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SUMMARY

Concurrent with the recent engineering efforts in developing advanced ceramics such as Si_3N_4 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 Si_3N_4 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 Si_3N_4, SiC, and a class of materials called SiAlONs. 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), O'-SiAlON (ref. 4), 15R-SiAlON (ref. 4) etc. However, most frequently, the term SiAlON refers to β-Si_3N_4 solid solution called β'-SiAlON. SiAlON 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, 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. 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 β'-SiAlON in the system Si_3N_4 - Al_2O_3 was first reported by Oyama and Kamigaito (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 Si_3N_4 - SiO_2 - Al_2O_3 (ref. 5) and Si_3N_4 - AlN - Al_2O_3 (ref. 3). Detailed compatibility and phase equilibria studies were reported by Gauckler et. al (ref. 8) and Jack (ref. 4) in the system Si_3N_4 - AlN - SiO_2 - Al_2O_3 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 β'-SiAlON region extends from the Si_3N_4 corner in the direction of $AlN.Al_2O_3$ along a line representing a constant metal/non-metal (M/X) ratio of 3:4 and can therefore, be described by the empirical formula $Si_{6-x}\ Al_x\ O_x\ N_{8-x}$ with x=0 to 4.2. In the oxygen rich part of the diagram, mullite and X-phase SiAlON (formula $Si_4Al_4O_{11}N_2$) 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 SiO_2-rich corner of the diagram and X-phase.

β'-SiAlON has a β-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 O'-SiAlON

(ref. 4) extends along the 2M/3X (metal/non-metal) line with the Si_2N_2O-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. Drew and Lewis (ref. 10) proposed a triclinic structure, while Gugel (ref. 11) proposed and orthorhombic lattice. Most recently, the unit cell has been determined to be monoclinic (ref.4).

Single phase β'-SiAlON forming regions in other systems such as Si_3N_4 - Al_2O_3 - Be_2SiO_4, Si_3N_4 -Al_2O_3 - Li_2O and Si_3N_4 - Al_2O_3 - MgO were reported by Jack (ref. 5), while Oyama (ref. 6) reported a β'-forming region in the system Si_3N_4 - Al_2O_3 - Ga_2O_3. Extensive ternary solid solutions were found to exist in all of these systems. Detailed phase equilibria in the system Si_3N_4 - SiO_2 - Be_3N_2 - BeO were reported by Huseby et. al (ref. 12) and are shown in Fig. 4. A large solubility of Be_2SiO_4 in β-Si_3N_4 and of BeO in $BeSiN_2$ was found to occur in this system. The solid solubility of Be_2SiO_4 in β-Si_3N_4 decreases with increasing temperature from 19 mol% at 1770 C to 11.5 mol% Be_2SiO_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 Si_3N_4 - SiO_2 - AlN - Al_2O_3 - Be_3N_2 - BeO, Gauckler (ref. 13) found that the single-phase solid solution with β-Si_3N_4 structure was restricted to the plane connecting the points Si_3N_4,Be_2SiO_4, $BeAl_2O_4$ and AlN:Al_2O_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 β-Si_3N_4 structure is located on this plane. No single-phase solid solution was found either above or below this plane.

In the quasiternary system Si_3N_4 - AlN - Be_3N_2 shown in Fig. 6, Gauckler et. al (ref. 13) found a complete solid solubility exists from AlN to $BeSiN_2$. 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 Si_3N_4 and SiC. Consequently, most early work on phase equilibria, structure, and property evaluation was conducted on β'SiAlONs fabricated by hot pressing. Table I lists starting materials for various β'-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 approximately 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 β'-SiAlONs. Characterization of the hot pressed materials has included phase equilibria, structure, and chemistry which have been discussed in the preceeding 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_3N_4 and Al_2O_3 mixture could be fabricated to dense single phase β'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 β'-SiAlON compositions having stoichiometries given by the formula $Si_{3-x}Al_xO_xN_{4-x}$ would not sinter. Layden (ref. 9) also reported that as a pure phase β'SiAlON could not be sintered to high final density. However, β' 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 $Si_{1.4}Al_{1.6}O_{1.6}N_{2.4}$ 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 temperatures above 1700 C. The "transient liquid phase sintering" was confirmed by Gauckler et. al (ref. 25) during sintering of β'-SiAlON compositions utilizing as starting materials only AlN and SiO_2 and no additives. Gauckleret. al concluded that different sintering kinetics would be expected for different sets of starting materials e.g. Si_3N_4, AlN, SiO_2 powders or Si_3N_4, AlN, Al_2O_3 powders or SiO_2 and AlN powders because of different reaction mechanisms (ref. 25). The formation of liquid facilitates densification and chemical reaction. Drew and Lewis (ref. 10) also observed the formation of liquid phase during sintering of Si_3N_4 and Al_2O_3 mixtures.

Recently, Arias (ref. 26) determined the effect of oxygen to nitrogen ratio (O/N) on the pressureless sinterability of SiAlONs of formula $Si_{2.55}Al_{0.6}O_yN_{4-0.667y}$ (where y varied from 0.57 to 1.92). Utilizing starting materials Si_3N_4, AlN, and SiO_2 plus a small amount of Al_2O_3 from the grinding media but no additive, 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 Si_3N_4 based ceramics. For example, Fig. 7 shows typical densification behavior of β'-SiAlON ($Si_{2.4}Al_{0.8}O_{0.6}N_{3.6}$) as a function of temperature (ref. 31). The starting materials used were Si_3N_4, AlN, and Al_2O_3 with 6 and 3 mol% of additives (Y_2O_3-SiO_2). The Y_2O_3 to SiO_2 molar ratio was constant at 1:2. Sintering was promoted by a liquid formed by an initial reaction between Y_2O_3, SiO_2 and Al_2O_3. 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 varied from 3.09 to 3.16 g/cc (ref. 17) depending on the location along the β'-homogeneity line (Fig. 2,3). 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. 10). Typical grain sizes of the hot pressed compositions were found to vary between 0.2 - 2 μm (ref. 10) 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 intercrystalline 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 Si - Al - O - N, while other systems e.g. Si, Be/N, O; 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-Si_3N_4 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

Arrol (ref. 7) reported the room temperature modulus of rupture (3-point MOR) of a hot pressed β'-SiAlON to be as high as 825 MPa. He also reported the strength of sintered β'-SiAlON to be 330 MPa. The compositions or formulations of neither material were defined. Other workers have reported the MOR of hot pressed and sintered β'-SiAlONs where the formulations or compositions 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). At 1370 C, the highest MOR for sintered materials was 375 MPa (ref. 29). Only one value 240 (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 β'-SiAlONs 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 β'-SiAlON compares favorably with room temperature strength of sintered Si_3N_4. On the other hand, the room temperature strengths of sintered β'-SiAlON are considerably lower than the room temperature strength of hot pressed Si_3N_4 (NC-132).

