$\text{SiAlON}$ forming regions in other systems such as $\text{Si}_3\text{N}_4$ - $\text{Al}_2\text{O}_3$ - $\text{Be}_2\text{Si}_2\text{O}_5$, $\text{Si}_3\text{N}_4$ - $\text{Al}_2\text{O}_3$ - $\text{Li}_2\text{O}$ and $\text{Si}_3\text{N}_4$ - $\text{Al}_2\text{O}_3$ - $\text{MgO}$ were reported by Jack (ref. 5), while Oyama (ref. 6) reported a $\epsilon^\prime$-$\text{SiAlON}$ forming region in the system $\text{Si}_3\text{N}_4$ - $\text{Al}_2\text{O}_3$ - $\text{Ga}_2\text{O}_3$. Extensive ternary solid solutions were found to exist in all of these systems. Detailed phase equilibria in the system $\text{Si}_3\text{N}_4$ - $\text{Si}_2\text{O}_3$ - $\text{Be}_2\text{N}_2$ - $\text{BeO}$ were reported by Huseby et. al (ref. 12) and are shown in Fig. 4. A large solubility of $\text{Be}_2\text{SiO}_4$ in $\epsilon^\prime$-$\text{SiAlON}$ and of $\text{BeO}$ in $\text{BeSiN}_2$ was found to occur in this system. The solid solubility of $\text{Be}_2\text{SiO}_4$ in $\epsilon^\prime$-$\text{SiAlON}$ decreases with increasing temperature from 19 mol% at 1770 C to 11.5 mol% $\text{Be}_2\text{SiO}_4$ at 1880 C. There are other single-phase materials in this system and all have moderate solubilities along lines of definite metal/non-metal (M/X) ratios and small solubilities perpendicular to these lines.

In the system $\text{Si}_3\text{N}_4$ - $\text{Si}_2\text{O}_3$ - $\text{AlN}$ - $\text{Al}_2\text{O}_3$ - $\text{Be}_2\text{N}_2$ - $\text{BeO}$, Gauckler (ref. 11) found that the single-phase solid solution with $\epsilon^\prime$-$\text{SiAlON}$ structure was restricted to the plane connecting the points $\text{Si}_3\text{N}_4$, $\text{Be}_2\text{SiO}_4$, $\text{BeAl}_2\text{O}_4$ and $\text{AlNAl}_2\text{O}_3$. This is shown in Fig. 5a. These four points are co-planar in the quaternary diagram. All composition points on this plane have a constant metal to non-metal ratio of 3:4. The plane of 3:4 is shown in Fig. 5b. A large area of single phase region with the $\epsilon^\prime$-$\text{SiAlON}$ structure is located on this plane. No single-phase solid solution was found either above or below this plane.

In the quaternary system $\text{Si}_3\text{N}_4$ - $\text{AlN}$ - $\text{Be}_2\text{N}_2$ shown in Fig. 6, Gauckler et. al (ref. 13) found a complete solid solubility exists from AlN to $\text{BeSiN}_2$. The lattice parameters in this solid solution with a wurtzite structure increase linearly with increasing Al concentration.

**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 $\text{Si}_3\text{N}_4$ and $\text{SiC}$. Consequently, most early work on phase equilibria, structure, and property evaluation was conducted on $\epsilon^\prime$-$\text{SiAlON}$s fabricated by hot pressing. Table I lists starting materials for various $\epsilon^\prime$-$\text{SiAlON}$ 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. $\text{MgO}$ 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 $\text{SiC}$. 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 $\epsilon^\prime$-$\text{SiAlON}$s. 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 1710-1760 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 $\text{Si}_3\text{N}_4$ and $\text{Al}_2\text{O}_3$ mixture could be fabricated to dense single phase $\epsilon^\prime$-$\text{SiAlON}$ bodies by pressureless sintering. However, other work (ref. 11) indicated that the resulting $\text{SiAlON}$ contained other phases. Morgan (ref. 24) predicted in a presentation cited by Layden (ref. 9) that single phase $\epsilon^\prime$-$\text{SiAlON}$ com-positions having stoichiometries given by the formula $\text{Si}_3\text{Al}_x\text{ON}_4$ would not sinter. Layden (ref. 9) also reported that as a pure phase $\epsilon^\prime$-$\text{SiAlON}$ could not be sintered to high final density. However, $\epsilon^\prime$ bodies formulated from starting materials that form some liquid at the sintering temperatures could be sintered to high density. For example, Layden introduced the term "transient liquid phase sintering" or TLP. In
this process, SiAlON bodies of composition Si1.4Al1.6O1.62 were formulated from two prereacted compositions, one of which was X phase which melts in the neighborhood of 1700 °C. The second composition was calculated from the lever rule to yield single phase β'-SiAlON when reacted with a predetermined amount of the X-phase at temperature above 1700 °C. The "transient liquid phase sintering" was confirmed by Cauckler et al. in sintering of β'-SiAlON compositions utilizing as starting materials only AlN and SiO2 and no additives. Cauckler et al. concluded that different sintering kinetics would be expected for different sets of starting materials e.g. Si3N4, AlN, Al2O3 powders or Si3N4, AlN, Al2O3 powders or Si3N4, AlN, Al2O3. The formation of liquid facilitates densification and chemical reaction. Drew and Lewis (ref. 10) also observed the formation of liquid phase during sintering of Si3N4 and Al2O3 mixtures.

