AN ANNOTATED BIBLIOGRAPHY ON SILICON NITRIDE FOR STRUCTURAL APPLICATIONS

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AN ANNOTATED BIBLIOGRAPHY ON SILICON NITRIDE
FOR STRUCTURAL APPLICATIONS

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PURPOSE - The increasing demand for engineering materials in high temperature applications has led to investigation of the use of ceramic materials in such applications. Silicon nitride has emerged as a ceramic material having outstanding corrosion resistance, thermal shock resistance, mechanical properties and chemical properties. Although the requirements for increasingly higher operating temperatures (2500 F) for gas turbines have created much of the interest in silicon nitride, there are other potential high temperature applications such as bearings and radomes for which silicon nitride is also under consideration.

The purpose of this bibliography is to summarize the research and development accomplished to date on the fabrication and properties of silicon nitride, particularly as it applies to structural uses of the material.

This bibliography is an attempt to present a comprehensive but not an exhaustive study of the literature in the field.

TIME PERIOD - The time period emphasized in the bibliography is 1961-1976, however, material prior to this period, as well as a few historic references, are included.

SCOPE - The scope of this bibliography includes work reported in the literature on the fabrication and properties of reaction-sintered and hot-pressed silicon nitride. Also included is work on silicon oxynitride and Si-M type oxynitrides having the silicon nitride structure. Whisker growth, chemical reactions, mechanical behavior, and other related topics relevant to the processing and applications of silicon nitride are also included.

Standard bibliographic reference tools including

- British Technology Index
- British Ceramic Abstracts
- Ceramic Abstracts
- Chemical Abstracts
- Defense Documentation Center, Technical Abstract Bulletin (TAB)
- International Aerospace Abstracts
- Metals Abstracts
- NASA Scientific and Technical Aerospace Reports (STAR)
- U.S. Atomic Energy Commission, Nuclear Science Abstracts
- U.S. Government Reports Announcements (GRA)

were the basic sources of information. Further references were found in texts, especially those publications covering the proceedings of conferences in the field.

LIMITATIONS - The vast body of literature on the preparation and properties of thin films of silicon nitride for electronic applications has been omitted because of its formidable size and because of its marginal relevance to the applications being considered.

ACKNOWLEDGMENTS - The technical assistance of Dr. William Croft, and the persevering efforts of Miss Michelle Matte in providing many of the references and her diligent proofreading of the manuscript, are gratefully acknowledged. The editorial and typing assistance of Mrs. Jeanne Pigeon are also gratefully acknowledged.
BOOKS


Physical and chemical properties of Si-Al-O-N (“Sialon”) materials are presented. Comments are made on the hot-pressing and sintering characteristics of these materials.


Bend strengths in air of hot-pressed and reaction-sintered Si₃N₄ were measured to 1450 C and results are related to structure and composition. Tensile test apparatus is described and results are given for short-term measurements on hot-pressed Si₃N₄. Tensile and bend data are compared in terms of Weibull concepts.


System for gravimetric measurement of nitridation kinetics is described. Fe at 50 ppm level affects nitridation of high purity Si powder. Effects of Fe content and N pressure on microstructure are considered in detail.


Internal or subsurface fracture initiation in hot-pressed Si₃N₄ was studied to establish critical defect sizes, fracture toughness, and failure strength. Data were used to establish surface finish criteria for various test systems.


The fracture toughness of reaction-bonded Si₃N₄ was measured in terms of $K_{IC}$, the critical stress intensity factor for the onset of cracking from a defect. Toughness was measured as a function of density and the α- and β-phase contents of the Si₃N₄. Density, Young's modulus, and plain bar bend strengths were also determined.


Rolling contact fatigue tests on hot-pressed Si₃N₄ containing bearings showed no failure at 600 k psi for up to 93 M stress cycles. Two types of bearings - one with steel races and Si₃N₄ rollers and the other with Si₃N₄ races and rollers - were successfully tested under accelerated conditions, i.e., 10,000 rpm and 2,500 lb load.

Hot-pressed $\text{Si}_3\text{N}_4$ was evaluated by means of fatigue testing on elemental components and testing of full-scale prototypes of bearings. $\text{Si}_3\text{N}_4$ has excellent fatigue life. Two types of precision 55-mm-bore roller bearings were designed, fabricated, and successfully tested under accelerated test conditions.


Fractographic studies of hot-pressed $\text{Si}_3\text{N}_4$ showed that room temperature strength is controlled by various types and sizes of inclusions. In test samples without severe surface damage most fracture originated internally at inclusions. The strength of $\text{Si}_3\text{N}_4$ was significantly increased with reduction of the size and frequency of inclusions.


Hot-pressed $\text{Si}_3\text{N}_4$ fails by spalling in a manner similar to bearing steels. Pores, inclusions, and residual grinding damage nucleate fatigue cracks. Their reduction should result in increased performance. The surface condition of $\text{Si}_3\text{N}_4$ is critical to rolling contact fatigue life.


The Gibbs free energies of formation of $\beta$-$\text{Si}_3\text{N}_4$ and $\text{Si}_2\text{ON}_2$ were determined at various temperatures. The Si-O-N system is discussed in terms of an equilibrium diagram with N and O pressures as variables. Conditions for the formation of $\alpha$- and $\beta$-$\text{Si}_3\text{N}_4$ were examined experimentally and it was found that the $\alpha$-phase is formed by a vapor phase mechanism and the $\beta$-phase by a direct reaction of N and Si. The latter is the thermodynamically stable phase at all temperatures.


