

Silicon Nitride and Related Materials

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Silicon nitride has been researched intensively, largely in response to the challenge to develop internal combustion engines with hot-zone components made entirely from ceramics. The ceramic engine programs have had only partial success, but this research effort has succeeded in generating a degree of understanding of silicon nitride and of its processing and properties, which in many respects is more advanced than of more widely used technical ceramics. This review examines from the historical standpoint the development of silicon nitride and of its processing into a range of high-grade ceramic materials. The development of understanding of microstructure–property relationships in the silicon nitride materials is also surveyed. Because silicon nitride has close relationships with the SiAlON group of materials, it is impossible to discuss the one without some reference to the other, and a brief mention of the development of the SiAlONs is included for completeness.

I. Introduction

(1) Review Structure

Silicon nitride (Si_3N_4) has been studied intensively for more than 40 years. There are two major ceramic forms of this material (reaction bonded and sintered) as well as the often overlooked, but extremely important, amorphous form normally used as a thin film. Each form has its own characteristic production routes, compositions, microstructures, and properties, and underlying all the forms are the fundamental physical and chemical properties of the basic structural unit itself, Si_3N_4 , which, at the atomic and unit-cell levels, provides the basis for many of the bulk property values. The ceramic forms are produced by variations of the traditional ceramic powder-processing routes (powder production, shaping, and consolidation), and each of these steps, in determining microstructural quality, has an important influence on the final properties (notably mechanical strength), which can completely override those of the more fundamental structural aspects. Practically all these features of the production of Si_3N_4 in its various

forms, including powder, have now received detailed attention, and the volume of information in the literature is enormous.

Many reviews on Si_3N_4 have been written. Here, a historical survey of the subject is presented: The reader seeking more-detailed information on specific aspects can find it in the review and the selected journal articles referenced. In putting the development of Si_3N_4 and related materials into historical perspective, the technical difficulty must be confronted of the intertwining of many strands of development, all of which cross-link to a large extent. The solution offered is to pry apart these strands and to treat each strand separately. The resulting structure separates primary scientific developments (determination of crystal structures and other intrinsic properties) from those of the development of the main forms of materials and their mechanical and other properties. The chronology of events shows that many of these activities took place more or less concurrently in different laboratories and that developments in one area were able immediately to influence those in other areas.

(2) Background

The recorded terrestrial history of Si_3N_4 spans just longer than 100 years. It must be assumed that in the earth's prehistory, when the atmosphere was chemically reducing and rich in ammonia, the crust contained large quantities of silicon and other nitrides (according to Lord Rayleigh's estimates,¹ there is far more nitrogen in the rocks of the earth's crust than in the atmosphere). Evidence for the natural existence of Si_3N_4 in the galaxy and with possible origins in supernovae comes from detailed analyses of particles of meteoritic rock,^{2,3} shown to contain $\alpha\text{-Si}_3\text{N}_4$ (nierite), which appears to have been nucleated on crystals of $\alpha\text{-Si}_3\text{N}_4$. The earliest report concerning a synthetic " Si_3N_4 " seems to be that of Deville and Wöhler in 1859;⁴ there was immediate speculation that, during the formation of the earth, silicon reacted with nitrogen to form Si_3N_4 , and the reaction of the red-hot Si_3N_4 with water may have been responsible for the formation of ammonia and, thereby, the introduction of nitrogen into organic compounds and life. A German patent of 1896⁵ describes the production of Si_3N_4 by the carbothermal reduction of SiO_2 . As a structural material, Si_3N_4 is, therefore, of approximately the same vintage as SiC, probably because of their similar chemistries and production routes. Simultaneously with reports of the technical developments appear discussions in the chemistry literature about the chemical formula and atomic structure of Si_3N_4 . The properties of a solid compound of silicon and nitrogen of stoichiometry close to 3:4 ("normal" Si_3N_4) was reviewed by Weiss and Engelhardt⁶ in 1910 and again by Wöhler⁷ in 1926. Reports of the usefulness of Si_3N_4

N. S. Jacobson—contributing editor

Manuscript No. 189742. Received November 1, 1998; approved October 4, 1999.
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Centennial Feature

as a refractory material appeared in the early 1950s: Patents⁸ were filed in 1952 by the Carborundum Company for mechanically strong articles "... consisting of and/or bonded by silicon nitride ...". These were made by the carbothermal reduction of SiO₂ in the presence of nitrogen and by the direct nitridation of silicon. By 1955, Si₃N₄ was an accepted refractory material, with applications including a bonding phase for SiC and oxide refractories, a mold wash resisting attack by molten nonferrous metals, and a thermo-couple sheath material withstanding >50 cycles of rapid (10 s) heating to 2500°F (1371°C), more than 4 times better than an equivalent Al₂O₃ article.⁹

The development of Si₃N₄ ceramics as potential high-temperature structural engine materials markedly accelerated in the early 1960s, the outcome of a deliberate and structured search for new materials with good high-temperature properties, of which resistance to thermal shock was most important. This work led to the development, successful testing, and, in some cases, commercial marketing, of a wide range of Si₃N₄ components for internal (piston and gas turbine) combustion engines. The result has been the attainment of a remarkable extent of refinement of understanding of the underlying basic science and production technology (and thus "maturity") of these materials, which, given subsequent further development, is, at present, probably unsurpassed in the structural ceramics area.¹⁰

In the 1950s, a series of review articles appeared examining the usefulness of Si₃N₄-bonded refractories and Si₃N₄ itself for use at temperatures >2500°F (1371°C), with applications such as atomic-energy jets and rockets.¹¹ Many of these articles were also concerned with Si₃N₄ whiskers and their potential applications in the reinforcement of metals. The period 1955–1964 saw intensive studies of all aspects of the production and properties of (what became known as) reaction-bonded Si₃N₄ (RBSN), which took place in the United Kingdom at the Admiralty Materials Laboratory (Poole; Norman Parr) and the British Ceramic Research Association (Stoke-on-Trent; Paul Popper) leading to a series of patents¹² and major conference and journal publications.^{13,14} An important breakthrough in the development of Si₃N₄ ceramics came in 1961, with the realization that a fully dense (and much stronger) form could be obtained by hot-pressing Si₃N₄ powder in the presence of small amounts of a metal oxide, such as MgO.¹⁵ Thirteen years later this development led to the production of dense, pressureless-sintered Si₃N₄.^{16,17}

In the 1970s, a very large program of development work on Si₃N₄ materials was started in the United States. It was internationally stimulated by the decision of Advanced Research Projects Agency (ARPA) of the U.S. Department of Defense in 1971 to initiate five year development programs with the Ford Motor Company (Dearborn, MI) and Westinghouse Electric Corporation (Pittsburgh, PA), with the objectives of demonstrating the practicability of stationary and mobile ceramic-containing gas-turbine engines, with Si₃N₄ as the leading candidate material.¹⁸

During the past 30 years, during which most of the considerable development work on Si₃N₄ has been conducted, primarily by the ceramics and electronics communities, many different aspects have been explored. This review examines five major strands of this development work: the fundamental physical properties of Si₃N₄, porous Si₃N₄, dense Si₃N₄, amorphous thin films, and powder production. Much of the work of the earlier period was summarized in an Admiralty Materials Laboratory report¹⁹ and later presented at conferences. Publications of 1969–1978 were brought together by Messer and Murphy of the U.S. Materials and Mechanics Research Center in their annotated bibliography containing 1386 entries.²⁰ A very useful summary of the electronic applications of Si₃N₄ has been provided by Arienzo and Orr-Arienzo²¹ of the Research and Technology Division of IBM. In recognition of the scientific and technological significance of the silicon nitrides, the Gmelin Institute (Frankfurt am Main, Germany) has reviewed, under the guidance of Schröder, the entire scientific literature on Si₃N₄ appearing up to 1992 for publication in the silicon supplement volumes of the *Gmelin Handbook of Inorganic and Organometallic Chemistry*. The contents of more than 26 000 selected publications deemed to be of adequate merit,

recorded in the Chemical Abstracts system of the American Chemical Society, are summarized in systematic format: The first silicon supplement volumes dealing with Si₃N₄ have appeared and others are planned.²²

Silicon nitride is chemically Si₃N₄. However, there are some difficulties in defining Si₃N₄ as a *materials* class, because of the blurring of the edges by the range of solid solutions (the "SiAlONs") between Si₃N₄ and Al₂O₃ (and other oxides), of which the α' and β' phases have received the most attention. The term SiAlON was originally coined to describe materials containing Si, Al, O, and N (and other metals), of a very wide range of compositions and crystal structures.²³ It now generally has the more-restricted meaning of the solid-solution phases with the α- or β-Si₃N₄ crystal structures (α'- and β'-SiAlONs). Because silicon and many Si₃N₄ powders generally do contain aluminum (with other metallic impurities) in at least trace amounts, there is no actual clear difference, as materials, between the silicon nitrides and the SiAlONs. Many Si₃N₄ materials are prepared by liquid-phase sintering, using Al₂O₃ as one of the additives, but the products are often regarded as silicon nitrides. However, from a scientific point of view, the important distinction between a Si₃N₄ and a SiAlON lies in the extended degree of microstructural freedom provided by the incorporation of Al₂O₃ (or other oxides) into the basic Si-N-O system and the wide range of M-Al-Si-N-O phases (including glasses) thereby made available. Many of these Al-O-containing phases crystallize and interconvert readily (possibly more readily than the pure silicates) during sintering of the materials and, therefore, are important in determining their microstructures and related properties. There also may be important consequences for grain-boundary film chemistries. Because of these close links with the silicon nitrides, a brief discussion of the SiAlONs (the "related materials"), primarily for historical completeness, must be included here. The SiAlONs have been reviewed in detail as a separate group of materials, e.g., by Ekström and Nygren.²⁴

II. Aspects of the Fundamental Properties of Silicon Nitride

(I) Crystal Structure

Early discussions concerned the composition of the compound obtained by heating mixtures of SiO₂ and carbon or by silicon alone in nitrogen: SiN₂, Si₂N₂, and Si₃N₄ were proposed⁶ as formulas, with "normal" Si₃N₄ being shown to have 3:4 stoichiometry. Detailed X-ray diffractometry (XRD) examinations in the mid-1950s proved the existence of two crystallographic modifications (α and β), both appearing to be hexagonal.²⁵ The *c*-axis dimension of the unit cell of the α phase was approximately twice that of the β phase, with the phenacite (Be₂SiO₄) structure, in which Be is replaced by Si and O by N. Therefore, there is nothing unusual in nitrides having crystal structures based on those of the oxides.²⁶ Each silicon was at the center of a tetrahedron, and each nitrogen in trigonal and approximately planar coordination by three silicons, so as to link three SiN₄ tetrahedra. The structures also can be regarded as puckered eight-membered Si-N rings joined to form sheets, which are, in turn, linked by bridging Si-N bonds (Fig. 1). The unit cell of β-Si₃N₄ consists of Si₆N₈, which Hardie and Jack²⁷ assigned to space group *P6₃/m* (Fig. 2). The structure of α-Si₃N₄ was determined to be closely related to that of β-Si₃N₄, consisting of alternate basal layers of β-Si₃N₄ and a mirror image of β-Si₃N₄, accounting for the doubled *c*-axis dimension, and a unit-cell composition Si₁₂N₁₆ (space group *P3₁c*) (Fig. 3). However, although the β structure was almost strain free, the α structure contained considerable strain, expressed by lattice distortion and the displacement of atoms from the idealized positions²⁸ (the amount of distortion of the Si-N bond angles in creating a model ball and pin α structure (Fig. 4) is immediately apparent to those who have struggled with this task). A further feature of the two structures is that the larger voids in each basal sheet created by the linking of six eight-membered Si-N rings align in the β structure to provide a continuous *c*-axis channel of

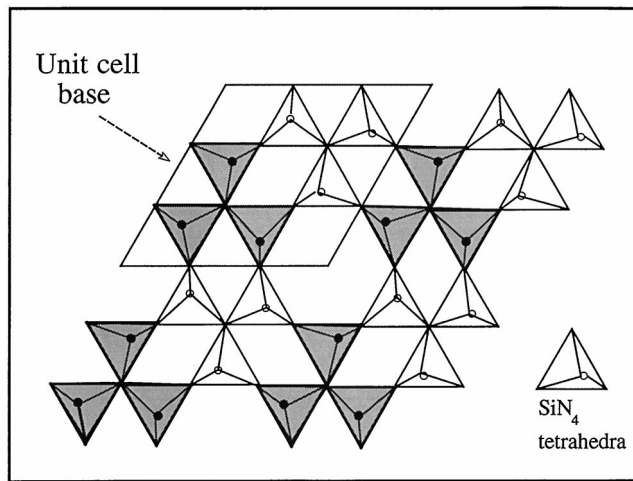


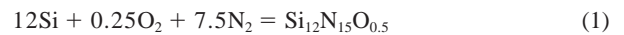
Fig. 1. Outline of Si₃N₄ crystal structure.

approximate diameter (300 pm), whereas, in the α structure, because of the operation of a c glide plane, the continuous voids are interrupted to form a series of large interstices, linked by 140 pm diameter tunnels. Later electron diffraction work on thick samples of β -Si₃N₄²⁹ suggested that the three silicon atoms coordinating N2(c) sites were not exactly coplanar, and the space group was probably $P6_3$. Neutron time-of-flight studies³⁰ subsequently suggested that, at higher temperatures (to 1000°C), the regular tetrahedra were unchanged, but the irregular became more uniform.

Careful XRD work had earlier revealed even-more-interesting aspects of the α -Si₃N₄ structure. Bond lengths in the α -Si₃N₄ structure were observed to be variable and much more so than in the β structure,³¹ and small but definite variations were observed in the unit-cell dimensions of materials obtained from different sources and with different particle morphologies.³² Moreover, small but definite variations in relative intensities of the 520 and 205 reflections were seen. It was concluded that α -Si₃N₄ had a range of homogeneity, which could be explained if it were assumed that it had a defect structure with $\sim 25\%$ nitrogen vacancies in the N(4) sites, and with partial replacement of nitrogen by oxygen in N(1) sites, with electrical neutrality being obtained by an appropriate number of silicon vacancies, or Si³⁺ species. The compositions suggested were thus approximately Si_{11.5}N₁₅O_{0.5}, or Si₁₀^{IV}Si₂^{III}N₁₅O_{0.5} (giving ~ 1.5 wt% oxygen). Density measurements using the flotation technique gave 3.169 ± 0.004 Mg·m⁻³, in good agreement with the calculated value of 3.168 Mg·m⁻³. Supporting evidence that α -Si₃N₄ was an oxynitride appeared to be provided by direct analyses for oxygen in Si₃N₄ samples of various α : β ratios, showing up to 2% oxygen for high- α material, but only 0.2% oxygen for low- α material. Moreover, nitrogen-isotope dilution analyses showed only 96.5% of the theoretical nitrogen for α material, even though 100% for β -Si₃N₄.³³ These reports triggered a debate over the nature of α -Si₃N₄ that was to last for many years.