Recently, Arias (ref. 26) determined the effect of oxygen to nitrogen ratio (O/N) on the pressureless sinterability of SiAlONs of formula Si1.53Al0.6CNY0.66Y (where Y varied from 0.57 to 1.92). Utilizing starting materials Si3N4, AlN, and SiO2 plus a small amount of Al2O3 from the grinding media but no additives, a maximum density of about 98% of theoretical occurred in the O/N ratio range between 0.2 and 0.3. It is very likely, that liquid formed in various phase fields according to the behavior diagram shown in Fig. 2 and promoted densification in all compositions as Y varied from 0.57 to 1.92.

In contrast to sintering by forming liquid within the system itself, additives which provide a liquid phase at the sintering temperatures are commonly used for densifying Si3N4 based ceramics. For example, Fig. 7 shows typical densification behavior of β'-SiAlON (Si1.4Al1.6O1.62) as a function of temperature (ref. 31). The starting materials used were Si3N4, AlN, and Al2O3 with 6 and 3 mol of additives (Y2O3-SiO2). The Y2O3 to SiO2 molar ratio was constant at 1.2. Sintering was promoted by a liquid formed by an initial reaction between Y2O3, SiO2, and Al2O3. In any case whether a liquid formed by the foreign additives or during sintering of bodies formulated with major constituents such that some liquid is formed at the sintering temperature, a grain boundary glassy phase is retained in the sintered body. It will be seen later that this glassy phase has a controlling influence on the high temperature properties of the sintered body (ref. 9).

**DENSITY AND MICROSTRUCTURE**

β'-SiAlON compositions have been fabricated to essentially theoretical density by hot pressing, while pressureless sintering has resulted in maximum densities close to 98% of theoretical, (ref. 30, 31). The density values of hot pressed β'-SiAlONs have ranged from 3.05 to 3.15 g/cc (ref. 17) depending on the location along the β'-homogeneity line (Fig. 2). The density of other phases has been found to be 3.05 g/cc for X-phase (ref. 18) and 3.08 g/cc for 15R polytype phase (ref. 18).

In general, the microstructures of both hot pressed and sintered materials consisted of β'-SiAlON as the predominant phase with some isolated porosity and metallic looking phase in a uniform β' matrix. In some cases isolated grains of X-phase and 15R polytype phases were also identified (ref. 19). Typical grain sizes of the hot pressed compositions were found to vary between 0.2 - 2 µm (ref. 19) while the grain size range 0.15 - 5.0 µm was observed in pressureless sintered compositions (ref. 31). The grain morphology in both sintered and hot pressed materials was characteristic of the presence of a liquid phase during densification. This liquid phase was retained in inter-crystalline spaces during cooling from the hot pressing (ref. 19) or sintering temperature (ref. 31) and formed a glassy phase at the grain boundaries.

**PROPERTIES**

Most of the mechanical properties reported in the literature are for β'-SiAlON in the system Si1.4Al1.6O1.62, while other systems e.g. Si3N4, AlN, O2, Si, Al, Be/N, O etc., have been examined primarily with respect to solid solubility, phase relationships, and structure. Because of their similar structures, the physical and mechanical properties of β'-SiAlON and β'-Si3N4 are also similar. In this review, the properties of various β'-SiAlON compositions in the system Si-Al-O-N are discussed.