First row stator elements for 30 MW gas turbine were designed and machined from $\text{Si}_3\text{N}_4$ and SiC. Discussion includes ground rules, philosophy, criteria, concepts, heat transfer, contact stresses, and thermal analyses as related to design.


Overview of progress on program aimed at application of ceramics to industrial gas turbines for electrical power generation.

The use of Ta wire reinforcements increased the Charpy impact strength of hot-pressed Si₃N₄ from 0.68-21.7 J (0.5-16 ft-lb) between room temperature and 1300 C. The mode of fracture was affected in such a way that interfacial splitting occurred together with ductile wire elongation. The Ta-Si₃N₄ composite system also exhibited a threshold energy, below which no damage occurs upon impact, that is considerably higher than that of the unreinforced Si₃N₄.


Discussion of progress in reaction-bonded Si₃N₄ in three areas: (1) the achievement of high strength (300 MN/m²) in Si₃N₄ prepared from flame-sprayed Si, (2) the potential of fiber reinforcement as a means of achieving high strength, high breaking strain, and fracture toughness in Si₃N₄, (3) the production of a mouldable form of Si powder compact by the use of polymeric additives.


Collection of 36 papers presented at the conference. Pertinent papers are annotated in this bibliography with each entry under the name of the specific author.


Si and Al powders were nitrided with NH₃ to produce ultrafine AlN, Si₃N₄, and Si-Al-O-N powders. Equipment design and powder characteristics are discussed.


(Si, Al) N alloys were deposited by reactive ion plating from Si and Al evaporation and NH₃ or NH₃ + 1% SiH₄ gas mixtures. The deposits had large columnar grains composed of smaller 0.2-0.6 μm grains. At substrate temperatures of 100-300 C during deposition there were no observable differences in the morphology of the deposits. Adhesion of the deposits was good. Deposition rates were comparable to those for high-temperature CVD processes.

Fabrication response of Si₃N₄ is similar to that of M50 tool steel presently used for aircraft engine bearings. Si₃N₄ can be satisfactorily lubricated by hydrocarbon and ester-base lubricants at temperatures to 260 C.


The properties and applications of hot-pressed Si₃N₄ of a higher strength form are discussed. The powder used in the hot-pressing operation is essentially 100% α- and the transformation to β- takes place during the densification.


Specimens of reaction-sintered Si₃N₄ (α/β ratio ~50/50), density 2.53 x 10³ kg m⁻³, were oxidized in air at temperatures from 1000 to 1400 C and characterized by measurements of weight gain, X-ray diffraction, and microscopy. The major oxidation product is cristobalite which forms around internal pores (Stage I) and eventually as a dense surface layer (Stage II). Strength was measured as a function of temperature after direct cooling from the oxidation temperature and after temperature cycling. Oxidation in Stage I has a small beneficial effect on strength at all temperatures, whereas oxidation in Stage II has a larger beneficial effect provided that the specimen is not cooled through the cristobalite inversion temperature at ~250 C.


Four-point bending apparatus was used to study creep of hot-pressed and reaction-sintered Si₃N₄ at 1200-1400 C. The primary creep stage is very marked. Creep curves are described by a power function of time. High temperature deformation of hot-pressed Si₃N₄ occurs by grain boundary sliding.


High-temperature slow crack growth processes in several ceramic systems, including Si₃N₄ at >1000 C, were examined under static and cyclic loading conditions. Data obtained at temperatures up to 1400 C are used for failure prediction and analysis of slow crack growth phenomena. Purity significantly affects slow crack growth and low frequency cycling does not affect its rate. Semiquantitative mechanisms that are discussed include dislocation motion and grain boundary sliding.

Thin films of reaction-sintered Si$_3$N$_4$ in both the as-fabricated condition and after deformation at 1400 C were examined in the Harwell MV microscope. The as-fabricated material consisted primarily of large grains of $\beta$-Si$_3$N$_4$ in a fine-grained matrix of $\alpha$-Si$_3$N$_4$ and pores which usually contain fibers. The fibers have the $\alpha$-Si$_3$N$_4$ structure often with an amorphous layer. The deformed material contained some heavily dislocated grains of $\beta$-Si$_3$N$_4$. Most dislocations have a Burgers vector <0001> and the remainder a vector of ~ <1123>. The observation of dislocation activity in the vicinity of cracks indicated that dislocation motion near the cracks contributes to the fracture surface energy.


Preparation of slip comprising Si powder suspended in H$_2$O with the aid of an alkaline deflocculent is described. Important variables include particle size, aging of slip, pH, and specific gravity. Correlations are discussed between processing variables and properties of resultant reaction-sintered Si$_3$N$_4$.


Experimental methods for MHz frequency, pulsed ultrasonic measurements at high temperatures are reviewed. Elastic property data are presented for Si$_3$N$_4$, SiC, and a Li-Al-Si glass ceramic.


Reaction of SiCl$_4$ and SiF$_4$ with NH$_3$ at 1-10 torr gave deposits which were glassy at 1100 C and which were crystalline $\alpha$-Si$_3$N$_4$ at 1500 C. Deposits showed preferred orientation and residual stresses. Material had outstanding resistance to oxidation and creep.