At high temperature (1370 C), the strength of sintered β'-SiAlON is equivalent to or higher than the strength of sintered Si_3N_4 but lower than the strength of hot pressed Si_3N_4 (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 β'SiAlON sintered with 6 mol% (Y_2O_3 - SiO_2) additive. Since the intended use of SiAlON has largely been for high temperature, high performance applications similar to those being attempted with Si_3N_4 and SiC, improvement in strength at high temperature is desirable.

Creep

Limited creep data are available on β'-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 Si_3N_4 (HS-110) and (HS-130), hot pressed SiC and reaction bonded Si_3N_4. These are shown in Fig. 10. 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. 11. The sintered SiAlON has a creep rate lower than that of hot pressed Si_3N_4 (HS-130), reaction bonded Si_3N_4 or Refel SiC but slightly higher than that of hot pressed SiC. Lumby further observed a strong dependence of creep behavior on AlN concentration. Creep after 20 hours at 1227 C and 77 MN/m^2 decreased from 0.275% strain for a β'-SiAlON composition contained 7.75 wt% AlN down to 0.06% 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 sintered SiAlON gave a steady state creep rate of 3.1×10^{-4} hr^{-1} at a stress level of 82 MN/m^2 at 1400 C. This value was below the compressional creep rate of hot pressed Si_3N_4 under these conditions which has been reported (ref. 36) to be 5.4×10^{-4} hr^{-1}. Layden also determined that the creep rate of the Y_2O_3 containing β' SiAlON bodies was about 6×10^{-5} hr^{-1} at 1370 C and a stress level of 69 MN/m^2 which was comparable to that of commercial hot pressed Si_3N_4 (HS-130) at the same stress and temperature. He observed that creep behavior was controlled by the properties of the grain boundary phases. For example, β'SiAlON compositions containing ZrO_2 additives exhibited slow crack growth during testing due to rapid flow of the grain boundary phases at stresses as low as 69 MN/m^2 at 1370 C. On the other hand, β'-SiAlON containing Y_2O_3 exhibited higher refractoriness of the grain boundary phases. Therefore, no slow crack growth occurred during testing to 345 MN/m^2 at 1370 C and the specimens failed by fast fracture .

Fracture Toughness

Fracture toughness (K_{Ic}) values reported in the literature for various SiAlON compositions are listed in Table IV. Generally, the values are lower than those of hot pressed Si_3N_4. For example, Wills et. al (ref. 37) found the fracture toughness values varying between 1.32 and 2.65 $MN/m^{-3/2}$ as compared with 6 $MN/m^{-3/2}$ for (HS-130) hot pressed Si_3N_4. 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) observed a high fracture toughness value (6.0 $MN/m^{-3/2}$) for a pressureless sintered SiAlON similar to (HS-130) hot pressed Si_3N_4 as well as hot pressed SiAlON, measured by the same technique (ref. 33). 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 increase in fracture toughness at higher temperatures was associated with the viscous deformation of the grain boundary phase. The variation in K_{Ic} 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 Arrol (ref. 7) reported that the oxidation resistance of β'-SiAlONs is better than that of hot pressed Si_3N_4 (HS-130). Layden (ref. 9) later confirmed this in his evaluation of oxidation behavior of TLP sintered SiAlON compositions. He observed that the oxidation rate of TLP $Si_{1.4}Al_{1.6}O_{1.6}N_{2.4}$ was an order of magnitude less than that of (HS-130) hot pressed Si_3N_4 at 1400 C (ref. 38). Layden (ref. 29) also made an ex-

tensive study on the oxidation behavior of β'-SiAlON compositions pressureless sintered with various additives such as CeO_2, Y_2O_3, ZrO_2, Y_2O_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 Si_3N_4 (HS-130). Similarly, Dutta (ref. 31) and Arias (ref. 30) reported a higher oxidation resistance in β'-SiAlONs doped with Y_2O_3-SiO_2 and Y_2O_3 respectively, as compared with HS-130. Very recently, Arias (ref. 32) determined the oxidation resistance of SiAlON-C ($Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$) 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 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 Si_3N_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 2.5×10^{-10} g^2/cm^4 hr^{-1} as compared with 2.67×10^{-8} g^2/cm^4 hr^{-1} for hot pressed Si_3N_4 and 1.96×10^{-9} g^2/cm^4 hr^{-1} for TLP SiAlON, indicating that SiAlON compositions can be produced with excellent oxidation resistance as compared with this hot pressed Si_3N_4. However, these sintered SiAlONs such as SiAlON - C and TLP SiAlON have poor room temperature strength as compared with hot pressed Si_3N_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 β'-SiAlON ($Si_3Al_{2.67}O_4N_4$) to be $2.7 \times 10^{-6}C^{-1}$ which was less than that of β-Si_3N_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 β-Si_3N_4. Gauckler observed an almost linear decrease of the thermal expansion coefficient with increasing Al concentration for the $Si_{6-x}Al_xO_xN_{8-x}$ SiAlON which is shown in Fig. 15.

Wills et. al (ref. 37) reported linear thermal expansion of three sintered SiAlON compostions. The expansion of the two compositions $Si_{4.94}Al_{1.06}O_{1.06}N_{6.94}$ and $Si_4Al_2O_2N_6$ was identical (3×10^{-6} C^{-1}) but the third composition β' + X showed greater expansion (3.3×10^{-6} C^{-1}) because of X - phase (ref. 37). However, collective data clearly indicated that the thermal expansion coefficients of β'-SiAlON compostions and of β-Si_3N_4 are quite similar.

Thermal Shock

Water quench thermal shock resistance (ΔT_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 ΔT_C values for β'-SiAlONs are comparable to those of various silicon carbide ceramics 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 β'-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 strengths of sintered β'-SiAlONs are equivalent to or higher than the strengths of sintered silicon nitrides but lower than the strength of hot pressed silicon nitride (NC-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 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 hub. To date hot pressed Si_3N_4 has been the favored material. 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.

*ΔT_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 those 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 Al_2O_3 concentrations. However, to select an optimum composition, a clear understanding of the phase equilibria of the particular system is essential.