The complexity of the α -Si₃N₄ structure was suggested by studies of the oxygen partial pressure (p_{O_2}) required to produce the α and β phases by nitridation of Fe(14%–20%)-Si alloys (the use of these alloys was chosen to lower p_{O_2} at the Si-Si₂N₂O phase boundary, for example, from $\sim 10^{-23}$ bar (10^{-18} Pa) (at 1300°C) to $\sim 10^{-20}$ bar (10^{-15} Pa), thus facilitating experimental studies). Conditions relating to the nitridation of pure silicon were then obtained by extrapolation. Data were obtained only for temperatures in the range 1200°–1300°C; at lower temperatures equilibria could not be established, and, at higher temperatures, rapid silicon volatilization occurred as SiO with the formation of AlN by reaction with alumina furnace tubing. These experiments allowed the creation of thermochemical diagrams, and the mapping of the conditions under which α - and β -Si₃N₄ and Si₂N₂O were formed by reaction of the alloy with nitrogen containing a predetermined

concentration of oxygen. If α -Si₃N₄ was assumed to be formed by the reaction (and containing 1.8 at.% oxygen),

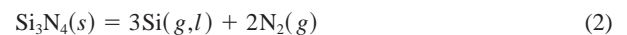


For $a_{\text{Si}} = 1$, the plot of $\log p_{O_2}$ as a function of $\log p_{N_2}$ defining the Si- α -Si₃N₄ boundary should have a slope of -30 . The experimental value of -45 was considered to be in good agreement, justifying the use of this formula to describe the α phase.³⁴ Studies of the precipitation of Si₃N₄ from Fe-Si alloys at temperatures in the range 550°–770°C led to the description of “high oxygen potential” (α) and “low oxygen potential” (β) phases, in preference to “low-temperature” and “high-temperature.”^{28,35} It was assumed that β -Si₃N₄ became unstable with respect to α -Si₃N₄ at $\sim 10^{-20}$ bar p_{O_2} at $\sim 1400^\circ\text{C}$. Despite the thermodynamic evidence, doubts about the necessity for oxygen in the only α -Si₃N₄ structure were immediately raised by direct measurements of oxygen content in α -Si₃N₄ crystals of various origins. The wide range of unit-cell dimensions for α -Si₃N₄ (774.91–775.72 pm and 561.64–562.21 pm), which was well outside experimental error,³² also suggested a possibly wider range of composition than the one originally proposed. α -Si₃N₄ materials with oxygen levels of 0.45%–0.61% were prepared,³⁶ and a sample of pure α -Si₃N₄ analyzed by Priest and colleagues³⁷ contained as little as 0.3% oxygen. These observations were supported by that of Kijima and colleagues,³⁸ who found almost zero oxygen. The lowest oxygen level so far measured is 0.05%,³⁹ giving $a = 781.8$ pm and $c = 559.1$ pm, with an $a:c$ ratio of 0.715, in agreement with the 0.715 measured for a macromodel of the α -/ β -Si₃N₄ structure from which oxygen is artificially excluded. A clear relationship between measured oxygen content and lattice parameter exists, with unit-cell volume increasing with decreasing oxygen content (Fig. 5).⁴⁰ Thus, there was no doubt that α -Si₃N₄ could accommodate oxygen within the crystal lattice, even though oxygen appeared not to be essential for the stability of the structure.³⁷

Recent, much-more-detailed examinations, using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) of a range of 100 nm dimension, of α -Si₃N₄ powders have shown that the oxygen can exist as a surface oxide-rich layer (of composition close to SiO₂) of average thickness 100–800 pm, depending on powder source^{41,42} and as internal oxygen. Of the total oxygen content (which, as expected, varies with particle specific surface area), between 3% and 30% has been estimated to reside in a surface layer. Therefore, most of the oxygen is normally internal; this aspect is returned to later.

Early attempts to convert α -Si₃N₄ to β -Si₃N₄ by prolonged annealing at 1800°C (and which failed)²⁸ indicated that more than oxygen loss was involved in the α -Si₃N₄ to β -Si₃N₄ transformation. It was suggested^{28,37} that the transformation was impurity controlled, and later shown readily to take place in the presence of a liquid phase through a reconstructive transformation.⁴³ This process involves breaking and reforming six Si-N bonds in each unit cell, with a change in position of one nitrogen and a small displacement of neighboring atoms.²⁸ Because the difference between the Gibbs function of formation of β -Si₃N₄ and that of α -Si₃N₄ is small (~ 30 kJ·mol⁻¹ at 25°C) and the activation energy high, the process apparently can proceed readily only in the presence of liquids (silicon, silicides, or silicates), which lowers the transformation activation energy. The reverse β -Si₃N₄ to α -Si₃N₄ transformation has never been observed, but it would be expected to be too slow to be detected at temperatures $< 1400^\circ\text{C}$. The formation and stability of α -Si₃N₄ is apparently thus largely controlled by kinetic factors.

Si₃N₄ does not melt but dissociates into silicon and nitrogen, with the nitrogen dissociation pressure reaching 1 bar (10^5 Pa) at 1880°C:



The silicon is also appreciably volatile:



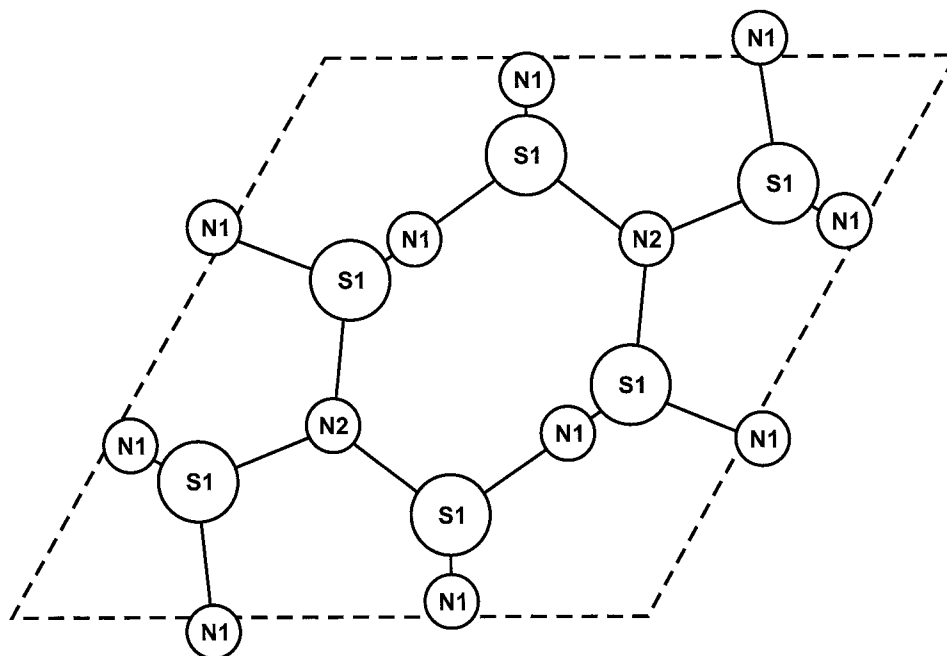


Fig. 2. β - Si_3N_4 unit cell. (After Wild *et al.*³³)

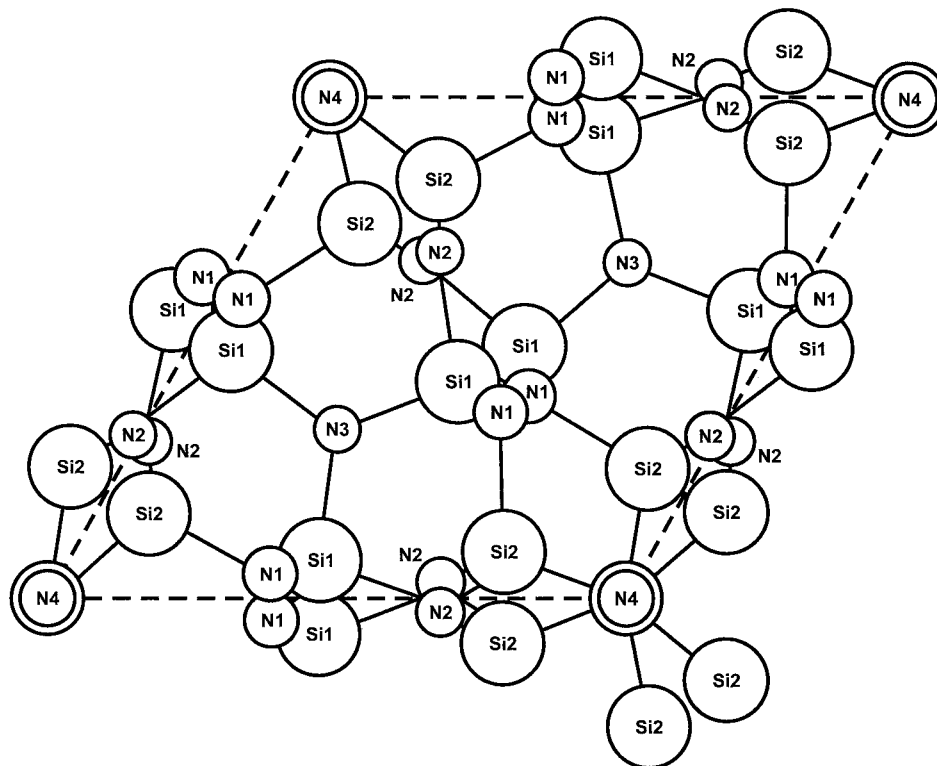


Fig. 3. α - Si_3N_4 unit cell. (After Wild *et al.*³³)

The pressures of silicon vapor over silicon and Si_3N_4 are shown as a function of temperature in Fig. 6.

(2) Lattice Diffusion and Defect Chemistry

Lattice diffusion in Si_3N_4 had long been suspected to be very slow because of the difficulties encountered in attempting to sinter powders. The generally accepted but unproved assumption was that covalent materials were "unsinterable." In principle, lattice diffusion should also be important for high-temperature creep, and the nitridation of silicon particles covered by Si_3N_4 films. Measurement of nitrogen and silicon tracer diffusion coefficients in

Si_3N_4 is not easy because of three major problems: the lack of large, high-purity, single crystals of α -phase and β -phase material; the high-temperature volatility of Si_3N_4 during diffusion anneals; and the limited range of suitable solid sources of silicon and nitrogen isotopes to eliminate the uncertainties of gas-phase–solid-phase boundary reactions. Measurements made on sintered or hot-pressed β - Si_3N_4 are unreliable indicators of self-diffusion in the Si_3N_4 lattice because of the continuous silicate intergranular phase. The first measurements of nitrogen diffusion were reported in 1976 by Kijima and Shirasaki⁴⁴ at the Japanese National Institute for Research in Inorganic Materials, using samples of

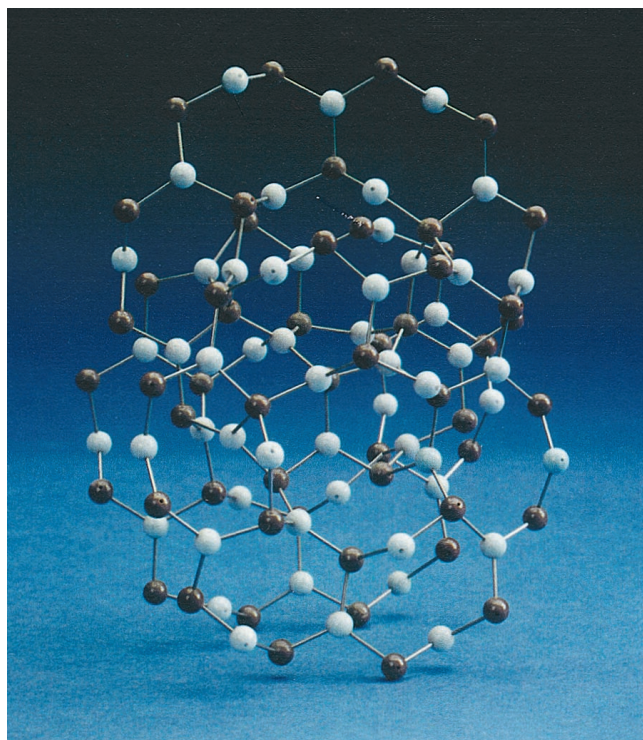


Fig. 4. Ball and pin model of α - Si_3N_4 showing 8- and 12-membered rings and structural layers ((brown) nitrogen and (blue) silicon).

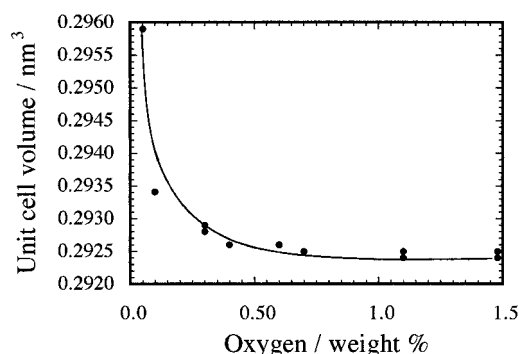


Fig. 5. Unit-cell volume of α - Si_3N_4 as a function of oxygen content.

RBSN and correcting for grain-boundary diffusion. Values for ^{15}N diffusion between 1200° and 1400°C were found to be

$$D_{\text{N}\alpha} = 3.7 \times 10^{-8} \exp(-233\text{kJ}\cdot\text{mol}^{-1}/RT) \quad \text{m}^2\cdot\text{s}^{-1} \quad (4)$$

$$D_{\text{N}\beta} = 6.8 \times 10^{10} \exp(-777\text{kJ}\cdot\text{mol}^{-1}/RT) \quad \text{m}^2\cdot\text{s}^{-1} \quad (5)$$

The difference between the two activation energies was surprisingly large, and the activation energy for the α phase surprisingly low, suggesting that all appropriate corrections might not have been made. However, the later availability of high-purity chemical vapor deposition (CVD) α - Si_3N_4 allowed a more precise determination to be made of ^{29}Si diffusion at the laboratories of the University of North Carolina, GTE, and Standard Oil.⁴⁵ Over the temperature range 1400°–1600°C, $D_{\text{Si}\alpha}$ was between 0.45×10^{-19} and $2 \times 10^{-19} \text{ m}^2\cdot\text{s}^{-1}$, with an apparent (and again low) activation energy of $\sim 197 \text{ kJ}\cdot\text{mol}^{-1}$. All these data are plotted in Fig. 7. Although there are significant differences, the values are consistent with the recognized lack of mobility of silicon and nitrogen in the Si_3N_4 lattice and suggest that nitrogen diffusion might be rate controlling in processes requiring the solid-state mobility of Si_3N_4 units. Many detailed measurements have been made of the mobility of other elements in amorphous Si_3N_4 thin films, particularly arsenic, boron, aluminum, gallium, and oxygen,

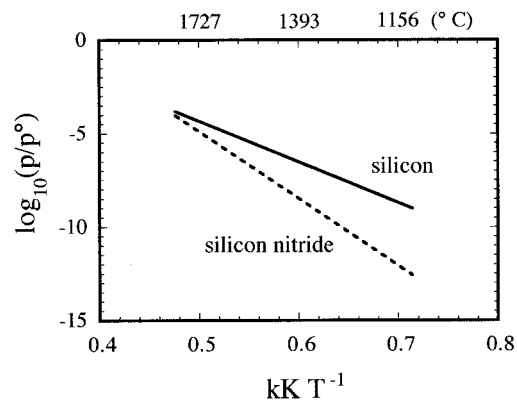


Fig. 6. Vapor pressures of silicon over pure silicon and Si_3N_4 , as a function of temperature.

in the context of the use of thin films as encapsulating or diffusion barriers in the preparation of electronic components.⁴⁶ It is difficult, however, to relate these values to those for diffusion coefficients in a crystalline material.