Stresses in reaction-sintered Si$_3$N$_4$ and other materials were calculated to determine the heat fluxes necessary to give maximum tensile stresses approximately equal to the tensile strength of the material. A one-dimensional finite element stress analysis was used to estimate stresses within 12%.


The properties of Si$_3$N$_4$ ceramics relevant to thermal shock are described, and results of testing and hardware trials are discussed. The technology of Si$_3$N$_4$ materials, and their potential for other hostile environments, is reviewed.

Ceramic materials that are strong and stable against oxidation at high temperatures have not been used extensively, because of their brittleness. The properties of candidate ceramic materials are presented and reviewed critically, as are the fabrication processes, in regard to future requirements for combustion chambers. Possible use of Si₃N₄ ceramics up to 1600 C is discussed and the potentialities of currently available fabrication techniques are described and illustrated.


Strength of reaction bonded Si₃N₄ is independent of maximum nitriding temperature (1350 C vs 1450 C) but it is dependent upon porosity. Oxidation at 1250 C reduces strength. Additions of Al₂O₃ reduce oxidation, but impair strength under certain conditions.


The problem of reducing friction and wear in hot oxidative or corrosive environments is discussed. The limitations on the use of metallic materials in hot oxidative conditions are considered and the use of inorganic metallic materials for bearings and lubricants is reviewed. Frictional data for Si₃N₄ ceramics are presented, showing they have a potential for use at temperatures at least as high as 700 C.


Study of the oxidation resistance of Si₂N₄ and SiC refractory materials at temperatures from 1000-1400 C. Results showed the oxidation resistance of these mixed materials to be lower than that of Si₃N₄ or SiC alone.


Reaction-sintered and theoretically dense hot-pressed Si₃N₄ materials have been bonded for components for turbine engine applications. Slip-casting techniques for bonding reaction-sintered Si₃N₄ components are discussed as are bonding techniques for hot-pressed Si₃N₄. Results of a bonding parameter study - including bond strength data and interface microstructures - are also presented. The bond between a reaction-sintered blade ring and a hot-pressed hub in a turbine rotor assembly can be as strong as the weaker of the two parent materials.

Kinetics of oxidation of Si$_3$N$_4$ and Si$_3$ON$_2$ were studied with powdered samples at 1100-1300 C and 0 pressure 15-170 torr. Interfacial and diffusion processes are shown with activation energies, 70 k cal/mole. 0 pressure did not influence the corrosion rate except at the beginning of the reaction.


Alpha- and beta-Si$_3$N$_4$ are not merely low- and high-temperature forms respectively but are "high oxygen potential" modifications. This explains the anomalies in preparative chemistry of Si$_3$N$_4$ and the difficulty of $\alpha$-$\beta$ interconversion.


Procedures and results obtained in an experimental study of the suitability of slip-cast reaction-sintered Si$_3$N$_4$ for radome applications are described. Results indicate outstanding thermal shock properties and rain erosion resistance superior to fused SiO$_2$. Remaining development problems are pointed out.


Preliminary evaluation of hot-pressed Si$_3$N$_4$ for ceramic vanes in large aircraft and industrial gas turbines. Prototype vane construction and testing was undertaken with closely related material characterization. Cyclic thermal stress and impact behavior need more attention. Establishing material performance criteria and comparing test data to them is also needed.


Changes in the solid reaction product were studied with respect to the axis of the jet, the dependence of the yield of AlN and Si$_3$N$_4$ on the size and conditions for the introduction of powdered particles, and on the composition of the high-temperature gas jet for the reaction of Al or Si with N. Highly dispersed powders which contained 10-98% AlN and 5-80% Si$_3$N$_4$ were obtained.


Si$_3$N$_4$ was prepared from powder mixtures comprising SiO$_2$ and C. Discusses conditions for formation of SiC and for varying $\alpha$/$\beta$ ratio. SiO overpressure reduces volatilization and favors formation of $\alpha$-Si$_3$N$_4$. 

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$\beta'$ structures are obtained with the general formula Mg$_{9x/4}$Si$_{6-x/4}$Al$_{x/2}$O$_x$N$_{8-x}$. Two new phases were found, both of which are lower symmetry modifications of the hexagonal AlN-type structure; unit cell dimensions and thermal expansion of $\beta'$ are independent of Mg content.


Four-point bend tests to determine fracture toughness showed that $K_{IC}$ varies slightly between 77 and 1273 K, having a minimum value of 4.5 MN/m$^{3/2}$ at room temperature. Above 1273 K, $K_{IC}$ rises sharply to 10.3 MN/m$^{3/2}$ at 1623 K. In general, fracture is transgranular at 77 K but is intergranular between room temperature and 1273 K. It is suggested that the high $K_{IC}$ at 1623 K is due to plasticity in the grain boundaries.


Fabrication technology of Si$_3$N$_4$ radome tips is discussed with emphasis on (1) choice of sintering aids, (2) equipment, and (3) optimum hot-pressing conditions. Bibliography is included.


The SiO$_2$ that is always present in Si$_3$N$_4$ powders leads to various amounts of extraneous phases in hot-pressed Si$_3$N$_4$. The "sialons" - silicon - aluminum oxynitrides - overcome this problem and offer the additional advantage of allowing fabrication by conventional shaping and sintering.