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TABLE I. - FABRICATION OF SiAlONs BY HOT PRESSING

Starting materials	Additives	Temperature, C	Time, min	Pressure, MN/m^2	Nature of investigation	Reference
Si_3N_4, Al_2O_3, Li_2CO_3	(a)	1750	20	29	Solid solubility	1
Si_3N_4, Al_2O_3		1700	60	(a)	Formation, structure and thermal expansion	2
Si_3N_4, AlN, Al_2O_3		1730	30	25	Solid solubility	3
Si_3N_4, Ga_2O_3, Al_2O_3		1730-1800	20-180	25	Solid solubility and thermal expansion	5
Si_3N_4, Al_2O_3, AlN, SiO_2		1760	60-300	30	Phase equilibria and comptability relation	7
Si_3N_4, AlN, Al_2O_3, SiO_2, Si_2N_2O		1500-2000	(a)	(a)	Phase equilibria, compatibility and structure	8
Si_3N_4, Al_2O_3		1700	60	15	Microstructure and phase analysis	10
Si_3N_4, Al_2O_3		1700	30	(a)	Phase analysis	11
Si_3N_4, Be_3N_2, BeO, SiO_2		1765-1880	60-120	28	Phase equilibria	12
Si_3N_4, Al_2O_3		1650-1850	6-60	25	Sintering, grain growth and phase equilibria	14
Si_3N_4, Al_2O_3	MgO	1750-1850	30-240	28	Fabrication, modulus of rupture and thermal properties	15
Si_3N_4, Al_2O_3	Si, Al, MgO, AlN, SiO_2, Kaolin	1500-2000	1-1440	28	Processing and properties	16
Si_3N_4, AlN, SiO_2	MgO	1750	60	20	Fabrication, chemistry and creep	17
Si_3N_4, Al_2O_3, AlN, SiO_2	MgO	1760	(a)	(a)	Physical, mechanical and thermal properties	18
Si_3N_4, AlN, SiO_2	MgO	1800	60	15	Formation, microstructure characterization	19
Si_3N_4, Al_2O_3	(a)	1500-1700	120	5.5-27.5	Effects of pressure and temperature on sintering	20
Si_3N_4, AlN, Al_2O_3	(a)	1600-1800	5-60	3.5-22	Modulus of rupture, dielectric properties and rain erosion	21
Si_3N_4, AlN, Al_2O_3	MgO	1700-1870	30-120	13.8-34.5	Electrical resistivity and comptability with W and Mo	22
Si_3N_4, Al_2O_3	(a)	1200-1700	120	27.6	Hot pressing and microstructure characterization	23

[a]Not reported.

E-[illegible]/2

TABLE II. - FABRICATION OF SiAlONs BY PRESSURELESS SINTERING

Starting materials	Additives	Temperature, C	Time, min	Nature of investigation	Reference
Si_3N_4, Al_2O_3	(a)	1700	60	Fabrication (slip casting) and sintering	2
Si_3N_4, Al_2O_3		1600-1850	15-720	Fabrication, modulus of rupture, creep, impact oxidation	9
Si_3N_4, Al_2O_3		1400-1800	60	Microstructure analysis	10
Si_3N_4, Al_2O_3		(a)	(a)	Phase analysis	11
Si_3N_4, AlN, Al_2O_3		1400-2000	0-180	Liquid phase sintering	25
Si_3N_4, AlN, SiO_2		1670-1830	240	Effect of oxygen to nitrogen ratio on densification	26
Si_3N_4, Al_2O_3, AlN		1775-1800	60	Fabrication and modulus of rupture	27
Si_3N_4, AlN, Al_2O_3		1740	60	Fabrication and modulus of rupture	28
β'-SiAlON	CeO_2, Y_2O_3, ZrO_2, $AlPO_4$, $GaPO_4$, ZrC, La_2O_3, Er_2O_3, Nd_2O_3 $(Sm,Gd)O_3$	1700-1800	60-180	Fabrication, modulus of rupture, creep and oxidation	29
Si_3N_4, SiO_2, AlN	Y_2O_3	1760	240	Fabrication, modulus of rupture and oxidation	30
Si_3N_4, AlN, Al_2O_3	Y_2O_3-SiO_2	1450-1750	60-120	Fabrication, modulus of rupture and oxidation	31
Si_3N_4, AlN, Al_2O_3	Y_2O_3, MgO-Y_2O_3, $MgAl_2O_4$	1750	240	Fabrication, modulus of rupture and oxidation	Current work by the author

[a]Not reported.

TABLE III. - MODULUS OF RUPTURE OF HOT-PRESSED AND SINTERED SiAlONS

Starting materials[b]	Basic formula	Fabrication method	Average 4-point modulus of rupture, MPa		Reference
			25° C	1370° C	
Si_3N_4, Al_2O_3	$Si_3Al_{2.67}O_4N_4$	Hot-pressed	310	a	4
Si_3N_4, Al_2O_3	a	↓	420	a	15
Si_3N_4, AlN, Al_2O_3, SiO_2 (MgO)	$Si_{2.67}Al_{0.30}O_{0.43}N_{3.57}$		[c]648	a	17
Si_3N_4, AlN, Al_2O_3	$Si_{2.25}Al_{0.75}O_{0.75}N_{3.25}$	↓	[c]510	[c]240	18
Si_3N_4, Al_2O_3	a	Sintered	250	a	15
Si_3N_4, AlN, SiO_2	$Si_{1.4}Al_{1.6}O_{1.6}N_{2.4}$	↓	208	180	9
Si_3N_4, AlN, Al_2O_3	$Si_4Al_2O_2N_6$		352	135	28
Basic $\beta'(Y_2O_3)$	$Si_{2.45}Al_{0.55}O_{0.55}N_{3.45}$		450	335	29
$\beta'(Y_2O_3)$	$Si_{2.7}Al_{0.3}O_{0.3}N_{3.7}$		460	375	↓
$\beta'(CeO_2)$	$Si_{2.45}Al_{0.55}O_{0.55}N_{3.45}$		400	a	
$\beta'(ZrO_2)$	$Si_{2.45}Al_{0.55}O_{0.55}N_{3.45}$		430	235	↓
Si_3N_4, AlN, SiO_2 (Y_2O_3)	$Si_{2.6}Al_{0.39}O_{0.4}N_{3.6}$		460	175	30
Si_3N_4, AlN, Al_2O_3 (Y_2O_3-SiO_2)	$Si_{2.4}Al_{0.8}O_{0.6}N_{3.6}$		483	228	31
Si_3N_4, AlN, SiO_2	$Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$		404	260	32
Si_3N_4, AlN, SiO_2 (MgO)	a		410	310	33
Si_3N_4, AlN, Al_2O_3 (Y_2O_3)	$Si_{1.8}Al_{1.6}O_{1.5}N_{3.0}$		404	65	Current work by the author
	$Si_{2.07}Al_{1.24}O_{1.2}N_{3.2}$		305	69	↓
	$Si_{2.4}Al_{0.8}O_{0.9}N_{3.4}$		295	95	
	$Si_{2.2}Al_{1.08}O_{1.08}N_{3.28}$	↓	395	135	↓

[a]Not reported.
[b]The additive or sintering aid is enclosed in parentheses.
[c]3-point MOR.