Very little is known with certainty about the defect chemistry of nominally stoichiometric α - and β - Si_3N_4 , although attempts at quantitative measurements have been made. The existence of dislocations in dense β - Si_3N_4 materials was reported (by Butler⁴⁷ in 1971), and dislocation behavior in β - Si_3N_4 is well documented from studies of mechanical properties. Disk-shaped features of $\sim 25 \text{ nm}$ diameter, assumed to be precipitates of SiO_2 , were reported by Jack and colleagues in 1983.³² More-recent work has drawn attention to other types of lattice defect in α - and β - Si_3N_4 . Dislocation loops clearly visible by high-resolution transmission microscopy (HRTEM) have been found in high concentrations in many α - Si_3N_4 particles (Fig. 8), although similar vacancy clusters have not been found in β - Si_3N_4 . The presence of loop-free zones close to grain boundaries in hot-pressed materials allowed rough estimates to be made of the nitrogen vacancy diffusion coefficient and the derivation of a Schottky-type defect formation energy of $680 \text{ kJ}\cdot\text{mol}^{-1}$. This value can be compared with the Si–N bond dissociation energy of $\sim 335 \text{ kJ}\cdot\text{mol}^{-1}$ and the heat of formation of Si_3N_4 at 1400°C of $730 \text{ kJ}\cdot\text{mol}^{-1}$.⁴⁰ On the assumption that nitrogen diffusion is rate controlling, the nitrogen vacancy diffusion coefficient has been estimated to be $\sim 10^{-18} \text{ m}^2\cdot\text{s}^{-1}$ at 1700°C. All these data are approximate, and the topic merits much-more-detailed exploration.

(3) Oxidation

Most actual and envisaged applications for Si_3N_4 materials required exposure to high temperatures, generally under oxidizing conditions (and sliding surfaces can also generate very high local

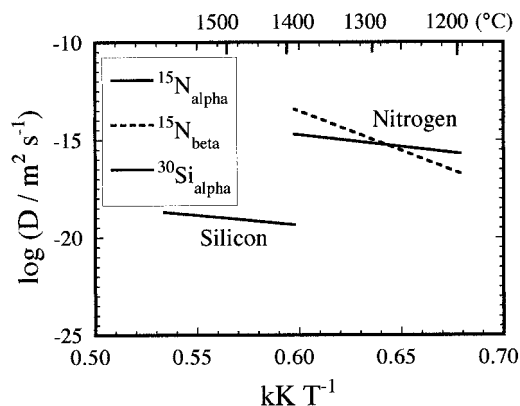


Fig. 7. Silicon and nitrogen diffusion coefficients in Si_3N_4 as a function of temperature.

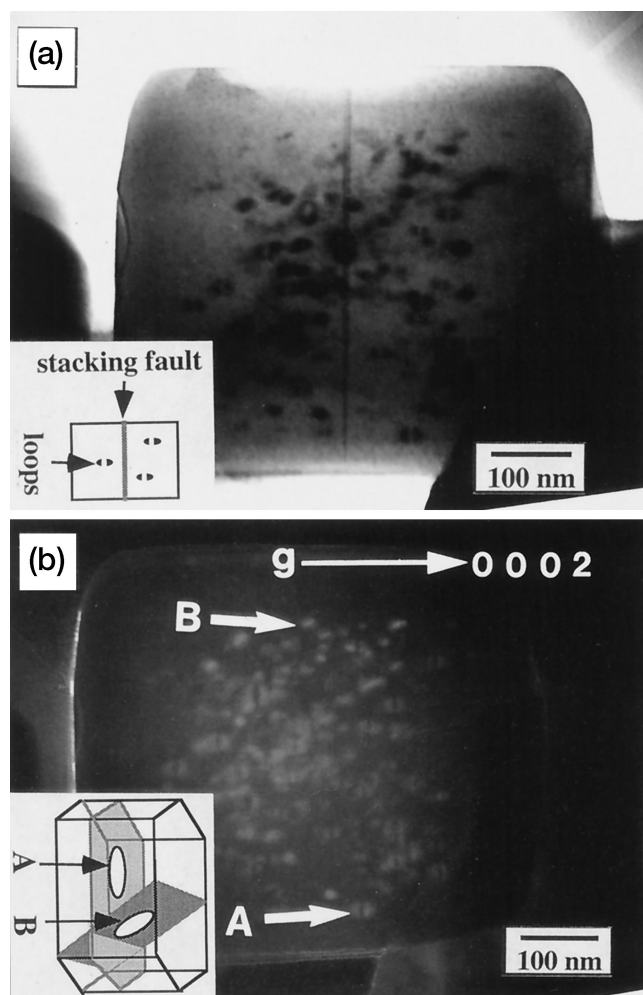
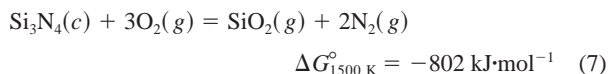
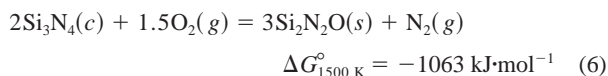


Fig. 8. Dislocation loops in an α - Si_3N_4 particle: (a) dark field and (b) bright field. (Courtesy of C. M. Wang.)

temperatures). Si_3N_4 is thermodynamically unstable with respect to oxidation under normal oxygen pressures, but is protected against catastrophic oxidation by a blocking surface oxide film able to impede oxygen transport to the nitride surface. Passive oxidation and the ability of Si_3N_4 ceramics to withstand high temperatures under oxidizing conditions without excessive oxidation therefore ultimately rests on the integrity and stability of the surface oxide layer. Two major reactions need to be considered:

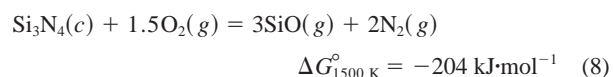


The production of compounds of nitrogen during reactions with oxygen and water vapor was also reported, suggesting complex interface reactions.⁴⁸

Passive oxidation of pure Si_3N_4 , commonly assumed to be controlled by the slow inward diffusion of oxygen through a surface SiO_2 film, leads to approximately parabolic kinetics. However, there were significant differences between the rates of oxidation of Si_3N_4 and silicon (and SiC). Si_3N_4 oxidized much more slowly than silicon in the temperature range 1000°–1400°C, with an activation energy of $\sim 486 \text{ kJ}\cdot\text{mol}^{-1}$, compared with $112 \text{ kJ}\cdot\text{mol}^{-1}$. Detailed TEM, XPS, and AES analyses showed that this is because the oxide film on silicon was amorphous SiO_2 , but, on Si_3N_4 , there was a nitrogen-containing duplex film consisting of an outer layer of amorphous SiO_2 and an interface layer of amorphous silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) (Fig. 9). The $\text{Si}_2\text{N}_2\text{O}$ was initially

considered to have an approximately constant $\text{SiO}_2\text{:Si}_2\text{N}_2\text{O}$ ratio,^{49–51} but subsequent detailed AES and Rutherford backscattering spectroscopy (RBS) profiling studies indicated a graded composition, merging seamlessly with the Si_3N_4 and SiO_2 .⁵² The $\text{Si}_2\text{N}_2\text{O}$ layer was clearly associated with the better oxidation resistance of Si_3N_4 (as compared with SiC), and it was suggested that oxygen permeation through the “suboxide layer” was the oxidation-rate-limiting process, with oxygen permeation and the substitution of oxygen for nitrogen in the suboxide highly impervious to oxygen^{53,54} as two interlinked steps. More studies of the behavior of oxygen in the $\text{Si}_2\text{N}_2\text{O}$ layer are now needed. Thicker films of SiO_2 on Si_3N_4 tend to crystallize, leading to changes in oxidation kinetics, and this feature also is in need of clarification. All these processes are highly sensitive to system purity (at the ppm level),^{55,56} and careful control of the experimental environment is essential.

Under low oxygen pressures ($\sim 10^{-2}$ bar (10^3 Pa) at 1000°C), active oxidation occurs, with formation of the less-stable but volatile and, therefore, nonprotective SiO :⁵⁷



Active oxidation has been less well studied, but is of importance when Si_3N_4 is used at high temperature under “reducing” conditions, which nonetheless contain low pressures of oxygen or oxygen-containing species, such as CO_2 or H_2O . Similar problems of the nonprotectivity of the product can result in sulfidizing environments.⁵⁸

III. Reaction-Bonded Silicon Nitride

(I) Production and General Properties

Early reports and patents referred to the bonding of particulate materials through the incorporation and nitridation of silicon powders. The higher-strength reaction-bonded form of single-phase material seems to have been developed mainly in the 1950s, from the nitridation of silicon powder, with the intention of producing Si_3N_4 powder.⁵⁹ By reaction with nitrogen, a very loosely packed silicon powder formed a coherent monolithic Si_3N_4 replica of the original shape of appreciable strength.¹⁴ The potential of the reaction-bonding process for the production of ceramic components was immediately recognized. During nitridation of the silicon particles, there had been simultaneous bonding, or sintering, of the product nitride. The ability to produce complex-shaped components without the need for time-consuming and expensive finishing operations was a major attraction (only matched subsequently by siliconized SiC materials). The material was porous (25%–35%), but strengths were a very respectable 200–300 MPa and appeared to improve slightly at temperatures between 1200° and 1400°C. These facts, coupled with the high creep resistance of a material free from glass, an ability to withstand thermal shock based on a low thermal expansion ($\sim 3 \times 10^{-6} \text{ K}^{-1}$), and resistance to attack by a wide range of molten

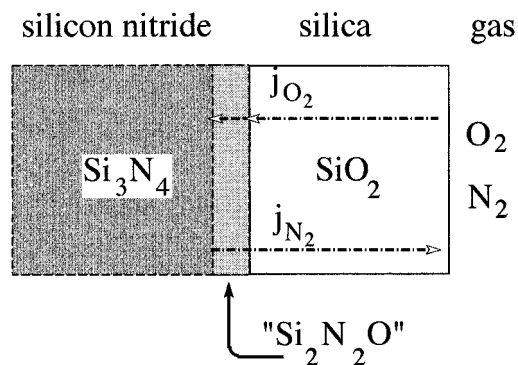


Fig. 9. Schematic of the oxide layer structure on oxidized Si_3N_4 .

metals, made the material immediately attractive for thermocouple sheaths and for handling molten aluminum.⁹ Moreover, because the material was formed from two of the most readily available elements in the earth's crust, silicon and nitrogen, it should have been relatively inexpensive—factors outweighed in practice, however, by the energy costs of a slow, high-temperature process and the difficulties of achieving microstructural quality.⁶⁰ RBSN was selected as a major material of the early ARPA ceramic-turbine development program for use in the hottest zones of a ceramic gas-turbine engine (although the highest mechanical stresses were at the cooler rotor center).⁶¹

(2) Microstructure

Major problems were encountered with the optimization of the properties of RBSN, and, in particular, the consistent attainment of good strengths.⁶² Silicon nitridation is very exothermic (~ 725 kJ·mol⁻¹ at 1400°C), and temperature increases during nitridation can be considerable. Silicon melts at 1410°C, and premature local melting of the powder with reduction of the surface area exposed to nitrogen made it impossible to attain complete nitridation. Nitrogen (and silicon) diffusion in the Si₃N₄ crystal lattice is, as noted above, too slow to give significant rates of nitride formation. On the other hand, if the temperature is held much below 1400°C, the reaction of conventional silicon powders becomes very slow and ultimately effectively stops; completion of nitridation thus becomes very difficult. The essential requirement for the formation of a satisfactory product was to allow initial nitridation to proceed to build up an adequate extent of restraining skeletal microstructure of bridging Si₃N₄, retaining the particulate silicon, and then to complete nitridation at a higher temperature, when the molten silicon particles were unable to fuse. This situation was achieved initially using a stepped, two- or three-stage time-temperature schedule. A commonly used program consisted of a slow ramp to $\sim 1300^\circ\text{C}$, followed by a hold until the reaction rate virtually ceased, followed by a final period at $\sim 1450^\circ\text{C}$ to complete conversion of the silicon to nitride. With the increasing availability of microprocessors, this type of program developed into those linking furnace heating to nitrogen uptake rate, to achieve linear reaction rates over the entire extent of the process. Ultimately, it became possible to exert very good control over the nitridation process, although total reaction times remained very long (12–36 h was common for commercial nitriding furnaces).⁶³

A fundamental feature of the silicon powder nitridation reaction is that the only reduction in void space in the compacted powder is the consequence of the molar volume expansion on conversion of silicon to Si₃N₄. There is no sintering in the normal sense, and the volume expansion is accommodated entirely within the pore structure of the nitriding powder. The density and molar volume of the silicon and Si₃N₄ are 2.32 and 3.19 Mg·m⁻³ and 0.363 and 0.440 cm³·mol⁻¹, respectively, and the overall reaction $3\text{Si}(c) + 2\text{N}_2(g) = \text{Si}_3\text{N}_4(c)$ thus results in a molar volume change of $+0.077$ cm³·mol⁻¹ (+21.2%). Through the initial fixation of the microstructure of the compacted silicon powder by a bridging nitride network, the microstructure of the silicon imprints itself strongly on that of the Si₃N₄ formed. Microstructural flaws—regions of low density and larger than average voids—become similar strength-controlling defects in the RBSN. The strength of the material was thus controlled by a combination of overall void fraction⁶⁴ and the largest void size. The intrinsic chemical reactivity of elemental silicon appeared to compound the problems, and aspects such as the conditions under which the silicon powder had been prepared could be of significance for microstructural quality and strength of RBSN. The silicon-powder-processing stage must, therefore, be near-perfect if maximum strength and consistency (Weibull modulus) in the RBSN are to be achieved.^{65,66}

(3) Nitridation Mechanisms

Considerable attention was soon focused on the details of the nitridation mechanism in order to understand better how reaction occurred, why reaction rates were so irreproducible, how the

bonding proceeded, and why no overall dimensional change occurred.²⁸ The microstructure of the material, the pore fraction, and the α -Si₃N₄: β -Si₃N₄ ratio seemed to be related to strength (although this last aspect was less certain⁶⁷). It quickly became evident that the nitridation-reaction-bonding process was extremely sensitive to impurities in the silicon powder and in the furnace environment: Reproducibility of product quality was extremely difficult to ensure.¹⁴ Contamination of the gaseous atmosphere by water or oxygen and additions of hydrogen had significant effects on nitridation rate, on the proportion of α -Si₃N₄ formed, and on overall microstructure. A major aspect of this problem was the unavoidable presence of oxygen contamination in the nitriding system, present as the SiO₂ films on the silicon particles and available as water vapor or oxygen impurity in the nitriding gas released from hot furnace oxide refractories. This in turn inevitably became linked to the question discussed above of the composition of the α - and β -Si₃N₄ and the requirement (or not) for oxygen.⁶⁸ Fluorides had been known from an early date to accelerate silicon nitridation,⁶⁹ and iron, a common constituent of earlier grades of silicon powder (introduced during milling), also acted (at the ppm level) as a catalyst for silicon nitridation in general and β -Si₃N₄ production in particular.^{8,70} The accelerating mechanisms were difficult to establish, but the consensus was that these species aided removal of protective surface SiO₂ films, the iron by forming liquid alloys with silicon and opening up a liquid-phase route to β -Si₃N₄. These particulate metallic alloys also could be an origin of large microstructural defects.^{71,72}

The very-high-purity silicon powders derived from silane were of great interest in this context. In the early 1980s, a laser-driven gas-phase synthesis technique was developed by Haggerty and colleagues at Massachusetts Institute of Technology for the production of nanosized, high-purity silicon (and other) powders. Such ~ 200 nm silicon powders developed nitride films at temperatures as low as 750°C.^{73,74} The nitride films also formed RBSN more readily and at lower temperatures than did conventional silicon powders with oxidized particle surfaces.⁷⁵ Fast, low-temperature nitridation appeared to be possible because of the absence of SiO₂ and Si₃N₄ film on the silicon particles; measured nitridation rates were comparable with silicon evaporation rates, indicating that silicon vaporization was rate limiting.