Mixtures of title components were formed from various compounds and heated at 1550-1700 C to form $\beta'$-structures. Limits of Li$_2$O solubility in $\beta'$ are given approximately by the Si$_3$N$_4$-LiAl$_5$O$_8$ join. At higher lithia concentrations phases appear that are isostructural with $\alpha$-Si$_3$N$_4$, Si$_2$N$_2$O, and eucryptite. $\beta$-structure transforms to $\alpha$- between 1550 and 1700 C.


The test facilities used to evaluate Si$_3$N$_4$ turbine stators for a regenerative gas turbine engine are described. Thermal response data for various stator vane systems are compared to theoretical values.

Important relationships between strength, N weight gain, and nitrided density have been established for reaction-sintered Si₃N₄. Definitive experiments on the deformation and optimization of reaction-sintered Si₃N₄ can now be conducted using these relationships to provide comparisons and assessments. The implications and use of these relationships are explained and discussed.


Variations of mirror radius with fracture stress in several materials including hot-pressed Si₃N₄ are compared and evaluated in terms of available theories.


High-cycle and low-cycle fatigue, creep, and stress rupture behavior data are presented for hot-pressed Si₃N₄ containing different levels of alkaline impurities, in particular Ca. Results indicate that the strain rate sensitivity of grain boundary sliding determines the temperature and strain rate dependencies of creep and fatigue in Si₃N₄. The effect of impurities on the viscosity of the grain boundary phase is related to the effect of alkaline elements on the creep and stress rupture strength of Si₃N₄.


X-ray radiography, ultrasonic, and dye penetrant detection techniques were used to identify the types of defects found in commercial hot-pressed Si₃N₄. High density defects such as metallic particles can be detected by X-ray radiography and cavities, low-density areas, and low-density defects by ultrasonic methods. Examples of defect detection in structural components are shown.


A review of SiC and Si₃N₄ as materials being chemically stable at high temperature and possessing those properties necessary for a reliable machine design. Fabrication parameters, microstructures, and properties are emphasized as are structural considerations, thermal-shock resistance, impact strength, and oxidation resistance. Directions for obtaining improved and new materials are discussed.


Subcritical crack growth in hot-pressed Si₃N₄ occurs by grain boundary sliding. Ca impurity in the glassy grain boundary phase severely decreases high temperature strength while Fe and Al have no apparent effect. Typical high purity of SiC powders (compared to Si₃N₄) may explain reduced susceptibility of hot-pressed SiC to subcritical crack growth.

The general problem of engine reliability is reviewed. Statistical models for strength and modulus for hot-pressed Si$_3$N$_4$ with regard to ceramic engine applications are discussed. A specific example is given of probability of failure computations for deterministic mechanical and thermal stresses in the first-stage rotor of the vehicular engine project.


Review of the literature concerning creep behavior of Si$_3$N$_4$. Preliminary observations of the tension and torsion response of hot-pressed Si$_3$N$_4$ are also reported. Tension response was explored for stresses up to 3500 psi and torsion behavior for up to 7400 psi. Shear deformation appeared to occur at fairly low stress levels and the initial and short-time creep strain rate was ~6.1 x 10$^{-4}$ in/in-hr.


A brief review of the preparation and properties of reaction-sintered Si$_3$N$_4$.


Review of potential advantages and disadvantages of the use of ceramic materials in gas turbine engines. The physical properties and fabrication techniques for six basic forms of Si$_3$N$_4$ and SiC are also reviewed.


Hot pressing or reaction sintering is usually used to fabricate Si$_3$N$_4$ into usable bodies. The properties of the two forms differ markedly at room temperature and at elevated temperatures. Results of some mechanical properties, modulus of rupture, elasticity, and impact strength, at elevated temperature are described. The influence of fabrication conditions on the retention of strength at high temperatures is mentioned.


The chemistry of sialons is discussed in relation to the degree of O and Al substitution. Reasons are suggested for multiphase products of reactions between Si$_3$N$_4$ and Al$_2$O$_3$. Properties are given for materials prepared from Si$_3$N$_4$, AlN, and SiO$_2$. Suggest Si$_{6.2}$Al$_2$N$_{8.2}$O$_2$ formula for expanded β-Si$_3$N$_4$ structure.

Bend testing was used to investigate creep of injection molded reaction-sintered Si₃N₄ and effects of impurity levels and nitriding atmospheres on the creep rate were evaluated. Creep rates and creep strains were decreased by reducing the Ca impurity level and by nitriding in a H environment. Test samples were analyzed by scanning electron microscopy and grain boundaries by Auger spectroscopy.


The planar growth faults of reaction-sintered Si₃N₄ were investigated. The structure and nature of three planar interfaces are described.


Overview of progress on program aimed at the application of ceramics to small vehicular gas turbine.


Considers effects of Si particle size and purity on strength of reaction-sintered Si₃N₄. Purity had no effect while strength was enhanced by fine particle size (-400 mesh) and low maximum firing temperature (1400 C). Strength controlling defects appeared to be “meltout” pores.


Dielectric properties of reaction-sintered and hot-pressed Si₃N₄ are dependent upon extraneous phases, particularly unreacted Si. Data are given for eight Si₃N₄ materials.


Use of ceramic nozzle guide vanes and shrouds considered for small radial flow gas turbines. Tests indicated feasibility of this approach.


Describes program on fabrication and testing of hot-pressed Si₃N₄ gas turbine vane platform (endwall).