**Modulus of Rupture**

Aaral (ref. 7) reported the room temperature modulus of rupture (3-point MOR) of hot pressed β'-SiAlON to be as high as 635 MPa. He also reported the strength of sintered β'-SiAlON compositions or formulae of SiAlON were defined. Other workers have reported the MOR of hot pressed and sintered β'-SiAlONs where the compositions or formulations are defined to varying degrees. These are summarized in Table III. In Table III, average values at room temperature and at 1370 °C are given for various β'-SiAlONs made from different starting materials. The highest room temperature strength of hot pressed β'-SiAlON bodies was found to be 648 MPa (ref. 17), while the highest strength obtained in pressureless sintered bodies was 483 MPa (ref. 31). The highest room temperature value was 580 MPa (ref. 29). Only one value 240 MPa (ref. 18) MPa is listed for a hot pressed β'-SiAlON at 1370 C.
Where data are available over a range of temperatures, the strength of sintered B'-SiAlON is compared with the strength of silicon nitride commercially produced in USA. This is shown in Fig. 8. As can be seen, the room temperature strength of sintered B'-SiAlON compares favorably with room temperature strength of sintered Si3N4. On the other hand, the room temperature strengths of sintered B'-SiAlON are considerably lower than the room temperature strength of hot pressed Si3N4 (NC-132).

At high temperature (1370°C), the strength of sintered B'-SiAlON is equivalent to or higher than the strength of sintered Si3N4 but lower than the strength of hot pressed 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 temperature. The grain boundary phase softens at high temperatures thus leading to slow crack growth and subsequent loss in strength. Fig. 9 shows an example of such typical slow crack growth failure (V-shaped area) in the fracture surfaces of a 1380°C MOR bar of B'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 temperature is desirable.

Creep

Limited creep data are available on B'-SiAlONs as compared with modulus of rupture data. Arol (ref. 7) determined the creep behavior of several hot pressed SiAlONs, and compared the data with hot pressed Si3N4 (HS-130) and SiC. Layden also determined that the creep rate of the Y2O3 containing B'-SiAlON 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 hot pressed Si3N4 (HS-130) at the same temperature. Layden observed that creep behavior was controlled by the properties of the grain boundary phases. For example, B'SiAlON compositions containing 2O2 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, SiAlON showed 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 compositions 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/m²/² as compared with 6 MN/m²/² 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. 2) determined high fracture toughness value (6.0 MN/m²/²) 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 temperature for both hot pressed and sintered SiAlONs which is shown in Fig. 12. Lumby suggested that the fracture toughness at higher temperatures was associated with the viscous deformation of the grain boundary phase. The variation of 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 technique.

Oxidation

Oxidation resistance is one of the key properties that must be satisfied by a material in order to be candidate for high temperature applications. Jack (ref. 2) and Arol (ref. 7) reported that the oxidation resistance of B'-SiAlONs is better than that of hot pressed Si3N4 (HS-130). Layden (ref. 9) later confirmed this in his evaluation of the oxidation behavior of TLP sintered SiAlON compositions. He observed that the oxidation rate of TLP Si1.4Al1.6O1.8 was about an order of magnitude less than that of (HS-130) hot pressed Si3N4 at 1400°C (ref. 38). Layden (ref. 29) also made an ex-
tentative study on the oxidation behavior of $\beta'$-SiAlON compositions pressureless sintered with various additives such as CeO$_2$, Y$_2$O$_3$, $ZrO_2$, Y$_2$O$_3$ - $ZrO_2$. These are shown in parabolic plots in Fig. 14. (ref. 22, 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 Si$_3$N$_4$ (HS-130). Similarly, Dutta (ref. 31) and Arias (ref. 30) reported a higher oxidation resistance in $\beta'$-SiAlONs doped with $Y_2O_3$-Si$_3$N$_4$ and $ZrO_2$ respectively, as compared with HS-130. Very recently, Arias (ref. 9) determined the oxidation resistance of SiAlON-C ($S_14.99A10.01N6$) to be even higher than that of TLP and $ZrO_2$ doped SiAlONs. This is shown in Fig. 14. The oxidation behavior of several SiAlONs is compared with that 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 Si$_3$N$_4$ 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 $2.5 \times 10^{-6} g^{2}/cm^4 h^{-1}$ as compared with $2.67 \times 10^{-6} g^{2}/cm^4 h^{-1}$ for hot pressed Si$_3$N$_4$ and $1.96 \times 10^{-8} g^{2}/cm^4 h^{-1}$ for TLP SiAlON, indicating that SiAlON compositions can be produced with excellent oxidation resistance as compared with this hot pressed Si$_3$N$_4$. However, these sintered SiAlONs such as SiAlONs and TLP SiAlON have poor room temperature strength as compared with hot pressed Si$_3$N$_4$. 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 ($S14.99A10.01N6$) to be $2.7 \times 10^{-6} C^{-1}$ which was less than that of $\beta$-Si$_3$N$_4$ ($3.5 \times 10^{-6} C^{-1}$). On the other hand, Gauckler et. al (ref. 18) reported an average value of $3.4 \times 10^{-6} C^{-1}$ which was in good agreement with the value for pure $\beta$-Si$_3$N$_4$. Gauckler observed an almost linear decrease of the thermal expansion coefficient with increasing Al concentration for the $S14.00A10.00N6$-$x$ 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 $S14.99A10.01N6.94$ and $S14.99A10.01N6.89$ ($3.3 \times 10^{-6} C^{-1}$) but the third composition $S14.99A10.01N6.82$-$x$ showed greater expansion ($3.3 \times 10^{-6} C^{-1}$) because of $X$-phase (ref. 37). Collectively, the data clearly indicated that the thermal expansion coefficients of $\beta'$-SiAlON compositions and of $\beta$-Si$_3$N$_4$ are quite similar.