First suggestions for the microstructure development mechanism²⁸ were that thin films of nitride initially formed on solid silicon surfaces and then spalled off into the voids as a result of compressive strain to form a microstructure consisting of high-surface-area flakes (“matte”) of Si₃N₄. This material seemed to be predominantly α -Si₃N₄. Above the melting point of silicon, an increased rate of formation of β -Si₃N₄ occurred. Thus, the material consisted of two phases: a whiskerlike or fibrous low-density phase consisting almost entirely of α -Si₃N₄ and a harder, higher-density, more-equiaxed phase, the development of which was promoted by higher reaction temperatures and the presence of liquids. The density of the matte was determined by the temperature and time of nitridation below 1410°C: The denser β -Si₃N₄ phase was assumed to result from the nitridation of liquid silicon. The microstructure was thus very strongly controlled by the details of the nitridation program and system purity.

Work establishing major reaction mechanisms was conducted by Moulson and colleagues⁷⁶ at the University of Leeds, using high-purity single-crystal silicon wafers. These earlier, detailed studies had also identified the importance of silicon evaporation and the formation and growth of nitride nuclei (Fig. 10). The vapor pressure of silicon (and rate of evaporation at ~ 1 mg·m⁻²·s⁻¹ at 1350°C) was more than adequate to sustain observed reaction rates. Apparently, an important aspect of the nitridation reaction is the nucleation and development of Si₃N₄ on silicon surfaces, with vapor-phase transport primarily from noncontacting silicon surfaces. The interlinking and bridging of nitride growth points then fixes a skeletal structure and the component external dimensions (those of the compacted silicon powder), to be filled in subsequently during succeeding stages of nitride production (Fig. 11). This essentially is the classical evaporation-condensation mechanism for sintering without shrinkage, with evaporation of silicon

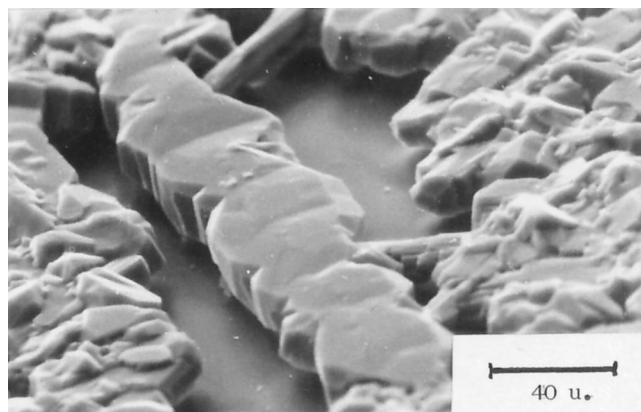


Fig. 10. Formation of Si_3N_4 crystals on single-crystal silicon. (Courtesy of A. J. Moulson.)

and condensation of Si_3N_4 ; it would also be consistent with the development of the considerable intrinsic strength of the material, which is otherwise difficult to explain on a pure spalling model. More recent, elegant TEM studies of developing Si_3N_4 films on silicon particles have also provided useful evidence regarding process mechanisms.⁷⁷

As with the question of the nature of the α - Si_3N_4 , there has been much controversy with regard to the role (if any) of the gaseous suboxide SiO in the nitridation reaction. In theory, SiO can be nitrided to Si_3N_4 but only in the presence of an effective sink for the low pressures of oxygen released ($\sim 10^{-20}$ bar (10^{-15} Pa)). In principle, silicon can act as this sink (thus recycling the oxygen as SiO), but it has been questioned whether kinetically the reaction can be fast enough (because of the low fluxes engendered by the low pressures of SiO).⁶² The need for the sink may, therefore, also explain the faster nitridations obtained in the presence of hydrogen.⁷⁸ In contrast, in the presence of excess oxygen, nitridation rates are slowed, and $\text{Si}_2\text{N}_2\text{O}$ becomes a significant product, although, because of the self-purging action of silicon, it is possible to nitride compacted powders in air. Although it is generally accepted that volatile silicon species are involved in the nitride formation reaction, the reason for the stepped increase in nitridation rate when the temperature is increased has not been satisfactorily explained, and the Si_3N_4 spalling model may have applicability.

Although research interest in the lower-strength RBSN has now declined in favor of higher-strength sintered materials, work is continuing in the nitridation mechanism and the production of Si_3N_4 powders for sintering. The reaction-bonded form also

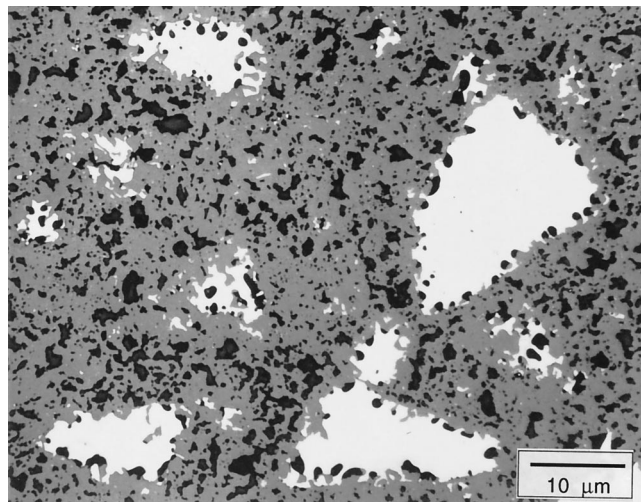


Fig. 11. Partially nitrided silicon powder, showing residual inner particle porosity. (Courtesy of A. J. Moulson.)

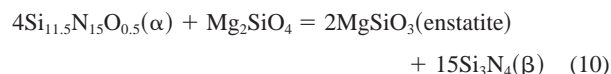
provides an important basis for sintered RBSN materials because of the higher green densities attainable in the reaction-bonded material compared with compacted Si_3N_4 powder.⁷⁹ Recent studies have been made using a fluidized-bed system as the basis of a possible route to the large-scale production of lower-cost Si_3N_4 powder.^{80,81} TEM examinations of nitrided, presintered silicon powder led to the suggestion that nitrogen penetration of the silicon-silicon grain boundaries occurs; stress-induced spalling of Si_3N_4 particles to expose fresh silicon surfaces was then postulated to occur, which agrees with the earliest suggestions for the silicon nitridation mechanism. Much work remains to be done in this complex area, particularly if mathematical modeling is to be satisfactorily achieved, and new techniques are being applied to these investigations.⁸²⁻⁸⁴

IV. Dense Silicon Nitride

(I) Hot-Pressed Silicon Nitride

(A) *Production:* Compacted Si_3N_4 powder does not densify appreciably under normal ceramic processing conditions; hot-pressing pure Si_3N_4 powder at 1750°–1900°C simply leads to the production of a porous material with properties similar to those of RBSN.⁸⁵ In 1956, SiC was successfully sintered with a liquid-forming additive (Al_2O_3),⁸⁶ and workers at the Plessey Co. laboratories in the United Kingdom attempted a similar procedure with Si_3N_4 . Oxide and nitride additives were tested, of which BeO, Mg_3N_2 , Al_2O_3 , and MgO were the most effective at allowing densification of α - Si_3N_4 powder at <23 MPa at 1850°C.⁸⁷ The best materials had room-temperature strengths of ~ 600 MPa and retained ~ 400 MPa at 1200°C. XRD examinations indicated a mixture of α - and β - Si_3N_4 . Strength depended markedly on Si_3N_4 purity, and higher-purity powders gave improved hot strength and creep resistance. It was judged that material prepared from 99.9%-pure Si_3N_4 had sufficient creep resistance at 1200°C to be acceptable as a gas-turbine blade material. Although its thermal-shock resistance was not as good as that of a Nimonic 90 alloy, it was better than those of high-density Al_2O_3 and SiC.

Questions were raised about the densification process, notably the intriguing role of the MgO additive, its ultimate location, and the interlinking of densification with the α - Si_3N_4 to β - Si_3N_4 transformation. An immediate suggestion was that the function of the MgO was to react with oxygen present in the system, either as a coating on the Si_3N_4 particle surfaces, or in the α - Si_3N_4 lattice and, thereby, forming magnesium silicates.⁸⁸



Densification began between 1500° and 1600°C, which corresponded closely to the liquidus temperatures of 1543° and 1557°C in the Mg– SiO_2 binary system and indicated that covalent Si_3N_4 could be dissolved in standard silicate systems. At temperatures >1600°C, conversion of α - Si_3N_4 to β - Si_3N_4 was rapidly completed, and, on cooling, the MgSiO_2 (nominally enstatite) remained mainly as an intergranular glass (and, therefore, not readily detectable by XRD examination). Much of the subsequent early development work on hot-pressed Si_3N_4 conducted using MgO additive was to provide the fundamental understanding of microstructure–property relationships in dense, hot-pressed Si_3N_4 , and which was 15 years later applied in the development of sintered Si_3N_4 .

(B) *Microstructure:* Considerable attention focused on the α - Si_3N_4 to β - Si_3N_4 “grain refinement” process, proceeding simultaneously with densification.⁸⁹ It was initially suggested that the lower stability of α - Si_3N_4 at temperatures >1400°C might accelerate densification, although it might not have been a requirement. The multiphase microstructures, consisting of β - Si_3N_4 grains, embedded in an amorphous or partially crystalline matrix, provided an excellent opportunity for optimization of materials

properties for specific applications.⁹⁰ A further aspect of fundamental importance was that the growth of the β - Si_3N_4 grains was strongly anisotropic, with the c -axis growth rates generally being much faster than those normal to the prism faces. Where grain growth was controlled by diffusion of silicon and nitrogen through the liquid phase, change of liquid-phase composition, modifying silicon and nitrogen diffusion rates, also affected grain-growth rate. It also was evident that the β - Si_3N_4 morphology and fraction of larger, elongated grains could be controlled by the presence of β - Si_3N_4 seeds. Equiaxed β - Si_3N_4 grains were produced from phase-pure β - Si_3N_4 powder, but, with predominantly α -phase Si_3N_4 powder, a low fraction of β - Si_3N_4 particles, acting as nuclei, gave larger, elongated β - Si_3N_4 grains in a matrix of finer α - or β - Si_3N_4 grains (shown in Fig. 12). Moreover, because prism plane growth rates are controlled by Si_3N_4 liquid interfacial energies, grain aspect ratio in particular was strongly controlled by liquid-phase composition. Thus, the Si_3N_4 microstructure could be varied over a very wide range by careful control of starting powder α - Si_3N_4 : β - Si_3N_4 ratio, particle size and size distribution, and liquid-phase volume and composition. The degree of control available over microstructure, in turn, had important implications for the control of mechanical properties. More-recent detailed work in this area has also shown the importance of the size of deliberately added β - Si_3N_4 seed particles.⁹¹

Because of the importance of the intergranular glass for high-temperature strength, considerable efforts were made to achieve glass crystallization through controlled postdensification annealing. This was, in large measure, very successful, and significant improvements in strength, at room temperature (to >1100 MPa) and high temperature (>800 MPa at 1300°C) were obtained,^{92,93} although it also quickly became evident that there were theoretical limits to the extent of crystallization possible.⁹⁴

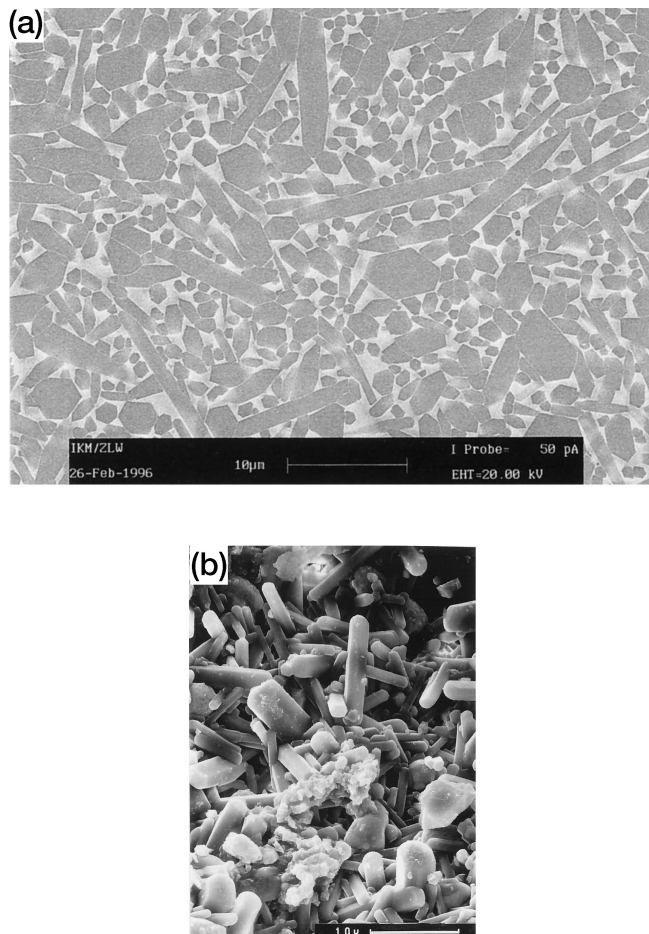


Fig. 12. Rod microstructures in β - Si_3N_4 : (a) etched surface (Courtesy of M. J. Hoffmann.) and (b) deliberately over-etched (Courtesy of P. Andrews.).

(C) *Mechanical Properties:* As a result of the early interest in hot-pressed Si_3N_4 as a high-temperature gas-turbine material, attention was directed to high-temperature strength and creep resistance. The major factor controlling hot strength appeared to be the intergranular glass derived from the densification aid and which, as indicated above, became the subject of intensive investigation. The importance of intergranular glass had been shown very early by the complete loss of strength at 1400°C in nitride prepared with 5% MgO: In contrast, RBSN with no intergranular glass showed no loss of strength at 1400°C .⁹⁵ At high temperatures, a viscous liquid must separate the Si_3N_4 grains (a “molasses and sand” picture) and that the grain-boundary phase was a silicate glass. High-temperature strength and creep strength were controlled by the intergranular glass and were very sensitive to its composition; maximum creep resistance was estimated to require <100 ppm calcium impurity.⁹⁶ The importance of cavitation at grain junctions for tensile creep behavior was quickly established,^{97–100} with the opening of the cavities into cracks and the interlinking of these cracks leading ultimately to failure. High-temperature failure by creep rupture through the viscous flow of the glass and the accumulation of damage in the form of cavities was also likely to determine the maximum application temperature. During tensile creep, the volume fraction of cavities increases; in contrast, compressive creep under similar conditions leads to very little cavitation, and the creep rate is only $\sim 1\%$ of that of tensile creep. This pattern has been modeled in terms of two quite different behaviors. Tensile creep produces cavitation at multigrain junctions, flow of silicate, expansion of the microstructure, and deformation. During tensile creep, the Si_3N_4 grains remain essentially undeformed. In compression, cavities cannot form, and solution–recrystallization of the Si_3N_4 is responsible for deformation. Conventional TEM, using lattice imaging, initially showed only clean grain boundaries,¹⁰¹ but later work was able to detect the presence of 1–2 nm glass films between most Si_3N_4 two- and three-grain boundaries, with the exception of low-angle subgrain boundaries and twin interfaces, irrespective of the additive system.¹⁰² As described in the following section on sintered Si_3N_4 , knowledge and understanding of grain-boundary compositions became refined to a remarkable degree.