The modulus of rupture and the modulus of elasticity of reaction-sintered Si₃N₄ were determined between room temperature and 1500 °C. The relationship between these properties and the isostatic pressing pressure of the Si powder was investigated. The micro-indentation hardness of the α- and β-Si₃N₄, Si, and SiC phases in impure Si₃N₄ was determined.


The manufacture of Si₃N₄ and its influence on the density of the product, the high thermal-shock resistance and its relation to the low coefficient of thermal expansion, the mechanical properties, and possible applications of Si₃N₄ are discussed.


Si₃N₄, although brittle at room temperature, has excellent oxidation resistance, good thermal shock resistance, and adequate creep strength at temperatures up to 1200 °C if stiffened with a very fine dispersion of SiC. Methods for producing the material in suitable form and in the best physical state for engineering designs have been fully explored by laboratory evaluation and field trials. Some applications are described and others suggested.


Results of microwave high temperature dielectric measurements combined with chemical, X-ray, micrographic, and other physical property investigations, performed on a variety of Si₃N₄ ceramics are reviewed. Si₃N₄ combines low dielectric loss with a low-temperatures coefficient of permittivity, both of which are desirable for radomes.


Room temperature fracture strength of 25 specimens of commercial hot-pressed Si₃N₄ was determined in four-point bending. Fracture strength was found to increase after exposure at temperatures >1173 K, relatively independent of the exposure environment. Strength increase is attributed to decrease of stress at crack tip resulting from localized plastic deformation. High fracture energy values on specimens annealed at >1500 K were close to values (39 J/m²) obtained by other investigators.

Studies of the microstructure of reaction-sintered Si$_3$N$_4$ reveal the presence of a number of phases which may be distinguished by their micro-hardness properties. The phases are identified by X-ray methods, and their relative proportions and distribution are considered in terms of the bulk density of material prepared in a number of ways. The influence of this microstructure upon the mechanical properties is indicated and some explanation of the good thermal shock resistance is given.


There is no appreciable solubility of Y$_2$O$_3$ in Si$_3$N$_4$. Principal phases in hot-pressed material are β-Si$_3$N$_4$ and tetragonal Y$_2$Si$_3$O$_3$N$_4$. Also identified were two intermediate phases that occur between 1000 and 1300 C. Y$_2$Si$_3$O$_3$N$_4$ accommodates impurities such as Ca; formation of low-melting glasses is thus avoided and Y$_2$O$_3$-Si$_3$N$_4$ hot-pressed material has high hot strength.


A review of the methods for fabrication of and improvement of engineering properties of Si$_3$N$_4$ refractories. Design of components made of this material is also included.


Ten SiC and five Si$_3$N$_4$ materials were exposed in a Mach 1 gas-velocity burner and cycle tested for up to 100 hours at 1200 C. One hot-pressed SiC, one reaction-sintered SiC, and three hot-pressed Si$_3$N$_4$ materials survived 100 one-hour cycle exposures. The other materials failed from thermal fatigue.


Results on hot-pressed Si$_3$N$_4$ test samples inspected with a conventional ultrasonic system were compared with those obtained with a computer-aided ultrasonic system. Test sensitivity and test resolution were improved using three data processing techniques.


Corrosion of hot-pressed Si$_3$N$_4$ and SiC were studied by static oxidation and also by corrosion-erosion tests in a pressurized turbine test passage. Static oxidation was parabolic for both materials at 1000-1400 C with impurities greatly influencing the composition of the oxide layer. Although both materials showed erosion in the dynamic tests at 1100 C, their strengths were unaffected by the gas turbine environment.

Cold-spin testing of Si₃N₄ "multidensity" rotors has been used for evaluation and for identification of failure conditions. A wide range of failure conditions have been identified during the testing phase allowing for the development of improved rotors suitable for subsequent hot testing and engine development.


A detailed analysis of the crystal structure of β-Si₃N₄ has been made, together with a partial analysis of the α-phase. Models of both have been made revealing the features of certain crystallographic planes. Some studies of the transformation from α- to β-Si₃N₄ at high temperatures have been made. The effect of temperature on the lattice parameters of Si₃N₄ has been studied using a high-temperature X-ray camera. The microstructure of reaction-sintered Si₃N₄ appears to consist of dense grains in a sea of interconnected flakes. Nitriding at temperatures above the melting point of Si leads to the growth of largely β-Si₃N₄ with only small amounts of α.


Creep tests in four-point bending performed on reaction-sintered Si₃N₄ in air and in vacuum at temperatures up to 1400 C. Creep deformations were very much smaller in vacuum than in air because of the formation of O-containing phases in the oxidizing atmospheres. Concentration profiles were obtained by X-ray analysis. Internal oxidation may be restricted in several ways.


Fracture is mostly intergranular and oxidation occurs after fracture. Photomicrographs illustrate fracture phenomena.


Thin foil and bulk Si₃N₄ samples were oxidized in air 1000, 1200, or 1400 C for 1-264 hours, and the oxidation products (SiON₂, β-SiO₂) and two amorphous phases were studied by electron microscopy using specimens prepared by ion thinning. Oxidation of the Si₃N₄ grains started at the grain boundaries.


Study on diffusion couples comprising α-Si₃N₄ and α-Al₂O₃ revealed new quaternary phase resembling γ- or δ-type Al oxides or oxynitrides. Unit cell of new phase is orthorhombic.