**Thermal Shock**

Water quench thermal shock resistance ($\Delta T_{cr}$) of several SiAlONs determined by various investigators are listed in Table V along with data for other silicon based ceramics for comparison. The collective $\Delta T_{cr}$ values for $\beta'$-SiAlONs are comparable to those of sintered 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 low 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 investigators have been working on the 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 strengths 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 (HC-132). 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 elevated temperatures. 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 Si$_3$N$_4$ or highly stressed in the low temperature region of the hot pressed Si$_3$N$_4$. 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.
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

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## Table I. Fabrication of Sialons by Hot Pressing

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<td>1765-1800</td>
<td>60-120</td>
<td>28</td>
<td>Structure</td>
<td>11</td>
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<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>MgO</td>
<td>1650-1850</td>
<td>6-60</td>
<td>25</td>
<td>Phase equilibria</td>
<td>12</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si, Al, MgO</td>
<td>1500-2000</td>
<td>1-1440</td>
<td>28</td>
<td>Sintering, grain growth</td>
<td>14</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>MgO</td>
<td>1750</td>
<td>60-240</td>
<td>25</td>
<td>and phase equilibria</td>
<td>15</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si, Al, MgO</td>
<td>1700</td>
<td>60</td>
<td>20</td>
<td>Fabrication, modulus of</td>
<td>16</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃, SiO₂</td>
<td>MgO</td>
<td>1760</td>
<td>(a)</td>
<td>(a)</td>
<td>rupture and thermal</td>
<td></td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃, SiO₂</td>
<td>MgO</td>
<td>1800</td>
<td>60</td>
<td>15</td>
<td>properties</td>
<td></td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>(a)</td>
<td>1500-1700</td>
<td>120</td>
<td>5.5-27.5</td>
<td>Phase equilibria</td>
<td>17</td>
</tr>
<tr>
<td>Si₃N₄, AIN, Al₂O₃</td>
<td>(a)</td>
<td>1600-1800</td>
<td>5-60</td>
<td>3.5-22</td>
<td>Mechanical and thermal</td>
<td>18</td>
</tr>
<tr>
<td>Si₃N₄, AIN, Al₂O₃</td>
<td>MgO</td>
<td>1700-1870</td>
<td>30-120</td>
<td>13.8-34.5</td>
<td>Properties</td>
<td>19</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>(a)</td>
<td>1200-1700</td>
<td>120</td>
<td>27.6</td>
<td>Electrical resistivity</td>
<td>20</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>and compatibility with</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W and Mo</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Not pressing and</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>microstructure</td>
<td>23</td>
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*Not reported.*
<table>
<thead>
<tr>
<th>Starting materials</th>
<th>Additives</th>
<th>Temperature, °C</th>
<th>Time, min</th>
<th>Nature of investigation</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td></td>
<td>1700</td>
<td>60</td>
<td>Fabrication (slip casting) and sintering</td>
<td>2</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td></td>
<td>1600-1850</td>
<td>15-720</td>
<td>Fabrication, modulus of rupture, creep, impact oxidation</td>
<td>9</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td></td>
<td>1600-1800</td>
<td>60</td>
<td>Microstructure analysis</td>
<td>10</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>(a)</td>
<td>1600-2000</td>
<td>0-180</td>
<td>Liquid phase sintering</td>
<td>11</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td></td>
<td>1670-1830</td>
<td>240</td>
<td>Effect of oxygen to nitrogen ratio on densification</td>
<td>25</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃, AIN</td>
<td></td>
<td>1775-1800</td>
<td>60</td>
<td>Fabrication and modulus of rupture</td>
<td>26</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃, AIN</td>
<td></td>
<td>1740</td>
<td>60</td>
<td>Fabrication and modulus of rupture</td>
<td>27</td>
</tr>
<tr>
<td>β'-SiAlON</td>
<td>CeO₂, Y₂O₃, ZrO₂, Al₂O₃, GapO₆, ZrC, La₂O₃, Er₂O₃, Nd₂O₃, (Sm,Gd)O₃</td>
<td>1700-1800</td>
<td>60-180</td>
<td>Fabrication, modulus of rupture, creep and oxidation</td>
<td>28</td>
</tr>
<tr>
<td>Si₃N₄, SiO₂, AIN</td>
<td>Y₂O₃</td>
<td>1760</td>
<td>240</td>
<td>Fabrication, modulus of rupture and oxidation</td>
<td>29</td>
</tr>
<tr>
<td>Si₃N₄, AIN, Al₂O₃</td>
<td>Y₂O₃-SiO₂</td>
<td>1650-1750</td>
<td>60-120</td>
<td>Fabrication, modulus of rupture and oxidation</td>
<td>30</td>
</tr>
<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>31</td>
</tr>
</tbody>
</table>