To maximize Si_3N_4 densification rates, yet maximize the viscosity of the residual intergranular glass, detailed attention has been paid to system composition. Marked differences in behavior were found in materials prepared from various Si_3N_4 starting powders, caused by contamination by metal oxides. This highlighted the need for very-high-purity Si_3N_4 powders. Of the major impurities found in earlier grades of Si_3N_4 powder, CaO was particularly deleterious, because, in the CaO–MgO– Si_3N_4 – SiO_2 system, the ternary eutectic temperature is reduced to $\sim 1325^\circ\text{C}$, with simultaneous reduction in intergranular glass viscosity.¹⁰³ Assuming that the grain-boundary liquid composition was that of the eutectic, for a given overall composition, the liquid content would increase with increasing CaO content. Even for a crystalline grain-boundary phase, there would be marked loss of strength at the eutectic temperature (as evidenced at the melting point of silicon in SiC–Si materials¹⁰⁴). The need for high-temperature strength therefore meant that the Si_3N_4 powder had to be of high purity with respect to calcium, sodium, and potassium.^{105,106}

Evaluation of strength at 1400°C as a function of MgO– SiO_2 molar ratio showed a minimum in strength at ratios between 1 and 2 (Fig. 13), ascribed to the composition of the Si_3N_4 -ternary eutectic (1515°C) join with a ratio of 1.6,¹⁰⁷ and significantly lower than those of the binary eutectics in the MgO– SiO_2 system because of the nitrogen dissolved and bonded in the liquid (Fig. 14). An important consequence was that it was necessary to know also the oxygen (“ SiO_2 ”) content of the starting Si_3N_4 powder, particularly if small amounts of densification aid oxide were being used; as described above, powder oxygen contents varied considerably according to production method and history of the powder. The oxygen content was of particular importance for those systems where it was necessary to avoid also the formation of oxidizable intergranular crystalline phases, as in the case of rare-earth-oxide densified materials. In this system, the ideal starting composition

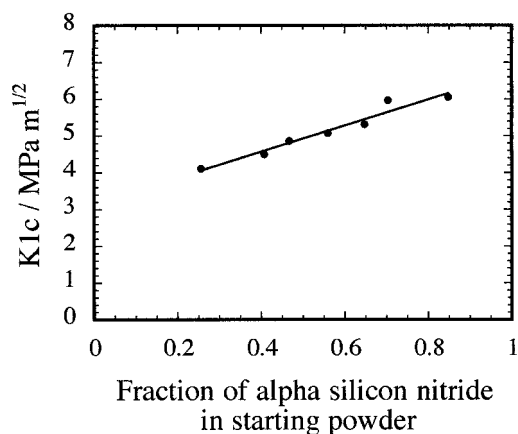


Fig. 13. Fracture toughness as a function of α - Si_3N_4 content of the starting powder. (After Lange.⁹⁰)

must lie within the Si_3N_4 - $\text{Si}_2\text{N}_2\text{O}$ - $\text{Y}_2\text{Si}_2\text{O}_7$ compatibility triangle near the Si_3N_4 corner, and careful control of the Y_2O_3 : SiO_2 ratio was needed.^{108,109}

Realization of the significance of intergranular glass viscosity quickly led to the exploration of the more-refractory and crystallizable Y_2O_3 - SiO_2 system as a replacement for the MgO - SiO_2 system, providing higher eutectic temperatures and more-viscous liquids.¹¹⁰ Using Y_2O_3 , strengths of 500–600 MPa could be retained at 1400°C. A range of similar systems containing the rare-earth lanthanide oxides was also thoroughly investigated.¹¹¹ The Be-Si-N-O system should be ideal, because it approaches the single-phase, solid-solution Si_3N_4 - Be_2SiO_4 composition,¹¹² but, because of the toxicity of BeO, it was never considered seriously as a densification aid. For long life at high temperatures under load, creep becomes important, and, as was the case for short-term strength, creep rates were related to the viscous grain-boundary glass phase. Tensile creep rates were 5–10 times faster than compressive creep, controlled by a combination of grain-boundary sliding, elastic deformation, and diffusional creep.

(D) *Oxidation*: As is the case with pure silicon and SiC, oxidation of pure Si_3N_4 was negligibly slow at temperatures <1200°C.¹¹³ However, hot-pressed materials containing metal-oxide sintering additives oxidized much more quickly, particularly as grain-boundary-phase eutectic temperatures were reached. The surface oxide film now consisted of SiO_2 , with metal silicates containing the sintering aid. The variations of oxidation rates with additive system and with overall composition within a given system led to the identification of cation diffusion to the surface under its chemical potential gradient as an important rate-controlling step of the reaction mechanism. Impurity elements (such as the calcium referred to above) of very low concentration in the Si_3N_4 grain boundaries became concentrated in the surface

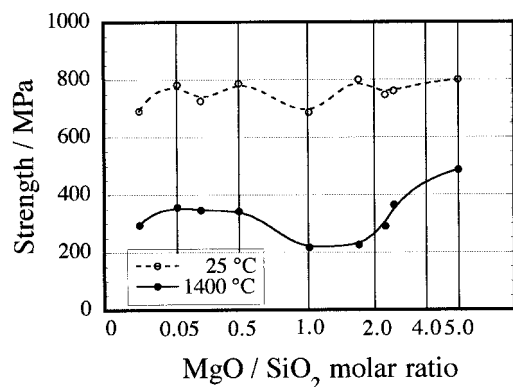


Fig. 14. Strength of hot-pressed Si_3N_4 as a function of composition. (After Lange.¹⁰⁷)

oxide film. The development of a model for oxidation of multiphase Si_3N_4 was based on important observations of Cubicciotti and Lau¹¹⁴ at the laboratories of Stanford Research Institute. Oxidation kinetics were apparently unaltered after removal by grinding of the surface oxide film from partly oxidized Si-Mg-N-O material. The oxidative weight gain continued more or less as though the film continued to exist (Fig. 15), implying that the rate-controlling step was not the inward diffusion of oxygen through the silicate film, but the outward diffusion of cations in the intergranular glass. Elemental analyses across sectioned, partially oxidized MgO-containing materials showed the concentration gradients and the depletion of intergranular cations toward the surface of the material.¹¹⁵ As a consequence, oxidation also influenced high-temperature creep rates, with the loss of intergranular phase, and compositional changes resulting from the incorporation of SiO_2 oxidation product and the loss of cations by outward diffusion, leading to a general stiffening of the material.^{116,117}

The influence of the intergranular glassy phase, its volume, and its composition in controlling oxidation became the basis for many detailed studies of all major densification systems. Later work developed the cation diffusion model to consider the oxidation of multiphase Si_3N_4 materials as interlinked steps: the simultaneous creation and dissolution of the incipient protective SiO_2 film. External and internal oxidation of Si_3N_4 occurs in the surface region by the arrival of oxygen, with the formation initially of SiO_2 . Subsequent reaction of the SiO_2 with the metal cations and oxide (or nitride) anions diffusing from the intergranular glass occurs, to form silicate liquids of much higher permeability toward oxygen.¹¹⁸ These two processes are regarded as establishing an equilibrium SiO_2 thickness, which then controls the inward supply of oxygen to the Si_3N_4 ; the overall reaction-rate constant is a composite of terms for outward cation diffusion and inward oxygen diffusion.¹¹⁹ However, refinement of models for these processes is needed.

Oxidation also involves molar volume changes. Examples of Y_2O_3 -based materials are given in Table I.¹²⁰ Stresses that result from the surface oxidation of Si_3N_4 to $\text{Si}_2\text{N}_2\text{O}$ or SiO_2 must be assumed to be relaxed at the free surface, but stresses resulting from the internal oxidation of nitrides located within the material subsurface zone (and particularly at temperatures below the eutectic) cannot be accommodated so readily. The effect of the volume expansion and the tensile stresses generated was to cause destruction of the outer layers of the material through surface cracking and spalling. Problems of this type were first reported by the Westinghouse group for materials made in the Si-Y-N-O system, for which the presence of the quaternary nitride Y_2O_3 - Si_3N_4 is most undesirable because of its large volume expansion.¹²¹ For this reason, the practicality of using Y_2O_3 as a densification aid was initially placed in doubt. However, identification of the cause of the catastrophic breakdown oxidation in certain temperature brackets and the involvement of quaternary nitrides enabled steps to be taken to prevent it by accurate control

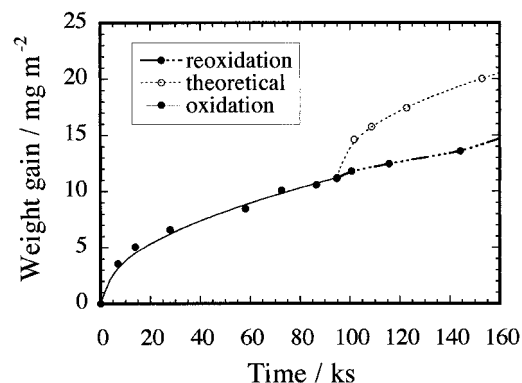


Fig. 15. Two-stage oxidation and reoxidation of Si_3N_4 . (Courtesy of P. Andrews.)

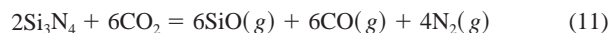
Table I. Molar Volume Changes during the Oxidation of Some Nitride Phases

Nitride	Products	Molar volume increase (%)
Si ₃ N ₄	SiO ₂	86
Si ₃ N ₄	Si ₂ N ₂ O	20
Y ₂ Si ₃ O ₃ N ₄	Y ₂ Si ₂ O ₇ , SiO ₂	30
YSiO ₂ N	Y ₂ Si ₂ O ₇ , SiO ₂	12
Y ₃ (SiO ₄) ₃ N	Y ₂ Si ₂ O ₇ , SiO ₂	4

of the Y₂O₃:SiO₂ ratio.¹²² Similar effects were reported by other groups for Si₃N₄ materials densified with the use of rare-earth oxides, such as Nd₂O₃ and Dy₂O₃, which could also form grain-boundary crystalline quaternary nitrides.¹²³ The use of MgO as a densification additive was soon largely replaced by that of Y₂O₃ because of the better high-temperature properties available in the Y₂O₃-densified materials.

More-recent work has focused attention on providing surface protective barrier layers that inhibit oxidation.¹²⁴ However, there has been only limited success, because, at the high temperatures of interest, the barrier layer itself, even if it retained its mechanical integrity under thermal cycling, tended to react with the underlying nitride or its oxidation products. Early work in this direction had investigated silicate glazes, but these effectively behaved similar to a silicate oxidation product and provided no improved protection. Thus, there remains a need to develop surface films of improved resistance to reaction at high temperatures with the substrate.

Because of interest in the potential use of Si₃N₄ in coal gasification and similar low-oxygen environments, oxidation and corrosion work on dense silicon nitrides now has been extended through detailed studies to the use of a wide range of gaseous atmospheres, including the oxidizing of CO₂ and H₂S. Earlier work with RBSN had suggested that oxidation in pure CO₂ was considerably slower than in dry air,¹²⁵ a feature demonstrated also in the oxidation of SiC by CO₂.¹²⁶ However, many of these systems appear to involve the faster active oxidation or sulfidation of Si₃N₄ through reactions of the type



Because these reaction products are volatile, protective barrier layers may not be formed, and corrosion may continue at a rate governed by the supply of oxidant.¹²⁷ All these processes require much-more-detailed investigation.

(2) Sintered Silicon Nitride

(A) *Production*: Early attempts to sinter Si₃N₄ powder under standard sintering conditions failed to yield material of significantly increased density or strength. It was recognized that this was mainly the consequence of the low lattice mobility of silicon and nitrogen and the high-temperature volatility of Si₃N₄, which led to microstructural coarsening but no density increase.¹²⁸ This classical "evaporation–condensation" mechanism for sintering, similar to surface diffusion, led to changes in particle shape and void distribution but no loss of void volume.¹²⁹ Even with the use of the standard liquid-forming additives successfully developed for hot-pressing, only small density increases were attainable. The physical loss of Si₃N₄ from pore surfaces in the component by decomposition to silicon vapor and nitrogen gas appeared also to counter the tendency for pore shrinkage to occur.

The accidental discovery at the Westinghouse laboratories by Terwilliger and Lange^{130,131} in 1976 that Si₃N₄ powder could be sintered without the need to apply mechanical pressure was a major step in the development of high-density Si₃N₄ ceramics. A graphite die "hot-pressing" experiment using MgO-doped Si₃N₄ powder was conducted at a higher than normal temperature without the application of the usual pressure, but significant shrinkage of the Si₃N₄ powder cylinder occurred. The reason was

that, in the confined space of the graphite die, loss of Si₃N₄ by evaporation had been restrained, and overall densification was, therefore, able to occur. In 1977, Mitomo,¹³² at the National Institute for Researches in Inorganic Materials in Japan, reported that they were able to obtain >90% density using 1 MPa of nitrogen pressure. Giachello and colleagues,¹³³ at the Fiat laboratories in Italy, then showed that the use of very high nitrogen pressure could be avoided if the compacted Si₃N₄ powder containing the sintering additive (MgO, for example) was immersed in a bed of loosely packed Si₃N₄ powder. In this way, the equilibrium vapor pressures of nitrogen, and equally importantly silicon, could be established over the component to suppress the outward fluxes of silicon vapor and nitrogen gas, leading to evaporation and pore growth. However, an outer skin of material, ~1 mm thick, failed to densify. This layer was deficient in MgO, and the longer the sintering time and the higher the temperature, the less MgO remained in the sample. At these high temperatures (>1500°C) and under the low oxygen pressures of the sintering environment, metal oxides also became significantly volatile, and loss of the essential liquid-forming additive occurred if steps were not taken to prevent it. In this case, incorporation of MgO into the surrounding powder bed (with BN powder to prevent simultaneous sintering of the bed) led to attainment of densities of >96% at 1800°C. At 1650°C, 98% density could be obtained in 5 h at 1 bar (10⁵ Pa) nitrogen pressure, using the powder bed technique to give a sintered Si₃N₄ of 500 MPa strength. Sintered silicon nitrides of high density are now readily obtained using a powder bed often supplemented with several bar nitrogen overpressures for good measure.