Room- and high-temperature properties of hot-pressed and reaction-sintered Si₃N₄ are listed and compared. Properties reviewed include density, elastic modulus, thermal expansion, tensile and bend strength, creep, oxidation and stress-rupture life.


A 3-D finite element stress analysis of a proposed ceramic rotor blade design is presented. Design considerations include thermal and centrifugal loading conditions. Also obtained were natural frequencies of the airfoil portion of the blade.


The dielectric, thermal shock, and erosion properties of reaction-sintered Si₃N₄ appear attractive for use in radomes at high-flight velocities. Fabrication techniques are also considered.


Collection of pertinent electrical, mechanical, and thermal property data for the hypersonic radome materials - slip-cast fused silica and reaction-sintered Si₃N₄. Effects of temperature and porosity are considered, and thermal shock and rain erosion are discussed in relation to porosity.


Data are presented for high-strength reaction-bonded Si₃N₄. Included are oxidation behavior in air at 1200 and 1375 C and flexural strength values from ambient to 1450 C. Flexural strength was >50,000 psi at 1450 C and no creep deformation occurred in 260 hours at 2260 C under a load of 20,000 psi.


Rain erosion resistance of Si₃N₄ appears adequate for radome applications.

Si₃N₄ materials tested had ΔT critical of about 400 C versus 300-375 C for SiC. Residual strength of the better SiC was twice that of the Si₃N₄.


Reaction formed new phase designated “X” that decomposes in two stages to form an aluminum oxynitride analog and, finally, α-Al₂O₃. “X” phase appears to be a quaternary phase in the system Si-Al-N-O.


The possible importance of ternary and quaternary phases and of related materials in Si₃N₄ technology is discussed.


The crystal structures of α- and β-Ge₃N₄ and α-Si₃N₄ were determined by X-ray powder methods and accurate atomic parameters were obtained. The parameters of β-Si₃N₄ agreed with previous determinations. Structural data shows that the α- “nitrides” are in fact oxynitrides with O replacing N in some sites and with N vacancies in others. α- and β- are not merely low-temperature and high-temperature structural forms of the same compound, but are “high oxygen potential” and “low-oxygen potential” modifications.


α-Si₃N₄ has a defect structure containing 0 atoms as well as vacant lattice sites. α- and β-Si₃N₄ are not merely low- and high-temperature forms. Phase relations α- and β-Si₃N₄, Si₂N₂O, and Si are discussed.


The thermodynamic conditions for the formation of α- “high-oxygen potential” and β- “low-oxygen potential” Si₃N₄ from Si have been established over a wide range of temperatures. Kinetic factors and the O “capacity” of the environment are equally important in determining the α/β ratio. In reaction with pure Si, α- is formed by a vapour-phase reaction. When β- is produced as a coherent layer on the metal surface, further reaction is retarded because of slow diffusion through the Si₃N₄. β-Si₃N₄ can be obtained by the equilibration of Si in Si-Fe alloys with appropriate N and O potentials at temperatures as low as 550 C, invalidating previous claims that it is a high-temperature phase.
X-ray studies were made of Si$_3$N$_4$ powders with various additions of MgO hot-pressed for 1 hour over a wide range of temperatures. At low temperatures, 100-1400 C, the MgO is converted to forsterite (Mg$_2$SiO$_4$). At higher temperatures the forsterite reacts with α-Si$_3$N$_4$ to produce enstatite (MgSiO$_3$) and β-Si$_3$N$_4$. Maximum changes as rapid densification, disappearance of forsterite, decrease in α:β ratio, and increase in strength, all occur at about 1557 C, the melting point of enstatite. That the enstatite phase acts as a bond between the Si$_3$N$_4$ particles explains the low high-temperature strength of hot-pressed Si$_3$N$_4$. 


Amorphous $\alpha$-Si$_3$N$_4$ coatings were directly deposited with SiH$_4$/NH$_3$ but with SiCl$_4$/NH$_3$ both amorphous and crystalline $\alpha$-Si$_3$N$_4$ coatings were obtained. Coatings deposited above 900 C were similar to Si$_3$N$_4$ composition, those below 900 C contained excess Si, all contained small amount of O. All amorphous coatings were cracked but the extent of cracking decreased with increasing deposition temperature and density.

96. Akio, K., Yoshihiro, O., Sanae, K., and Isao, M., Yogyo Kyohai Shi, 80 (3), 28-34 (1972). (See Entry No. 409)


Discussion of the problems that must be overcome, primarily stress concentrations, in ceramic materials before they can be successfully used in gas turbine engines. Reviews the physical properties - density, elastic modulus, coefficient of thermal expansion, thermal conductivity, and specific heat - of four potential materials including hot-pressed and reaction-bonded Si$_3$N$_4$ and SiC.


Report of the influences of raw materials and processing variables on the preparation of Si$_3$N$_4$ by reaction bonding. Gas permeation was rate-limiting and the degree of nitridation increased with temperature from 1300-1400 C. Oxygen impurities enhance formation of $\alpha$-Si$_3$N$_4$.


Cyclic fluidized-bed quenching was used to evaluate the thermal fatigue resistance of hot-pressed Si$_3$N$_4$. Finite element analysis showed that behavior of wedge-shaped specimens simulated that of turbine vane. Thermal fatigue can limit the application of hot-pressed Si$_3$N$_4$ in transient high-temperature environments. When analyzed in terms of slow crack growth mechanisms, thermal fatigue life is sensitive to strain level and duration above 1000 C.