TABLE IV. - FRACTURE TOUGHNESS (K_{Ic}) OF SIALON MATERIALS

Starting materials	Basic formula	Fabrication method	Fracture toughness (25° C) $MN/m^{-3/2}$	Reference
Si_3N_4, Al_2O_3	[a]	Hot-pressed	1-2	15
Si_3N_4, AlN, SiO_2	$Si_{2.25}Al_{0.75}O_{0.75}N_{3.25}$	Hot-pressed	4	18
Si_3N_4, MgO	Si_3N_4 (HS-130)	Hot-pressed	6.0	33
Si_3N_4, AlN, SiO_2 (MgO)	[a]	Sintered	6.0	33
Si_3N_4, AlN, Al_2O_3	$Si_4Al_2O_2N_6$	Sintered	2.2-2.7	37
[a], X	[a]	Sintered	1.32	37

[a]Not reported.

TABLE V. - WATER QUENCH THERMAL SHOCK RESISTANCES (ΔT_c) OF SiAlON, Si_3N_4 and SiC CERAMICS

Material	Basic formula	ΔT_c	Reference
Hot-pressed SiAlON	$Si_{2.25}Al_{0.75}O_{0.75}N_{3.25}$	320	18
Sintered SiAlON	$Si_{2.4}Al_{0.8}O_{0.6}N_{3.6}$	460-480	31
Sintered SiAlON	[a]	510	33
Reaction sintered SiC	SiC	305	40
Hot pressed SiC	SiC	415	40
Reaction sintered Si_3N_4	Si_3N_4	440	40
Hot pressed Si_3N_4	Si_3N_4	750	18

[a]Not reported.

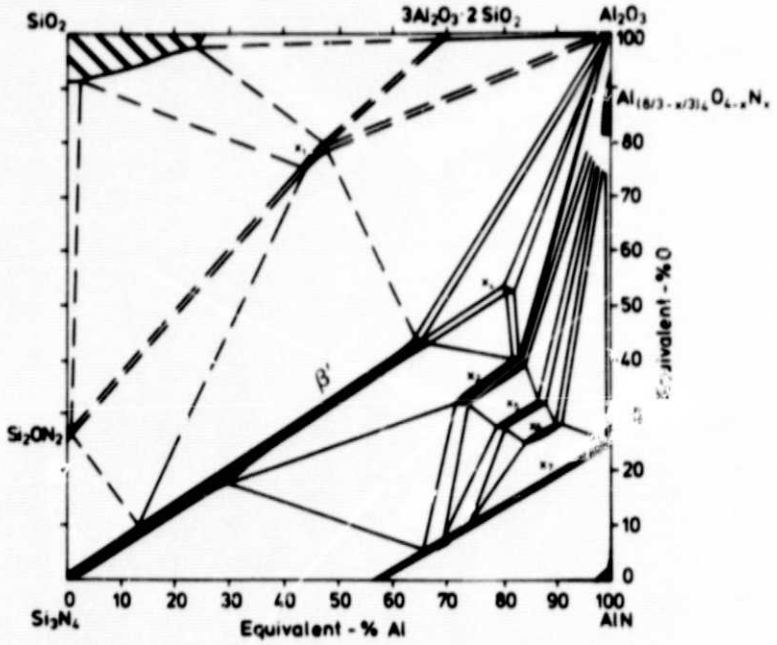


Figure 1. - Isothermal section Si_3N_4 - AlN - Al_2O_3 - SiO_2 of the system Si-Al-O-N at 1760° C (ref. 8).

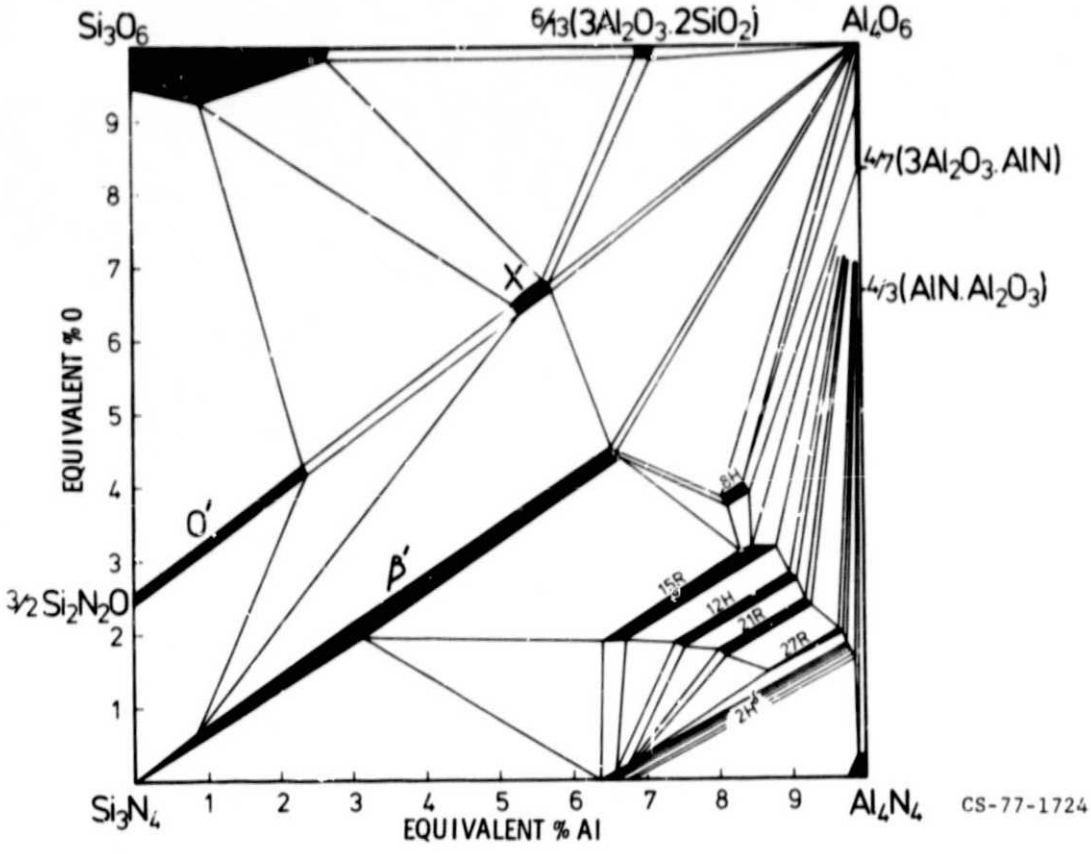


Figure 2. - The Si_3N_4-AlN-Al_2O_3-SiO_2 system (ref. 4).