(B) *Densification Mechanisms*: Studies of the liquid-phase sintering mechanism through application of the classical Kingery models for liquid-phase sintering led to the belief that, following particle rearrangement, the major stage II rate-controlling step was either the diffusion from particle–particle contact points or solid–liquid interface reactions (solution and crystallization).¹³⁴ With Y₂O₃ additive, diffusion through a viscous nitrogen-containing liquid appeared to be rate controlling. With MgO additive, interface reactions appeared to be rate controlling, although this interpretation of data has been regarded as too simple because of changes in system composition and microstructure during sintering and difficulties of interpreting log–log plots.¹³⁵ A wide range of sintering additives for Si₃N₄ now has been explored, generally based on systems successfully developed for hot-pressing. Those most commonly used were MgO and Y₂O₃, often with incorporation of Al₂O₃. Although the amounts of additive used were usually similar, sintering temperatures had to be 200°–300°C higher than those used for hot-pressing, and 1850°–1900°C were not uncommon. Important additional processing conditions for the attainment of high density were identified as thorough mixing and homogenization of the powder (involving attritor milling over many hours) and the use of very fine (<200 nm) Si₃N₄ powder.

Many studies have been made of the influence of gas pressure on densification, including the staged application of pressure. It was realized that there were conflicting microstructural requirements for densification and subsequent property attainment. For rapid densification, a fine-grained equiaxed microstructure was needed to give maximum viscous flow grain-boundary sliding and rapid solution–crystallization. For good mechanical properties (e.g., toughness and strength), a high-aspect-ratio (although fine) grain microstructure was required.¹³⁶ A critical point in the densification process was a relative density of ~0.91 of theoretical, when pore closure occurred. Above this density, high gas pressures could be applied to accelerate sintering (gas-pressure sintering). The exact timing of pressurization was important, as was heating rate in the first stage to achieve early pore closure (and loss of surface area) and to minimize mass loss by evaporation. Onset of pore closure was also favored by high temperatures, despite the higher volatility, and this controlled temperature–pressure schedules. Significant densification rates were obtained by controlled increases of the gas pressure to 10 MPa. This

two-stage technique allowed the production, using 3%–6% sintering additive, of materials with grain sizes $\sim 0.5 \mu\text{m}$, aspect ratios of ~ 5 , and room-temperature bend strengths of $\sim 1000 \text{ MPa}$.

As a further refinement of the production process to improve purity and thereby microstructural quality, the processing of powders under clean-room conditions has been explored. This has been directed especially at reducing foreign-particle defects, and one pilot study has reported significant ($>10\%$) strength improvements over those obtained from standard laboratory conditions.¹³⁷

(C) *Mechanical Properties:* As with hot-pressed Si_3N_4 , developments that led to markedly improved properties were optimization of the $\beta\text{-Si}_3\text{N}_4$ grain size and aspect ratio. Microstructural development was as discussed in Section IV(1)(B) above, controlled by the properties of the Si_3N_4 powder ($\alpha\text{-Si}_3\text{N}_4$: $\beta\text{-Si}_3\text{N}_4$ ratio and $\beta\text{-Si}_3\text{N}_4$ particle-size distribution), additive composition, and sintering temperature and time. The composition of the intergranular glass was clearly important for the development of microstructure; examination of the changes of lanthanide (Ln) element in a $\text{Ln}_2\text{O}_3\text{-Al}_2\text{O}_3$ sintering system showed a marked influence of lanthanide size on grain aspect ratio and grain-size distribution, indicating its influence on Si_3N_4 plane interfacial energies.¹³⁸ Most Si_3N_4 materials were prepared using $\alpha\text{-Si}_3\text{N}_4$ -rich powders that transformed during sintering to $\beta\text{-Si}_3\text{N}_4$, with aspect ratios comparable to whiskers if there was no strong steric hindrance. Such high-aspect-ratio $\beta\text{-Si}_3\text{N}_4$ materials could be regarded as whisker-reinforced ceramics, and the rodlike $\beta\text{-Si}_3\text{N}_4$ grains acted to toughen the material.

For maximum fracture toughness and strength, a high proportion of high-aspect-ratio $\beta\text{-Si}_3\text{N}_4$ grains was required. Early studies on hot-pressed Si_3N_4 had shown a marked correlation between $\beta\text{-Si}_3\text{N}_4$ grain aspect ratio and fracture toughness (Fig. 16),¹³⁹ and, as expected, a similar correlation existed for sintered Si_3N_4 . This was achieved by control of $\beta\text{-Si}_3\text{N}_4$ nuclei density and $\beta\text{-Si}_3\text{N}_4$ particle size, and the highest-strength materials were obtained from Si_3N_4 powders containing a high proportion of α phase. Starting powders containing a high proportion of $\beta\text{-Si}_3\text{N}_4$ gave fine-grained but equiaxed $\beta\text{-Si}_3\text{N}_4$, of lower toughness and strength. Extensive work showed that fracture toughness (K_{Ic}) could be increased from $\sim 3 \text{ MPa}\cdot\text{m}^{1/2}$ using starting powder containing 70% $\alpha\text{-Si}_3\text{N}_4$ to $6 \text{ MPa}\cdot\text{m}^{1/2}$ using starting powder containing 100% $\alpha\text{-Si}_3\text{N}_4$. $\beta\text{-Si}_3\text{N}_4$ grain aspect ratios of $>10:1$ were achieved by controlled annealing treatments.¹³⁸ Si_3N_4 containing large-diameter ($>1 \mu\text{m}$) elongated $\beta\text{-Si}_3\text{N}_4$ grains developed toughness of $\sim 10 \text{ MPa}\cdot\text{m}^{1/2}$. Therefore, such materials could be regarded as early examples of ceramic-reinforced ceramic-matrix composites, for which close control of interfacial bond

strength was important. Weak interfaces favored high toughness, but the debonding of very large β grains resulted in the development of fracture origins and loss of strength. Current best room-temperature values for K_{Ic} and strength for as-formed sintered materials are in the region of $7\text{--}10 \text{ MPa}\cdot\text{m}^{1/2}$ and 1100 MPa .^{140,141}

However, the microstructural design of these materials must also take account of the effects of silicate phase composition and content on creep, fatigue, and oxidation resistance.¹⁴² Other practical advantages of high toughness values are resistance to machining damage and improved fatigue behavior, K_{Ic} increasing with the volume fraction of elongated grains, and scaling with $(\text{grain size})^{1/2}$, an effect attributed to crack wake mechanisms, such as crack bridging, grain rotation, and grain pullout.

As with other whisker/fiber composites, the $\beta\text{-Si}_3\text{N}_4$ -glass interfacial bond strength and the suppression of debonding led to increased transgranular fracture and reduced toughness. This was also controlled by intergranular phase composition, with decreasing $\text{MO}:\text{Al}_2\text{O}_3$ ratio and increased nitrogen content leading to increased interfacial bond strength.^{143,144} Improvements in toughness resulting from the development of large grains minimized reductions in strength as the size of the larger elongated grains increased: 1983–1993 saw significant improvements in strength and fracture toughness.

A combination of fine grain size and intergranular glass also allowed high-temperature superplastic behavior to be developed.¹⁴⁵ An additional aspect of superplasticity was that, as a result of alignment of the high-aspect-ratio $\beta\text{-Si}_3\text{N}_4$ grains during superplastic forging treatments, highly anisotropic microstructures could develop. As a possible result of reduction in flaw size and steep *R*-curve behavior, bend strength values $>2 \text{ GPa}$ and very high fracture toughnesses ($>8 \text{ MPa}\cdot\text{m}^{-1/2}$) were achieved when the stress was applied perpendicularly to the pressing direction.¹⁴⁶

(D) *Grain-Boundary Chemistry:* Considerable attention has been directed to the nature of the grain-boundary films in sintered Si_3N_4 using HRTEM.^{147–149} It had long been recognized for hot-pressed Si_3N_4 that glass films at grain faces and junctions were important for high-temperature creep behavior (and posed the question of why they were not squeezed out during hot-pressing¹⁵⁰). It became evident that amorphous films derived from the liquid-phase sintering additives were present at almost all Si_3N_4 grain faces (Fig. 17). High-purity Si_3N_4 densified with SiO_2 alone produced films 1.0 nm thick, independent of Si_3N_4 grain orientation and SiO_2 volume fraction (the excess was present at grain edges and corners). Materials densified with liquid-forming metal oxide additions had grain-boundary thicknesses and compositions characteristic of the additive system, and there was strong dependence of film thickness (typically in the range $0.5\text{--}1.5 \text{ nm}$) on chemical composition. Subsequent annealing treatments leading to crystallization of “bulk” grain edge material may have, in turn, led to changes in interface chemistry and film thickness.

These observations provide support for the Clarke^{151,152} steric model for an equilibrium film thickness, controlled by a balance of forces: attractive van der Waals and repulsive steric forces resulting from distortion of the SiO_4 tetrahedra in the SiO_2 glass. To these can be added an electrical (“double layer”) force, influenced by the presence of charged species (cations). Increasing cation concentration is believed to lead to increased electrical double layer forces and an increase in film thickness (by 30% for 0.25 vol% additions of CaO); it is evident that small changes in interfacial chemistry strongly affect the grain-boundary film thicknesses and may lead to degradation of high-temperature properties. Recently, evidence has been obtained that these film thicknesses can be perturbed (to the extent in some cases of complete squeezing out) as a result of redistribution of the grain-boundary liquid during high-temperature plastic deformation.¹⁵³ This work reflects a remarkable analysis for the variations in chemical composition of a material on the scale of $<1 \text{ nm}$, but nonetheless vitally important for an understanding of the mechanical properties of Si_3N_4 .

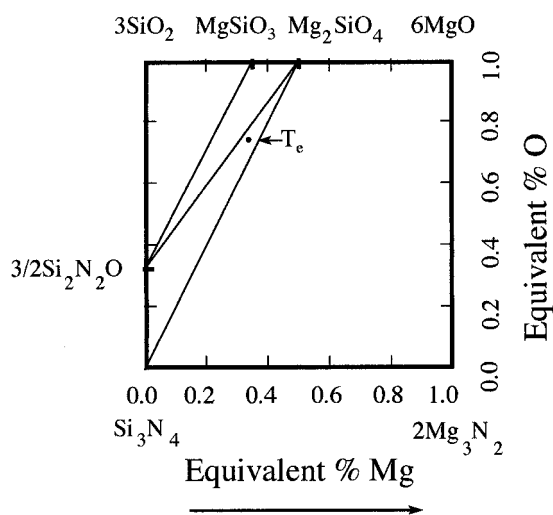


Fig. 16. $\text{Si}_3\text{N}_4\text{-MgO}$ system. (After Lange.¹⁰³)

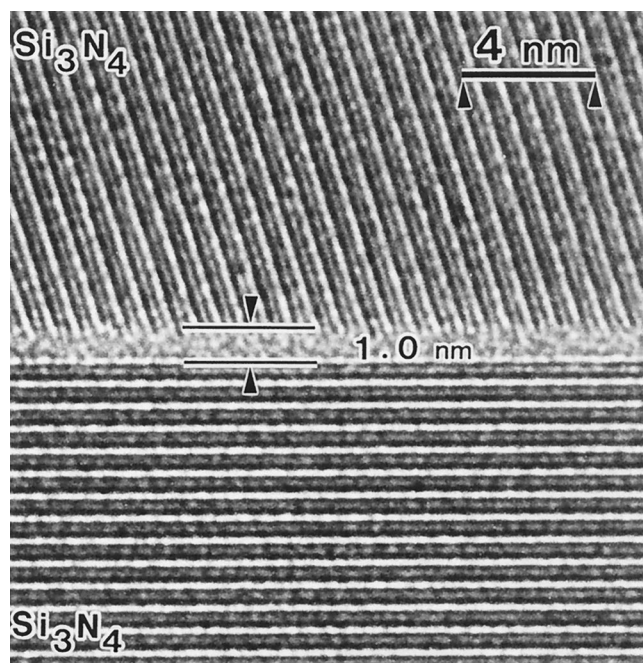
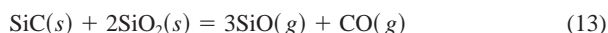


Fig. 17. Si_3N_4 - Si_3N_4 boundary in hot-pressed Si_3N_4 , showing the amorphous film. (Courtesy of C. M. Wang.)

V. Silicon Nitride Powders

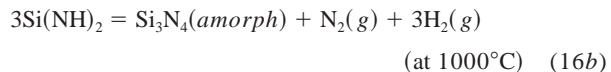
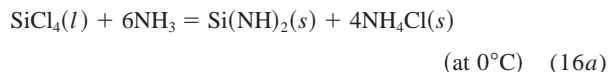
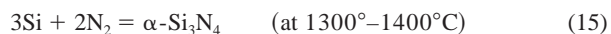
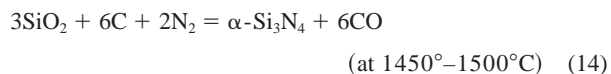
The need for high-purity Si_3N_4 powders for hot-pressing and sintering was recognized since the significance of impurity cations for the high-temperature strength of hot-pressed Si_3N_4 was first appreciated.^{154,155} Other essential requirements for a sinterable powder, it was quickly realized, were a small mean particle size (<200 nm),^{128,156} a narrow particle-size distribution, an equiaxed morphology, and the absence of agglomerates. Other important factors affecting sinterability and microstructural quality were the α - Si_3N_4 : β - Si_3N_4 ratio (90%–98% being optimum) and the carbon and oxygen contents.

Oxygen is present in each particle as internal oxygen and as a nanometer surface layer of $\text{SiO}_2/\text{Si}_2\text{N}_2\text{O}$. High-surface-area powders have a higher oxygen content and a greater proportion of surface oxygen. However, >50% of the oxygen is within the particle and is not removable by HF washing or high-temperature treatment under hydrogen.^{42,157,158} Because oxygen is involved in liquid formation with the densification additives, the amount present needs to be accurately known. Carbon may be present as SiC and can lead to loss of the oxygen at high temperature through the reaction



There was no disagreement about desirable powder characteristics; however, there was a choice of production routes. The three commercially used for powder production were silicon powder

nitridation, carbothermal reduction of SiO_2 under nitrogen, and high-temperature decomposition of silicon diimide.¹⁵⁹



The carbothermal reduction of SiO_2 powder under nitrogen was the earliest used method for Si_3N_4 production and is now considered by some as the most-cost-effective industrial route for the production of high-purity α - Si_3N_4 powder; it is now a standard commercial process. It also has been possible to develop the fluidized bed technique as a route to the larger-scale production of material.¹⁶⁰ The nitridation of silicon powder was developed in the 1960s, following the “rediscovery” of Si_3N_4 and was the first large-scale method for powder production. Earlier grades of Si_3N_4 powder made by this route, as indicated above, suffered from contamination by impurities (silicates and iron) in the silicon source powder. The development of the long-known but little-used silicon amide route¹⁶¹ relied on the increased availability of low-cost silicon tetrachloride. Silicon diimide decomposition gives initially amorphous Si_3N_4 , which is converted to the α - Si_3N_4 form by heating under nitrogen at 1400°–1500°C; this is now the second-most-important route for commercial production.

Each form of powder has its own characteristics and trace impurities, some of which may be introduced as contaminants from the milling of agglomerates. Comparative reviews made of production methods and general powder properties have established that the wide differences in Si_3N_4 densification behavior are related to powder characteristics, of which α - Si_3N_4 content, ultimate crystallite size, and oxygen content are important factors.¹⁶² A selection of typical properties and compositions for Si_3N_4 powders is shown in Table II.