Work on the strength of hot-pressed and flame-sprayed reaction-sintered commercial types of Si$_3$N$_4$ is described. Variation in the rupture modulus and elastic modulus at temperatures from 30-1450 C are described. The plasticity of hot-pressed Si$_3$N$_4$ at temperatures 1200 C and above are also described. Initial results on the delayed fracture of hot-pressed Si$_3$N$_4$ are presented. A brief account of high-temperature creep is included.


Indentation hardness of refractory borides, carbides, and nitrides was determined at temperatures up to 2000 C. Most of the refractory solids are very brittle at low temperatures. Above a critical temperature (half absolute melting point) they become ductile and the hardness falls as the temperature increases. Si$_3$N$_4$ and SiC are the only materials having an indentation hardness above 100 kg/mm$^2$ at 1500 C.

Temperature distributions occurring in Si$_3$N$_4$ powder compacts, 5 cm diam x 5 cm long, were measured as a function of time during nitridation at temperatures from 1295 to 1330 C. The temperature distributions were shown to be determined by a rise in surface temperature allowing heat to be radiated and the establishment of a temperature gradient.


Results of nitriding of Si powder compacts containing up to 50 w/o Si$_3$N$_4$ indicate that gas diffusion is the rate-determining step. Additions of Al to the Si compacts increased nitridation rate and amount of β-Si$_3$N$_4$ formed at 1350 C.


Results of a study to determine to what extent N flow into the compact controls the overall reaction rate during the nitriding of Si powders. The reaction rate was measured using thermogravimetry as a function of compact pore structure, Si particle size, compact (spherical) size, up to 5 cm diameter, and reaction temperature. Evidence points to the reaction between Si and N and not the rate of flow of N into the compact as being the rate-determining step.


A mechanism is proposed for the nitridation of Si powder based on the untypical microstructure of a partially nitrided Si compact. Microstructural examination shows that nitridation does not occur at the Si-Si$_3$N$_4$ interface but that it proceeds via a pore migration mechanism.


Growth and morphology of Si$_3$N$_4$ on high-purity Si indicate that the process involves vapor-phase transport and/or surface diffusion rather than solid state diffusion.


A model is presented to explain kinetic data for the nitridation of pure Si at 1250-1370 C and N pressures of 20-760 torr. The initial linear kinetics are associated with the growth of individual nitride nuclei. The reaction rate steadily decreases as the nuclei coalesce and falls to zero when the Si is completely covered with nitride.


Using a static system the kinetics of the thermal decomposition of Si$_3$N$_4$ were studied. At 1400-1750 C, Si$_3$N$_4$ decomposed to liquid Si and N gas, following first-order kinetics during the initial stages of dissociation and the Jander solid-state kinetic law in the latter stages. The activation energies for the first-order and Jander kinetics were 93.0 ± 6.6 kcal mol$^{-1}$ and 186 ± 10 kcal mol$^{-1}$ respectively. Excess Si metal and a N atmosphere in the reaction system inhibited the decomposition reaction.
The reaction of Si and N at high temperatures produced only the nitride \( \text{Si}_3\text{N}_4 \). Si and N begin to react at temperatures above 1240°C. The reaction is slow between 1250 and 1315°C. Between 1315 and 1385°C, a logarithmic rate law obtains. Above 1385°C, the rate of reaction is very rapid. The crystal structure of \( \text{Si}_3\text{N}_4 \) is orthorhombic.

The new phase \( \text{SiAl}_4\text{N}_4\text{O}_2 \) was prepared by heating mixtures of \( \text{Si}_2\text{O}_2\text{N}_2 \) and \( \text{Al}_2\text{O}_3 \) in Ar atmosphere at 1650-1700°C. It is regarded as the thermolysis product of the solid solution \( \beta'\text{Si}_3\text{N}_4 \).

The addition of 30 v/o W wires to hot-pressed \( \text{Si}_3\text{N}_4 \) increased the Charpy impact strength at 1300°C from 0.25 ft-lbs to 2.25 ft-lbs. At this temperature the interfacial shear strength is low enough to allow the energy absorbing mechanism of fiber pullout to be operative. At room temperature, however, the tungsten silicide layer formed at the W-\( \text{Si}_3\text{N}_4 \) interface rendered W reinforcement ineffective. Means of solving this problem are discussed.

Lists the physical and chemical properties of Si₃N₄. In the nitriding process the Si should be powdered to a fineness of at least 40 μm. Formation of Si₃N₄ begins at 970 C; the rate of formation reaches a maximum at 1600 C and drops sharply above 1700 C. Metallic impurities are eliminated by boiling in a 50% solution of HCl. Data on the influence of the nitriding temperature and the concentration of N are shown.


Porous Si forms prepared by flame-spray deposition of Si powder were nitrided to produce Si₃N₄ bodies. This method provides for economic production of accurate and intricate shapes of Si₃N₄.


Concludes from experiments and thermodynamic analysis that Si₃N₄ should not be used as electrical insulator in contact with Ti at temperatures >1200 C.


Dislocations in β-Si₃N₄ generated by fracture at room temperature were examined by transmission electron microscopy. The dislocations lie on [1010] and are near edge orientation with Burgers Vector c[0001].