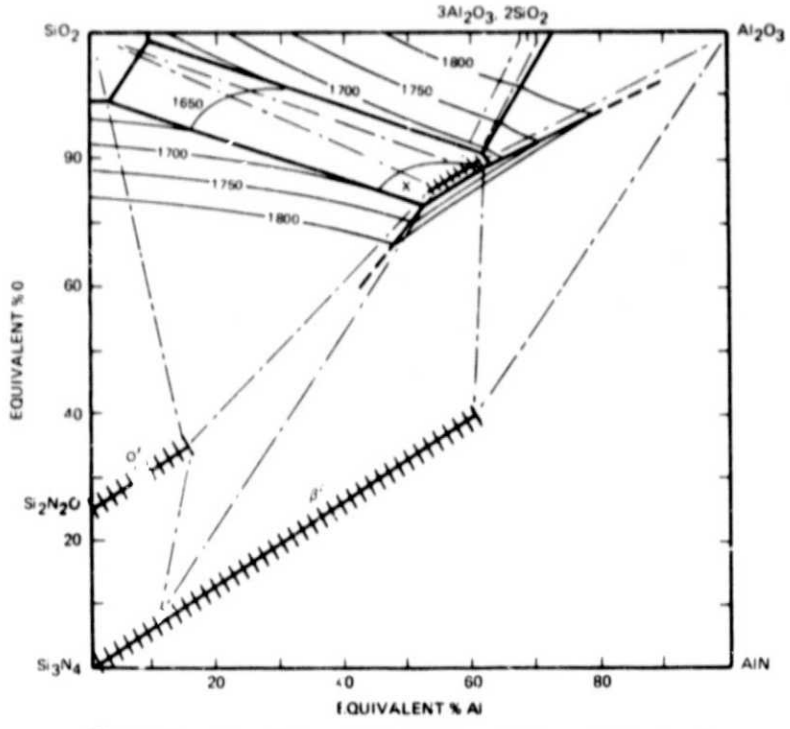


Figure 3. - The Si_3N_4-AlN-Al_2O_3 - SiO_2 system showing liquidus isotherms (1650° - 1800° C) between the SiO_2 corner and X-phase (ref. 9).

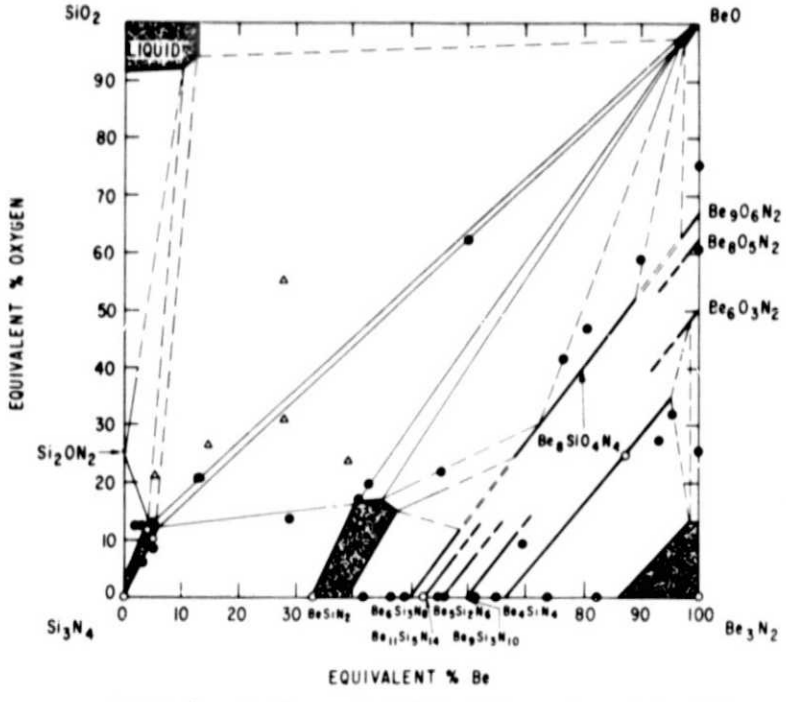


Figure 4. - Isothermal section of the system Si_3N_4-SiO_2-BeO-Be_3N_2 at 1780° C (ref. 12).

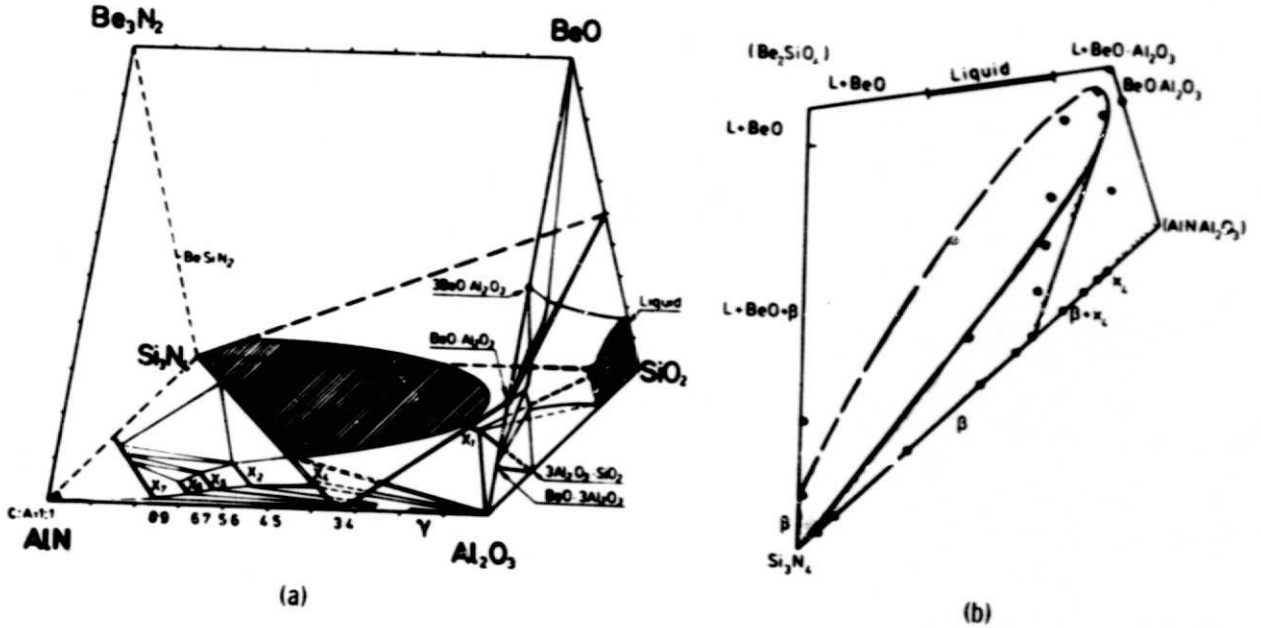


Figure 5. - Phase diagram of the quaternary system Si_3N_4 - AlN - Al_2O_3 - Be_3N_2 - BeO at 1760° C (ref. 13).