*Not reported.*
### TABLE III. - MODULUS OF RUPTURE OF HOT-PRESSED AND SINTERED SIALONS

<table>
<thead>
<tr>
<th>Starting materials&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Basic formula</th>
<th>Fabrication method</th>
<th>Average 4-point modulus of rupture, MPa&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₃Al₁.26O₁.₂₄N₄</td>
<td>Hot-pressed</td>
<td>310&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>a</td>
<td></td>
<td>420&lt;sup&gt;a&lt;/sup&gt;</td>
<td>a</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.67Al₀.₃O₀.₄N₃.₅₇</td>
<td></td>
<td>648&lt;sup&gt;a&lt;/sup&gt;</td>
<td>a</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₂₅Al₀.₇₅O₇.₇₅N₃.₂₅</td>
<td></td>
<td>510&lt;sup&gt;a&lt;/sup&gt;</td>
<td>18</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>a</td>
<td></td>
<td>240&lt;sup&gt;a&lt;/sup&gt;</td>
<td>15</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₄Al₂O₆N₆</td>
<td>Sintered</td>
<td>208</td>
<td>9</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₄₅Al₀.₅₅O₅.₅₅N₃.₄₅</td>
<td></td>
<td>352</td>
<td>28</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₇Al₀.₃O₀.₃N₃.₇</td>
<td></td>
<td>460&lt;sup&gt;a&lt;/sup&gt;</td>
<td>29</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₄₅Al₀.₅₅O₅.₅₅N₃.₄₅</td>
<td></td>
<td>400&lt;sup&gt;a&lt;/sup&gt;</td>
<td>a</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₄₅Al₀.₅₅O₅.₅₅N₃.₄₅</td>
<td></td>
<td>430</td>
<td>235</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₄₅Al₀.₃O₂O².₃₅N₃.₄₅</td>
<td></td>
<td>460</td>
<td>175</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₄₅Al₀.₅₂O₂O₂.₃₅N₃.₄₅</td>
<td></td>
<td>483</td>
<td>228</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₅₅Al₀.₆O₂O₆.₇₂N₃.₅₂</td>
<td></td>
<td>404</td>
<td>260</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₅₅Al₀.₆O₂O₆.₇₂N₃.₅₂</td>
<td></td>
<td>410</td>
<td>310</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₅₅Al₀.₆O₂O₆.₇₂N₃.₅₂</td>
<td></td>
<td>404</td>
<td>65</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₅₅Al₀.₆O₂O₆.₇₂N₃.₅₂</td>
<td></td>
<td>305</td>
<td>69</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
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<td></td>
<td>295</td>
<td>95</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₅₅Al₀.₆O₂O₆.₇₂N₃.₅₂</td>
<td></td>
<td>395</td>
<td>135</td>
</tr>
<tr>
<td>Si₃N₄, Al₂O₃</td>
<td>Si₂.₅₅Al₀.₆O₂O₆.₇₂N₃.₅₂</td>
<td></td>
<td>395</td>
<td>135</td>
</tr>
</tbody>
</table>

<sup>a</sup>Not reported.