All these methods involve low-cost raw materials and yield high-purity high- α - Si_3N_4 powders, but the need for very careful control over the production process and subsequent milling and purification steps ultimately result in high prices (~40–300 US\$/kg) for the relatively small quantities of powder currently required. The cost of materials represents 30%–50% of the cost of a sintered Si_3N_4 component, and the high cost of Si_3N_4 powder is one reason for the slow acceptance of Si_3N_4 ceramic components in the market.¹⁶³

In principle, the reactions of vapor-phase species, which can be obtained in a very pure state, should yield equally high-purity Si_3N_4 powders and avoid the need for extended milling. Later attempts to produce nanosized powders use CO_2 laser and plasma-energized reactions of silane and ammonia:



Table II. Typical Silicon Nitride Powder Properties[†]

Property	Route		
	Silica/carbon	Silicon/nitrogen	Diimide
Specific surface area (m^2g^{-1})	12	22	12
α content (%)	99	98	98
d_{50} (μm)	1.63	0.63	0.65
Oxygen (%)	2.2	1.9	1.7
Carbon (%)	0.8	0.2	0.1
SiC (%)	2.5	0.5	<0.2
Chlorine (ppm)	<10	40	500

[†]References 159 and 160.

Particle sizes of the amorphous product are typically 10–25 nm, from which equiaxed α - Si_3N_4 is produced by crystallization at 1400°C.¹⁶⁴ Production rates are, however, very slow, and the commercial viability of this route seems questionable.^{165,166}

VI. Amorphous Thin Films

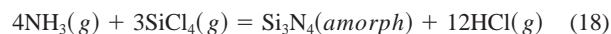
Because pure Si_3N_4 powder could not be sintered to full density, CVD methods successfully applied for the production of thin-section SiC ¹⁶⁷ were also explored in the case of Si_3N_4 . One immediate objective was to provide dense, stable, crystalline ~ 100 μm coatings to seal the surfaces of porous RBSN.¹⁶⁸ Later work was directed at the production of thicker deposits as precursors for thin-wall components for applications at high temperature. Considerable efforts were made over an extended period at laboratories in Japan¹⁶⁹ and in the United States^{170,171} to develop this route to the production of dense, high-purity polycrystalline Si_3N_4 , which was expected to have good high-temperature strength and oxidation resistance because of the complete absence of intergranular glass.

Amorphous and crystalline (normally α phase) Si_3N_4 could be produced at temperatures $>1200^\circ\text{C}$ from a range of silicon-bearing reactants, such as SiH_4 , SiF_4 , and SiCl_4 and NH_3 (reactions (18) and (19) below). Thin polycrystalline films formed using this method at $\geq 1200^\circ\text{C}$ and at low rates (<35 $\text{nm}\cdot\text{h}^{-1}$) were generally theoretically dense α - Si_3N_4 , of grain size 0.1–1 μm , and uncracked. Later work showed that, provided the reactant gas pressures were sufficiently low (less than ~ 0.1 bar (10^4 Pa)), much thicker (>4 mm) uncracked deposits of polycrystalline CVD Si_3N_4 could be obtained on graphite formers at rates of up to 0.4 $\text{mm}\cdot\text{h}^{-1}$. The quality and microstructure of the product depended critically on the production conditions of temperature, reactant gas partial pressure, and total gas pressure and flow rate. It was also shown to be possible to produce CVD β - Si_3N_4 by this method in the presence of TiCl_4 vapor.¹⁷² However, the CVD form of Si_3N_4 has, to date, remained undeveloped for structural applications, mainly because the low pressures of reactants necessary result in slow rates of material production and the limitations in the dimension and shape capabilities of the CVD technique.

In contrast, the CVD production of very thin amorphous Si_3N_4 films rapidly became extremely important in the semiconductor

device field,^{24,173,174} and much of the success of silicon-integrated circuits has been due to the properties of Si_3N_4 , combined with those of SiO_2 . From ~ 1960 – 1970 , amorphous Si_3N_4 , usually in the form of 100–200 nm films, was extensively developed as a high-dielectric-strength material and as impervious dielectric films to replace or supplement SiO_2 films in semiconductor device production and use, which permitted multistage production of integrated-circuit components containing controlled doped layers (Fig. 18). Amorphous Si_3N_4 is now widely used as a passivation layer or a barrier to alkali or moisture diffusion, as a masking layer to prevent oxidation or diffusion in underlying materials in patterned areas, and as a final protection layer to finished devices because of its hardness and radiation resistance.¹⁷⁵

The amorphous form of Si_3N_4 has the fundamental SiN_4 and NSi_3 structural units of the crystalline forms, but lacks the longer-range ordering. There is also a tendency for its stoichiometry to depart from the 3:4 ratio. The density of amorphous Si_3N_4 is less than the crystalline forms, but increases with production temperature and can reach ~ 3 $\text{Mg}\cdot\text{m}^{-3}$ (95% of the value for crystalline Si_3N_4). The most important properties of amorphous Si_3N_4 are its low permeability toward sodium, oxygen, H_2O , and hydrogen (because of the rigid covalent structure), high electrical resistivity (10^{12} $\Omega\cdot\text{m}$), hardness, and good resistance to chemical attack.^{174,176} Very thin amorphous films can readily be obtained by the direct nitridation of silicon by NH_3 at temperatures up to 950°C . However, this reaction is self-limiting to ~ 10 nm thicknesses because of the low diffusivity of nitrogen in Si_3N_4 . Thicker films can be obtained readily by CVD reactions of NH_3 and SiCl_4 or SiH_4 with nitrogen carrier gas:



SiCl_4 is thermally more stable and, therefore, more useful for the higher temperature and faster production of thicker deposits. Below $\sim 1100^\circ\text{C}$, smooth films are obtained, but films of thickness >200 nm tend to develop cracks, particularly during annealing and crystallization at $\sim 1500^\circ\text{C}$.

Amorphous Si_3N_4 films are generally nonstoichiometric, and the compositions are best represented as $\text{Si}_x\text{N}_y\text{H}_z$, where z is between 0 and 0.1, and the N:Si ratio is between 0.5 and 1.6. The

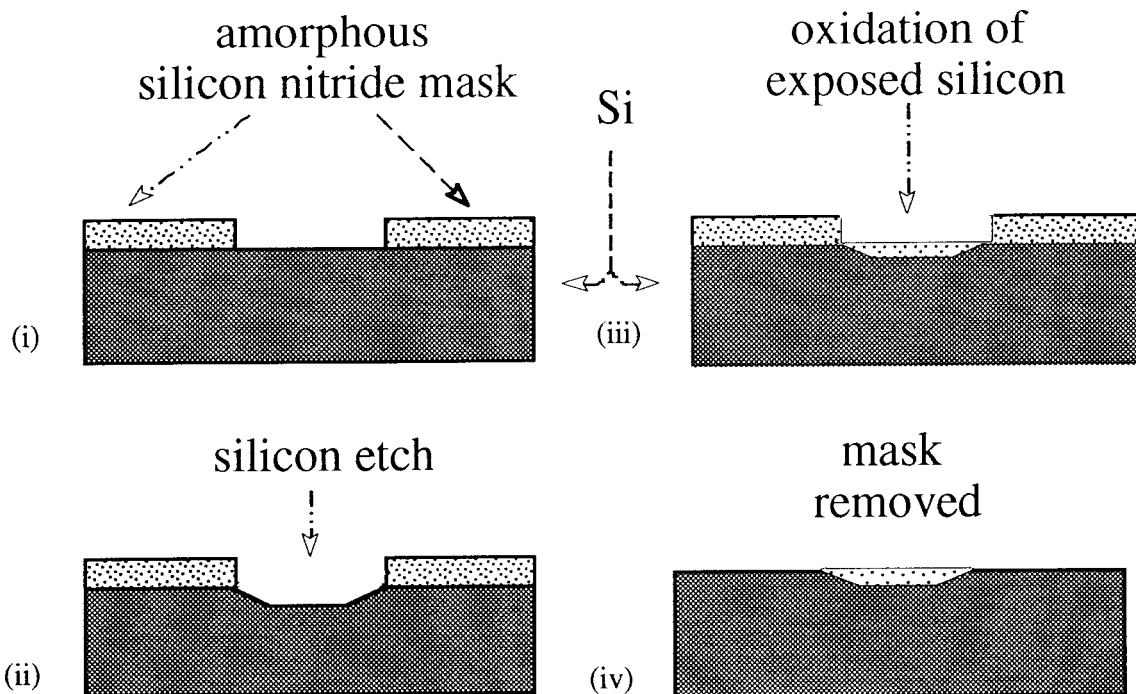


Fig. 18. Schematic showing stages in the use of a Si_3N_4 mask in the construction of a recessed oxide pattern on a silicon surface.

structural hydrogen is important for density, etch rates, and permeability. CVD has been the most common production method used, conducted either at atmospheric pressure (APCVD) or at pressures between 10^{-4} and 10^{-2} bar (10 and 10^3 Pa) (LPCVD). Until ~1974, the standard deposition reaction used SiH_4 and NH_3 at 1 bar (10^5 Pa) pressure in a cold-wall reactor with temperatures between 700° and 900°C to give deposition rates of >10 $\text{nm}\cdot\text{min}^{-1}$. More-modern LPCVD hot-wall reactors use dichlorosilane (SiCl_2H_2) and NH_3 at 700° – 800°C with pressures of 10^{-4} – 10^{-3} bar (10 – 10^2 Pa).¹⁷⁷ This method is now routinely used in conjunction with complex molecular excitation systems, such as plasma enhancement (PECVD), laser enhancement (LECDV), and ultraviolet photon enhancement (PHCVD), as well as microwave and electron cyclotron resonance, for the high-speed and large-scale production of Si_3N_4 films on silicon and other substrates (to reduce stress levels in CVD Si_3N_4 films on a silicon substrate, 5–50 nm buffer layers of pyrolytic SiO_2 are normally first put down). With PECVD, deposition temperatures can be as low as 200° – 300°C with 10^{-3} bar (10^2 Pa) 30 kHz to 13 MHz glow discharge energization, giving growth rates of the order of tens of $\text{nm}\cdot\text{min}^{-1}$.

VII. SiAlONs

The solid solubility of Al_2O_3 in the β - Si_3N_4 lattice was discovered independently at about the same time (1971–1972) in the United Kingdom at the University of Newcastle-upon-Tyne (Jack and Wilson²³) and in Japan (Oyama¹⁷⁸). One of the reasons for exploration of this system was to determine if a material could be produced that would combine the good thermal-shock resistance of Si_3N_4 with the sinterability of Al_2O_3 . The major product of the reaction between Al_2O_3 and Si_3N_4 had the β - Si_3N_4 crystal structure, a low thermal expansion coefficient, and appeared to be more readily densified by hot-pressing. It was at first proposed that the β' -SiAlON region extended along the Si_3N_4 – Al_2O_3 and Al_2O_3 – Si_3N_4 joins and filled the region between them¹⁷⁹ and that the readier densification behavior was influenced by the lattice vacancies in a defect structure. This range of lattice substitution appeared to be possible because of the similarities in bond lengths between Si–N (175 pm) and Al–O (175 pm) and between Al–N (187 pm) and Si–O (162 pm). However, after initial uncertainties resulting from compositional drift caused by loss of volatile material (SiO and N_2) at reaction temperatures in the region of 1750° – 1800°C ,¹⁸⁰ the phase composition (based on a unit cell of Si_6N_8) was shown to be $\text{Si}_{(6-z)}\text{Al}_z\text{O}_z\text{N}_{(8-z)}$, retaining the 3:4 metal:nonmetal ratio, with z values in the range 0–4.2 (equivalent to ~70 wt% Al_2O_3), and the single-phase form continued not to be readily sintered.¹⁸¹ Much detailed work conducted mainly at Newcastle and Stuttgart and published four years later (1975–1976)^{179,182} established that β' -SiAlON extended only along the Si_3N_4 – Al_2O_3 join from $z = 0$ to $z \approx 4.2$ (Fig. 19). Doubts had, in

fact, earlier been expressed about the β' -SiAlON homogeneity range by creep measurements,¹⁸³ suggesting that the compositions along the Al_2O_3 – Si_3N_4 join contained glass and that materials of composition 3M:4X had minimum creep rates. Other Al-Si-N-O phases were subsequently identified in the Si_3N_4 – SiO_2 – Al_2O_3 –AlN system, and phase behavior relationships were mapped out in detail.^{182,184,185} The high-temperature reaction of Si_3N_4 and Al_2O_3 usually gave β' -SiAlON and an SiO_2 -rich “X-phase,” a “nitrogen mullite” of approximate composition $\text{Si}_3\text{Al}_6\text{O}_{12}\text{N}_2$.^{186,187} X-phase melted at $\sim 1670^\circ\text{C}$ and, therefore, in principle, provided an inbuilt liquid-phase-sintering system for SiAlON compositions based on starting powders in the Si_3N_4 – SiO_2 – Al_2O_3 –AlN pseudoquaternary system (and lacking in the simpler Si_3N_4 – SiO_2 system), allowing hot-pressing to be conducted without the need for extra metal oxide additive. The amount of X-phase could be decreased as a result of the evaporation of SiO_2 at temperatures $>1800^\circ\text{C}$.¹⁸⁸ In practice, densification by pressureless sintering of β' -SiAlON materials was more readily achieved through the use of metal oxide additives, such as MgO ¹⁸³ and Y_2O_3 , developed for hot-pressing, and these and related additives became included in powder formulations.

The production of SiAlON phases containing other metal oxides was established in 1972.²³ Reactions of Si_3N_4 with, for example, Al_2O_3 and Li_2O , provided a β' -SiAlON and a phase with the α - Si_3N_4 crystal structure (α' -SiAlON). Oxides providing the α - Si_3N_4 structure were those of lithium, magnesium, calcium, yttrium, and lanthanides of $Z > 58$. The α' -SiAlONs had the general composition $\text{M}_x\text{Si}_{12-(m+n)}\text{Al}_{(m+n)}\text{O}_n\text{N}_{(16-n)}$, where x is determined by the valence of M and typically is <2 .¹⁸⁹ Because of the established role of Y_2O_3 as a densification aid for hot-pressing of Si_3N_4 ,¹⁰⁹ the Y-Si-Al-O-N and rare-earth oxide systems were explored in considerable detail.¹⁹⁰

A distinguishing feature of the α' -SiAlON– β' -SiAlON system is that the α' to β' phase transformation is fully reversible, and the two phases have characteristic morphologies: The β' phase forms with the elongated grains typical of β - Si_3N_4 and gives increased fracture toughness, whereas the α' -phase grains tend to be small and equiaxed. The mechanical properties of these materials, therefore, can be controlled by the α' -SiAlON: β' -SiAlON ratio and, in turn, by production conditions.^{24,191–194} A further important feature of the α' -SiAlON– β' -SiAlON relationship is that the α' phase appears to be more stable at lower temperatures. The phase composition can be controlled by heat-treatment procedures when rare-earth oxides are used as sintering aids. Because the α' phase can accommodate metal oxides, whereas, in general, the β' phase does not do so readily, metal oxides are rejected to the intergranular regions during the α' -SiAlON to β' -SiAlON transformation, a process expressed by the general phase equation

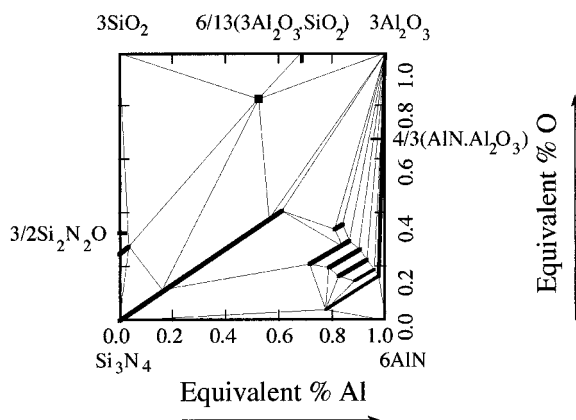
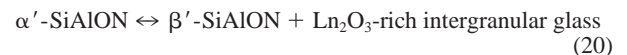


Fig. 19. Phase relationships in the SiAlON system. (After Jack.¹⁸⁰)

Because of the release of glass on conversion of the α' -SiAlON to β' -SiAlON, the high-temperature properties of the SiAlONs may deteriorate. However, in principle, the transformation provides a mechanism for optimizing phase content and microstructure merely by appropriate heat treatments, and a range of hardness, strength, and toughness values can be obtained from a single starting composition.²⁴

Thus, the SiAlON systems, containing Al_2O_3 , with the related possibilities for the inclusion of other elements in the Si_3N_4 lattice, in contrast with the Si_3N_4 -based materials, have greater phase complexity and more degrees of freedom to permit the development of specific microstructures and sets of properties. The SiAlON systems have been examined in parallel with Si_3N_4 materials, which do not contain Al_2O_3 , in establishing the better understanding needed to obtain optimum processability and properties of these materials. There remains much work to be done in both classes of this system.