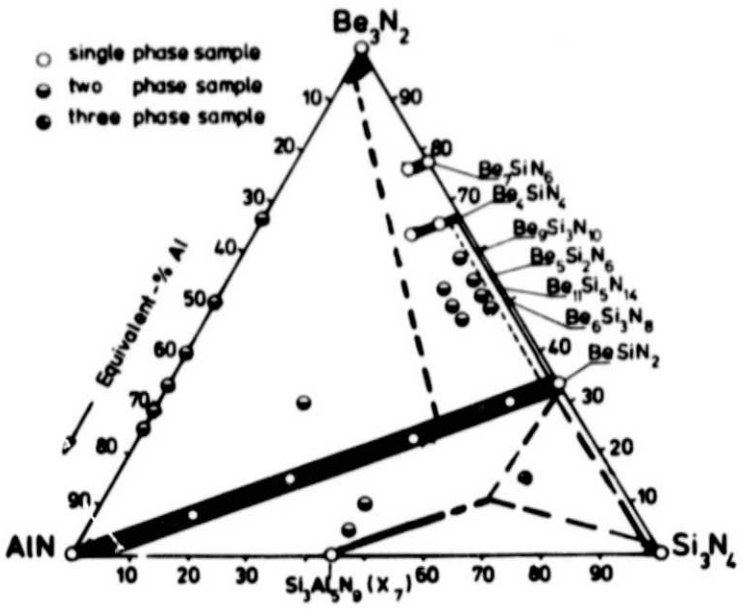


Figure 6. - The systems Si-Al-Be-N at 1780° C (ref. 13).

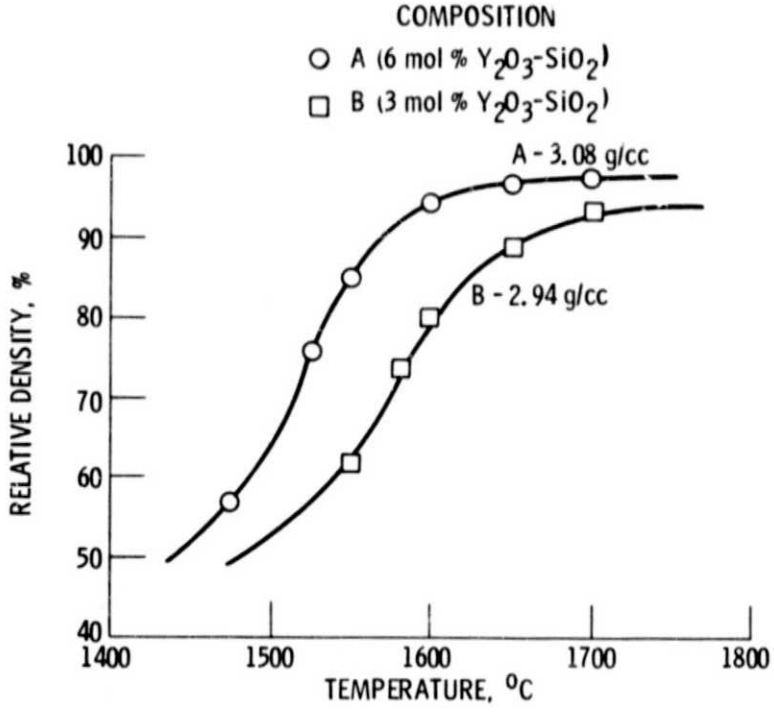


Figure 7. - Density of sintered β' - SiAlON for 1 hour at different temperatures (ref. 31).