<sup>b</sup>The additive or sintering aid is enclosed in parentheses.

<sup>c</sup>3-point NQR.
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 ($\sqrt{{\text{m}}/\text{m}^2}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>Hot-pressed</td>
<td>1.2</td>
<td>15</td>
</tr>
<tr>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>Hot-pressed</td>
<td>1.2</td>
<td>15</td>
</tr>
<tr>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>Sintered</td>
<td>6.0</td>
<td>33</td>
</tr>
<tr>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>Sintered</td>
<td>6.0</td>
<td>33</td>
</tr>
<tr>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>Sintered</td>
<td>2.2-2.7</td>
<td>37</td>
</tr>
<tr>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>Sintered</td>
<td>1.32</td>
<td>37</td>
</tr>
</tbody>
</table>

*Not reported.*

TABLE V. - VAPOR QUENCH THERMAL SHOCK RESISTANCES ($\gamma T_s$) OF SIALON, $\text{Si}_3\text{N}_4$, and $\text{SiC}$ CERAMICS

<table>
<thead>
<tr>
<th>Material</th>
<th>Basic formula</th>
<th>$\gamma T_s$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot-pressed SIALON</td>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>325</td>
<td>18</td>
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<tr>
<td>Sintered SIALON</td>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>340-440</td>
<td>31</td>
</tr>
<tr>
<td>Sintered SIALON</td>
<td>$\text{Si}_2\text{Al}<em>6\text{O}</em>{12}$</td>
<td>510</td>
<td>33</td>
</tr>
<tr>
<td>Reaction sintered $\text{SiC}$</td>
<td>$\text{SiC}$</td>
<td>305</td>
<td>40</td>
</tr>
<tr>
<td>Hot pressed $\text{SiC}$</td>
<td>$\text{SiC}$</td>
<td>615</td>
<td>40</td>
</tr>
<tr>
<td>Reaction sintered $\text{Si}_3\text{N}_4$</td>
<td>$\text{Si}_3\text{N}_4$</td>
<td>610</td>
<td>40</td>
</tr>
<tr>
<td>Hot pressed $\text{Si}_3\text{N}_4$</td>
<td>$\text{Si}_3\text{N}_4$</td>
<td>750</td>
<td>18</td>
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</tbody>
</table>

*Not reported.*
Figure 1. - Isothermal section Si₃N₄ - AlN - Al₂O₃ - SiO₂ 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 Si₃N₄·AlN·Al₂O₃·SiO₂ system showing liquidus isotherms (1650° - 1800° C) between the SiO₂ corner and X-phase (ref. 9).

Figure 4. - Isothermal section of the system Si₃N₄·SiO₂·BeO·Be₃N₂ at 1780° C (ref. 12).
Figure 5. Phase diagram of the quaternary system $\text{Si}_3\text{N}_4 - \text{Al}_2\text{O}_3 - \text{Be}_3\text{O}_2 - \text{Be}_4\text{N}_2$ at 1700°C (ref. 131).
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).

<table>
<thead>
<tr>
<th>COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (6 mol % Y2O3-SiO2)</td>
</tr>
<tr>
<td>B (3 mol % Y2O3-SiO2)</td>
</tr>
</tbody>
</table>

- O single phase sample
- ■ two phase sample
- ■ three phase sample
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 β'-SIAION (Si_2.4A_1.8O_0.6N_2.6) bend bar. V-shaped area indicates slow crack growth (ref. 31).

Figure 10. - Creep of various ceramic materials. 1227°C, 77 MN/m².
(After Arrol^7).

*Composition not defined.
Figure 11. - Comparison of creep (4-pt. bend) behavior of Si₃N₄, 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 (Si₃₋ₓAlₓOₓN₄ₓ₋ₙ) 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°C and 1000°C for β'- Si₆₋ₓAlₓOₓNₓB₋ₓSiAlON (after Gauckler, ref. 18).