VIII. Ceramic Applications

(1) Overview

Two sets of important features underpin the applications of Si_3N_4 ceramics: the intrinsic properties of good resistance to thermal shock and refractoriness and the other specific qualities characteristic of material type. For sintered Si_3N_4 , these are a fibrous and fine-grained microstructure giving high fracture toughness, high strength, and very good tribological and wear characteristics, and, for RBSN, an intrinsic and extremely useful complex shape fabricability (Fig. 20).

Cost is always an important factor determining applications, and, at the present time, the price of high-purity sinterable Si_3N_4 nanopowder is $\sim 50\text{--}200$ US\$/kg. Additional factors tending to increase production costs are the necessity for very careful Si_3N_4 powder processing and blending stages to secure the dense, homogeneous, and fibrous sintered microstructures necessary for achieving maximum mechanical property values and reproducibility: The cost of the very-high-temperature controlled atmosphere sintering also has to be taken into account. High-quality, micrometer-sized silicon powder, which is widely used in the metallurgical area, is much less expensive (4 US\$/kg), but this factor is offset by the length of time required for the controlled nitriding process at $1200^\circ\text{--}1450^\circ\text{C}$. Cost limits the use of Si_3N_4 -based materials to applications where the performance benefit is so great that it justifies the premium price or where the size of the ceramic component is so small that raw-material cost does not dominate the overall price. However, a wide range of niche markets now has been established for RBSN and dense-sintered Si_3N_4 materials.^{11a,195}

Si_3N_4 was first commercially developed in the 1950s, initially as a refractory bonding phase; nitride-bonded SiC refractories continue to be a very important commodity,¹⁹⁶ with world sales approaching 20 000 tonnes/year. If only 5% of this material is considered to be a Si_3N_4 bonding phase, this is, strictly speaking, the single biggest application for Si_3N_4 . In contrast, the worldwide annual output of sinterable Si_3N_4 powder is currently estimated to be between 300 and 350 tonnes, to which can be added ~ 30 tonnes of RBSN. The resistance to attack by molten metals of Si_3N_4 is also appreciated and leads to applications for RBSN components in molten aluminum handling and casting.⁹

However, the major driving force for the development of Si_3N_4 ceramics in the 1960s and 1970s was, without doubt, the enticing prospect of high-efficiency ceramic gas-turbine and reciprocating

engines running at very much higher temperatures than were possible with conventional metallic engines, thereby achieving significantly higher thermodynamic efficiency, lower engine weights, and improved fuel consumption. This extremely demanding application required high hot strength, creep, thermal shock, and oxidation-resistant materials of high reliability: Si_3N_4 and SiC were identified as prime candidates for development. SiC proved to be more difficult to produce to full density and had low fracture toughness: The theoretical advantage of its better thermal-shock resistance through higher thermal conductivity did not, in practice, adequately offset these disadvantages. Therefore, Si_3N_4 became the major engine hot-zone candidate material: SiC-silicon composite materials were, however, extensively developed as pump seal materials, gas-turbine combustion chambers, and industrial heat exchangers. A selection of sintered Si_3N_4 components is shown in Fig. 21.

(2) Automobile

Much of the work conducted on Si_3N_4 in the 1960s and 1970s was directed at the introduction of dense-sintered and porous RBSN hot-zone components into a new range of advanced gas-turbine and reciprocating engines, with projected significantly higher operating temperatures and efficiencies.¹⁹⁷ Many test engines were developed and satisfactorily evaluated, but major barriers to the incorporation of Si_3N_4 components into standard engines were the costs of processing and the severe technological problem of the mass production of complex ceramic components with a very high degree of reproducibility and long-term reliability.¹⁹⁸

The control of reproducibility and reliability is not a problem unique to Si_3N_4 ceramics: It has its roots in the fundamental aspects of the ceramic-powder blending and sintering processes. However, because of the inherent difficulty of sintering Si_3N_4

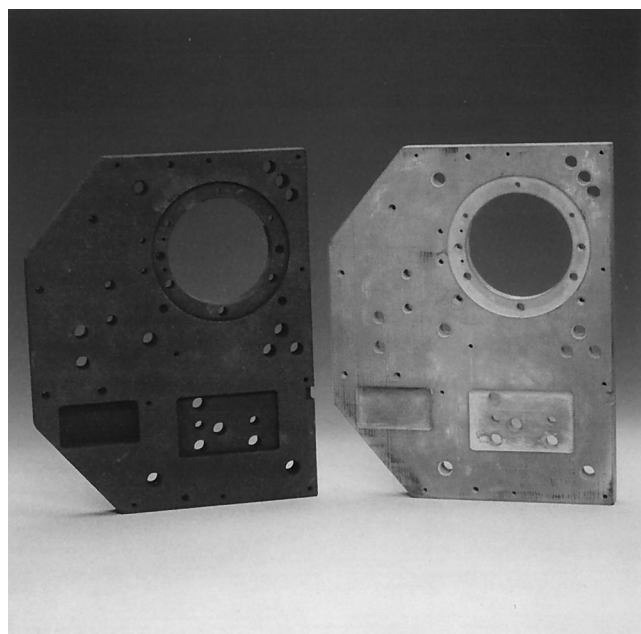


Fig. 20. RBSN: (left) presintered silicon and (right) nitrided component. (Courtesy of Morgan Matroc, plc.)



Fig. 21. Sintered Si_3N_4 components. (Courtesy of Ceradyne, Inc.)

powder to full density and the retention of the essential microstructure of the silicon powder in RBSN, both forms of this material are particularly unforbearing of defective powder processing.

The original ceramic engine programs were expensive and have been estimated to have cost several thousand million dollars¹⁹⁹ during almost 40 years of effort, at the end of which there was no commercial ceramic engine. That a complete ceramic engine did not materialize was, in part, the result of the lack of adequate reliability and high materials costs,^{164,200} set against the severe difficulties of making any type of major change in engine design or component material. Thus, the early programs have been regarded, in a very strict sense, as failures.²⁰¹ Nonetheless, routine and large-scale use is now made by some manufacturers of automobile diesel engines of small, dense, sintered Si_3N_4 components, e.g., glow plugs, swirl chambers, and turbocharger rotors, where stresses and temperatures are relatively low and the consequences of failure not catastrophic for the engine as a whole. Table III lists some applications of Si_3N_4 in production (diesel or spark-ignited) reciprocating engines.

The range of Si_3N_4 components now used in engines of many types would not have been the case without the improvements to the materials and their processing generated by these intensive development programs. In terms of understanding the Si_3N_4 ceramics and, particularly, the dense, sintered forms of material, can today be regarded as the most mature of all the technical ceramics.

The largest current market for Si_3N_4 components is in reciprocating (diesel and spark-ignited) engines.²⁰² Most of these components are manufactured in the United States and Japan, although considerable development work also has been conducted in Germany and other European Union countries. In the United States, the driving force for the use of ceramic-engine components has been emissions reductions, in Japan improved performance.

It is estimated that >300 000 sintered Si_3N_4 turbocharger rotors are manufactured annually.¹⁹⁹ In Japan, most applications are in light-duty engines, in the United States medium- and heavy-duty diesel engines. These applications are not the very-high-temperature applications originally envisaged, but rely on the low density (and mass and inertia) of the Si_3N_4 component coupled with high strength and toughness required to withstand impact damage.²⁰³ Current development work concerns the cautious further introduction of Si_3N_4 components to diesel and spark-ignited engines, in locations where low mass and improved wear resistance are required, such as exhaust valves, valve spring retainers, bucket tappets, rocker arm pads,²⁰⁴ and valve springs (Fig. 22).

(3) Bearings

The wear resistance, low friction, high stiffness, and low density of Si_3N_4 has led to the development, in the sintered form, of high-temperature and unlubricated roller and ball bearings. Friction and rolling contact fatigue rates are low; this gives Si_3N_4 bearings longer life than conventional higher-density steel and



Fig. 22. Si_3N_4 springs. (Courtesy of NHK Spring Co., Ltd.)

hard-metal bearings. Applications include abrasive environments in oil drilling, vacuum pumps, and sterilizable and unlubricated dental drills.¹⁷⁶

(4) Metal Working

The possibility of high-speed metal cutting was demonstrated in the 1970s, and Si_3N_4 and SiAlON cutting tips entered commercial production in the 1980s. Sintered Si_3N_4 cuts cast iron, hard steel, and nickel-based alloys with surface speeds up to 25 times those obtainable with conventional materials, such as WC. Considerable use is made of Si_3N_4 -based cutting-tool inserts for machining cast iron in the automotive industry and for machining nickel-based superalloys for the aero industries. The advantages of Si_3N_4 over Al_2O_3 -based materials are its significantly higher toughness and its ability to withstand rapid temperature changes. Therefore, silicon nitrides have a small proportion of the ceramic cutting-tool market (the bulk of which uses fine-grained Al_2O_3). Diamond-coated Si_3N_4 cutting tools also have been evaluated.²⁰⁵

(5) Industrial

One of the earliest applications for RBSN was as a thermocouple sheath materials for use in hot-metal-processing areas, and a small but steady demand continues. A larger market is for components used for the handling and die-casting of low-melting and reactive aluminum, for which the increasing requirements for aluminum purity make the use of metallic components less desirable. Internally threaded shroud nozzles, for inert-gas welding and cutting torches, developed in the 1980s, also provide a steady market for RBSN because of its strength and electrical resistance, and its better thermal-shock resistance compared with Al_2O_3 . On a smaller scale, specialized kiln furniture of low thermal mass and

Table III. Silicon Nitride Engine Applications[†]

Component	Year introduced	Benefits
Glo-plugs	1981–1985	Faster start-up
Precombustion chamber	1983–1986	Lower emissions, lower noise, faster start-up
Rocker-arm pads	1984, 1987	Lower wear
Turbocharger	1985–1989	Lower inertia lag
Fuel injector link	1989	Reduced wear, lower emissions
Cam roller follower	1991	Increased injection pressure, lower emissions
Fuel injector check ball	1992	Reduced wear, lower emissions
Compression brake master	1993	Reduced wear on cylinder wear face
Exhaust gas control valve	1993	Increased acceleration, reduced gas leakage

[†]After Katz.²⁰²

thermal shock resistance has been satisfactorily produced in RBSN: It finds application, for example, in dental porcelain firing trays and supports, where repeated cycling of the furniture to firing temperature is required. Weld location pins to assist in the precision welding of small components are widely used in sintered Si_3N_4 on the basis of thermal-shock characteristics and strength at high temperature.

IX. The Future

Si_3N_4 has, during the past 40 years, developed into a range of very well-established materials with many very useful properties, of which resistance to thermal shock, high-temperature stability, hardness, and wear resistance are, at the moment, the most important. These properties have led to the establishment of many applications, using, at the present time, relatively small quantities of material.

Considerable over-optimism and the over-promotion of Si_3N_4 ceramics in the early days of their development as very-high-temperature structural materials for internal combustion engine applications generated some disillusionment, but many steady markets have now been developed, where the materials are better than other established ceramic options, such as Al_2O_3 , cordierite, ZrO_2 , or SiC , in terms of one or more of the important criteria of fabricability, properties, and price. By way of partial realization of the early high hopes for Si_3N_4 as an engine ceramic, several automobile components are now standard ceramic production items. This limited acceptance and the better appreciation and understanding of the qualities and shortcomings of these materials gained on relatively large-scale production lines, must lead to improvements in production technology and engineering confidence.

The full incorporation of Si_3N_4 as engine hot-zone moving components remains many years away: Serious obstacles are the lack of detailed knowledge about the long-term reliability of the components and their high cost. Cost remains a major barrier to the more-widespread use of Si_3N_4 materials, and will do so until larger-scale supplies of less-expensive raw materials, particularly high-quality Si_3N_4 powder, can be established. The problem is that cost and quantity are interrelated: This is a vicious circle, from which an escape is needed. One route might be generated if social or economic forces were to swing strongly against current materials or engine systems: Then a wider use of ceramic components might be seen to be one solution to economic or materials supply problems. The more likely scenario is that of a slow, but steady, increase in the range of Si_3N_4 components and applications, extending over the next 10–20 years before any major surges in demand occur. Amorphous Si_3N_4 thin films face no such problems, and their widespread use in the microelectronics area has become completely accepted: The absolute quantities needed are very small, and the technology for the production of this type of the material is very well established.

The separate major challenge to the ceramics community now is to apply the knowledge and understanding gained with regard to the principles underlying the powder processing, microstructure development, thermomechanical properties, and quality control of Si_3N_4 ceramics to achieve comparable improvements in quality, engineering acceptability, and marketability in other ceramic materials.

Acknowledgments

The willing assistance of many colleagues, associates, and former students with the provision of detailed information concerning many aspects of the production, properties, and applications of Si_3N_4 and illustrations (not all of which could be used) is gratefully acknowledged.

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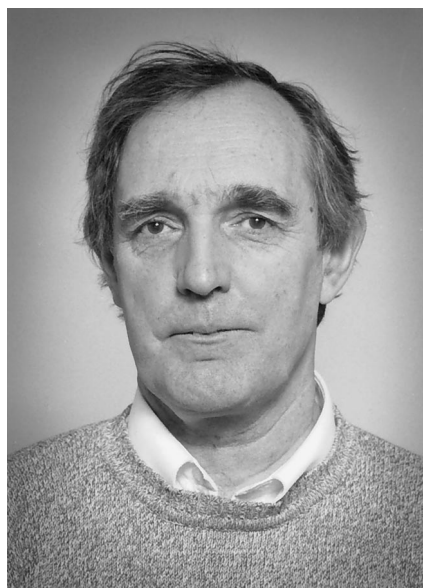
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