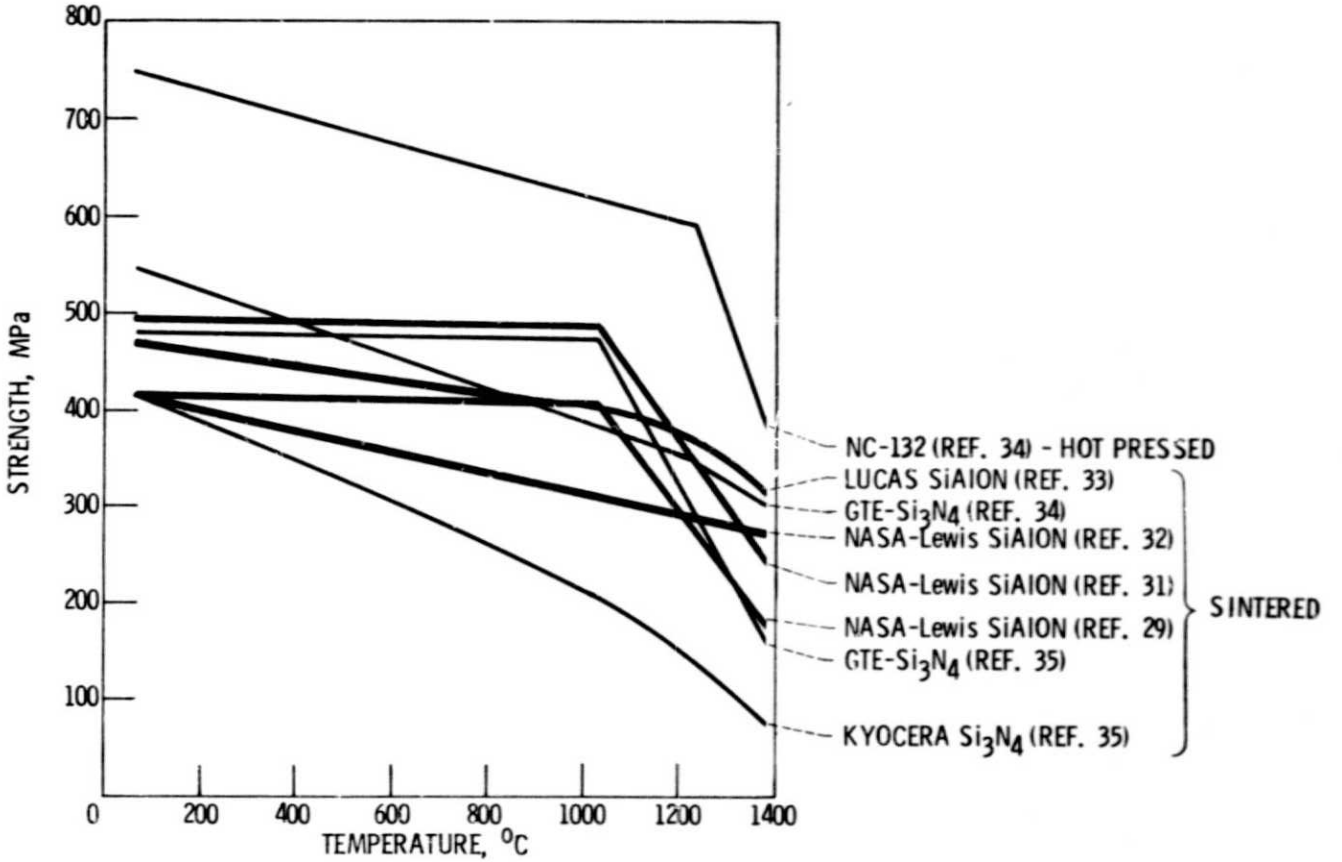
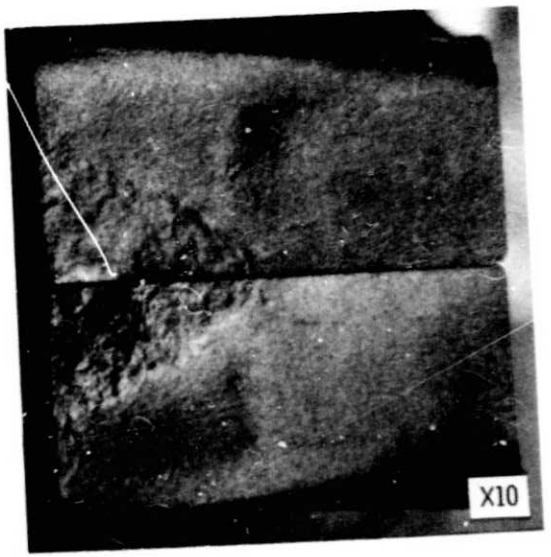


Figure 8. - Comparison of strength behavior of β' SiAlON and Si_3N_4 materials.



A - 6 mol% Y_2O_3-SiO_2

Figure 9. - Fracture surface (1380° C) of sintered β'-SiAlON ($Si_{2.4}Al_{0.8}O_{0.6}N_{3.6}$) bend bar. V-shaped area indicates slow crack growth (ref. 31).

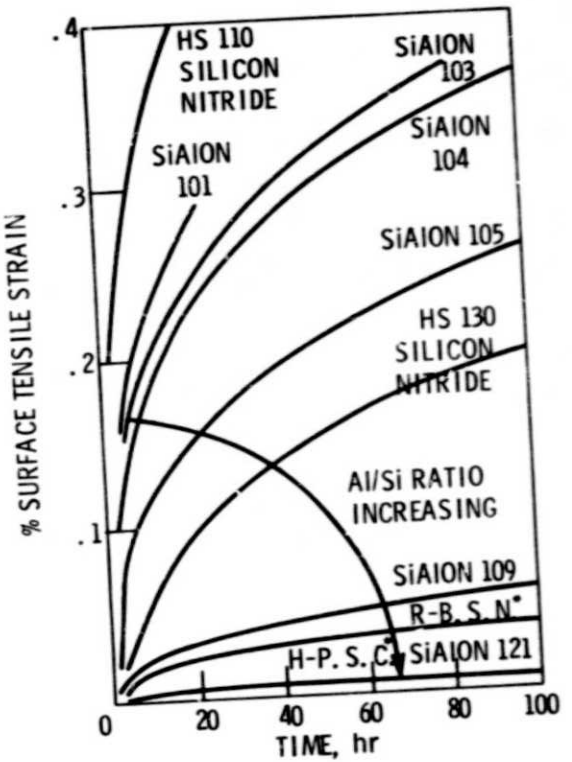


Figure 10. - Creep of various ceramic materials. 1227° C, 77 MN/m^2. (After Arrol[7]).

* Composition not defined.

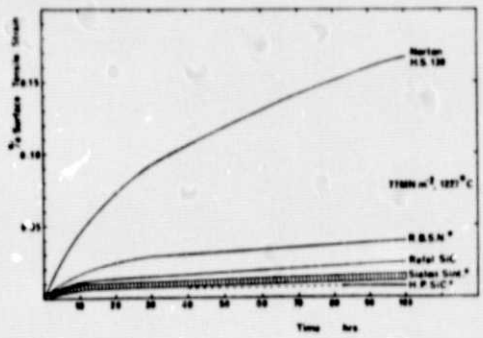


Figure 11. - Comparison of creep (4-pt. bend) behavior of Si_3N_4, SiC, and SiAlON (ref. 33).

*Composition not defined.

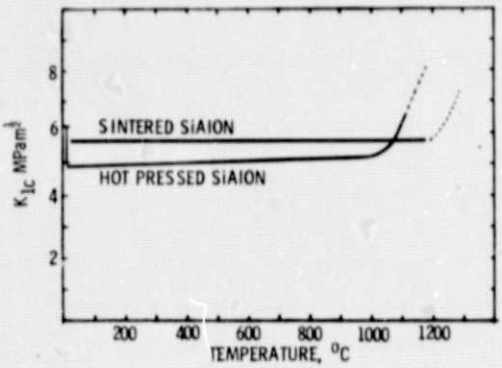


Figure 12. - Variation of fracture toughness with temperature for hot-pressed and sintered SiAlONs (ref. 33).

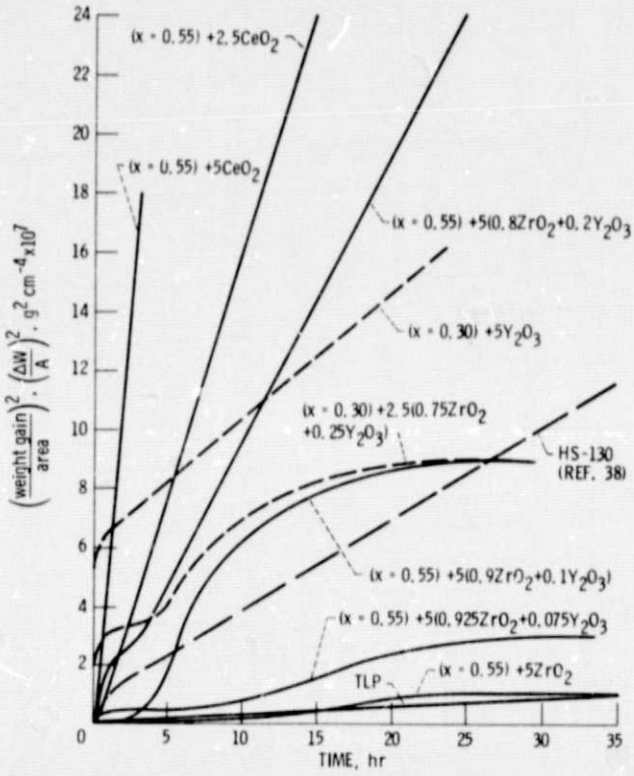


Figure 13. - Weight gain in air at 1400^0 C (2550^0 F) of various SiAlON compositions ($Si_{3-x}Al_xO_xN_{4-x}$) after Layden (ref. 29) and Ashbrook (ref. 39).

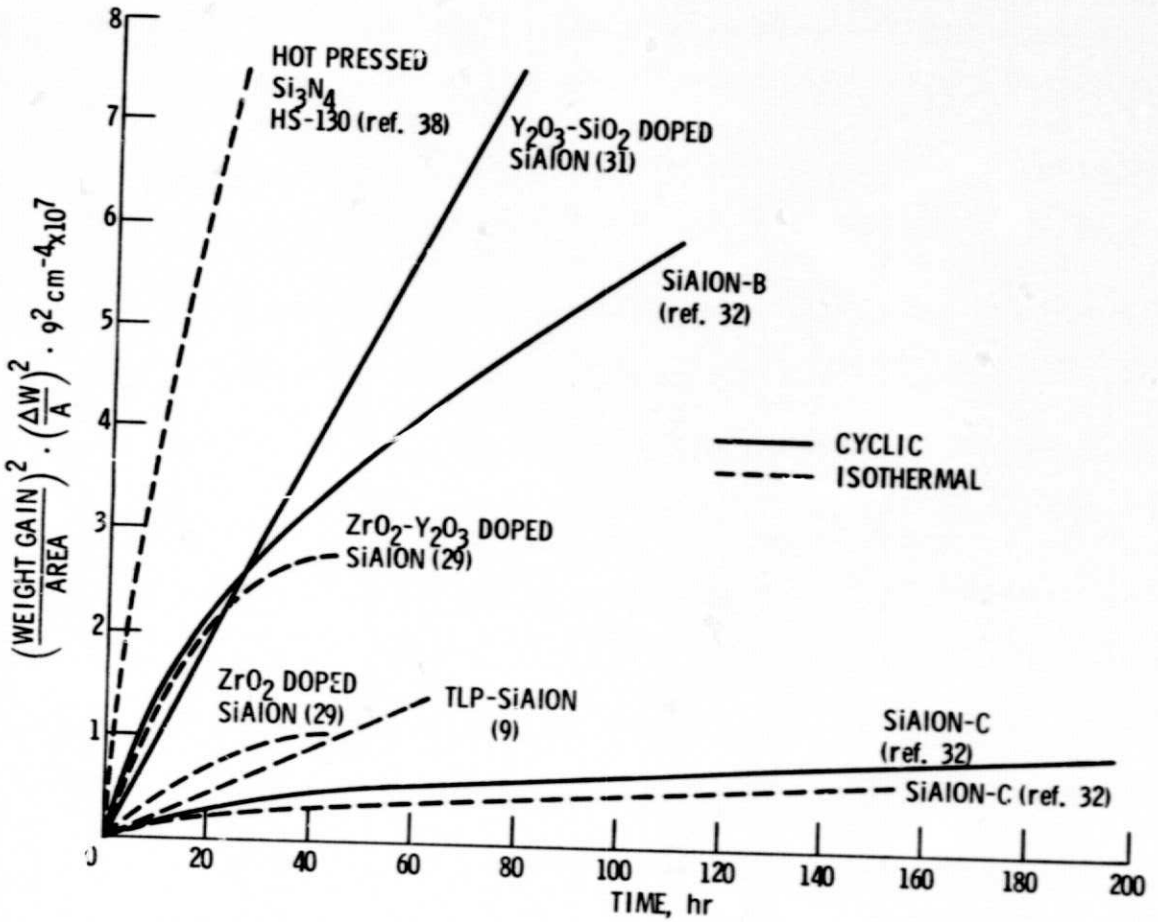


Figure 14. - Parabolic plots of the oxidation of various Si_3N_4 ceramics at 1370^0 to 1400^0 C.

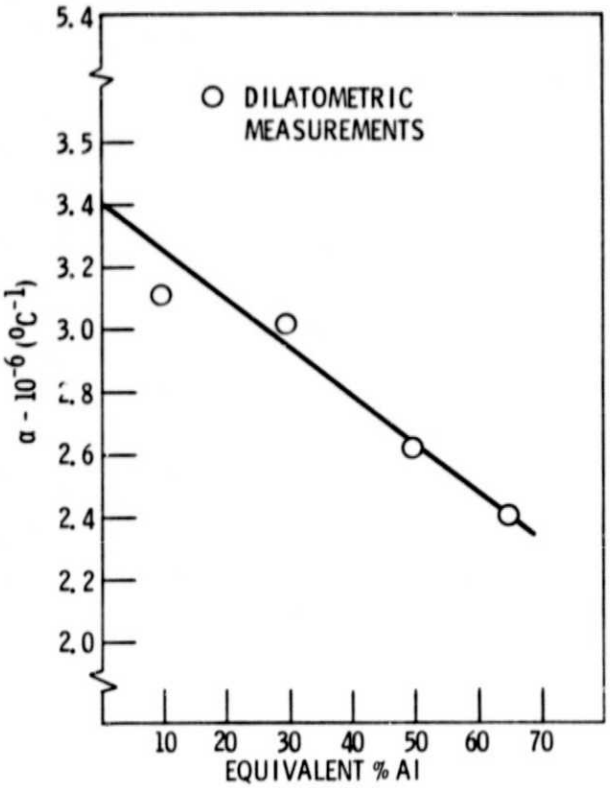


Figure 15. - Linear coefficient of thermal expansion between 25^0 and 1000^0 C for β' - $Si_{6-x}Al_xO_xN_{8-x}$ SiAlON (after Gauckler, ref. 18).