A review with 16 references.


Effects of alumina refractories on nitridation are discussed. Formation of α-Si₃N₄ is related to presence of SiO₂ in compact being nitrided. Role of metallic impurities in nitridation is also considered.


Reaction-sintering and hot-pressing techniques for the manufacture of Si₃N₄ components are discussed. Reaction sintering is best carried out at 1300-1400 C for 40 hours using fine Si powder containing some Fe. Hot pressing should be done at 1650 C for 60 minutes at 500 kg/cm².


Review of development and properties of Si₃N₄ for structural applications and discussion of modified materials having β-Si₃N₄ structure.

Review of Advanced Materials Engineering's work with reaction-bonded Si$_3$N$_4$ in automotive applications such as diesel pistons and turbocharger impellers.


Calculations indicate that Si$_3$N$_4$ can withstand higher temperatures than SiC for short thermal fatigue life under certain conditions, but also that SiC is superior for long-term thermal fatigue.


Characterization of micro crystals of Si$_3$N$_4$ formed by high pressure heat treatment of bulk Si$_3$N$_4$ in N. Extensive optical results were confirmed and complemented by electron microscopy and X-ray diffraction analysis. Found were $\alpha$-Si$_3$N$_4$ pseudo-morphs of $\beta$-Si$_3$N$_4$ as well as apparent twins of each phase.


The temperature dependence of flexural strength and fracture toughness ($K_{1C}$) of Si$_3$N$_4$ hot pressed with addition of MgO, Al$_2$O$_3$, and ZrO$_2$ was investigated. The Al containing material showed greater high-temperature strength, but lower fracture toughness than the material containing Mg. ZrO$_2$ additions increase toughness of the Al material, and ZrO$_2$ particles control crack propagation.


Circumferential displacements that occur when hot-pressed Si$_3$N$_4$ cylinders are sliced longitudinally indicated strain. Residual stresses affect reproducibility of mechanical properties and no treatment has been found for eliminating them.


Techniques for fabrication of Si$_3$N$_4$ by pressing, slip-casting, and extrusion are discussed. All techniques yield articles approximately 72% of the theoretical density. Physical properties, electrical and thermal properties, chemical properties, oxidation resistance, and applications of Si$_3$N$_4$ are reviewed.


Chemical methods for determining the amorphous SiO$_2$ covering the particles in $\alpha$-Si$_3$N$_4$ powders are given and the results compared with O analysis by neutron activation. Pseudo-isostatic hot pressing of Si$_3$N$_4$ is described. The effect of additives on the surface SiO$_2$ is explained; MgO and Al$_2$O$_3$ additives reduce its effects, C reacts with SiO$_2$ to produce CO which converts Si$_3$N$_4$ to SiC.

Thermodynamic measurements for phases in the Si-N-O system were made at 50 C intervals in the range of 1200-1500 C and the limiting conditions for each phase formation are expressed in terms of N and O partial pressures. Experimental data are not sufficiently accurate to predict the exact temperature at which transformations will occur between the phases in the Si-N-O system. Data confirms that α-Si₃N₄ is an oxynitride with a limited range of homogeneity $\text{Si}_{11.4}N_{15}O_{0.3} - \text{Si}_{11.5}N_{15}O_{0.5}$.


Fracture surface energies of four hot-pressed and two reaction-sintered Si₃N₄ materials were measured from -196 to 1400 C by work of fracture technique. Fracture energy first decreased with increasing temperature and then, at higher temperature, increased rapidly. Hot-pressed materials had higher fracture surface energies than the reaction-sintered materials.


Review of the properties of Si₃N₄ important to utilization at high temperatures such as crystal structure, density, thermodynamics, thermal expansion, and strength. Some of the areas needing more detailed investigation are pointed out.


Si₃N₄ can be lubricated satisfactorily by conventional lubricants. Its abrasive wear coefficient is high compared to other ceramics. Rolling-contact fatigue and spalling behavior were compared to steel. Attempts were made to reduce severity of surface interactions between Si₃N₄ and M50 steel.


Fracture strengths to 1600 C were measured on reaction-sintered materials varying in pore size, α/β ratio, and density. $\gamma$ values were determined by crack growth and double torsion techniques. Agreement between measured and calculated values suggests that largest pores control strength.


Microstructure of reaction-bonded Si₃N₄ was studied during nitridation, using scanning and transmission electron, and optical microscopy. At temperatures below the melting point of Si the pores of the compact became filled with needles which form the background matte of α-Si₃N₄. At temperatures above the melting point there is increased growth of β-Si₃N₄ resulting in formation of a two-phase structure.

Review of high-strength ceramics, oxides, nitrides, and carbides, with potential high-temperature applications. A unified materials science approach to strength which can be applied to promote a fundamental understanding of the strength of any ceramic material is presented. Three ranges of fracture behavior were identified: (Region A) fracture from inherent flaws, (Region B) fracture from flaws generated by small amounts of plastic deformation, (Region C) fracture after considerable plastic deformation. In case of Si₃N₄ temperature has very little effect on strength if plastic effects are absent.


Results of strength studies on Si₃N₄ specimens are analyzed by Weibull function and the applicability of this function is assessed. A more general theory including Weibull theory as a special case is outlined.


Review of Westinghouse's ceramic R and D program for the design application of brittle materials for high-temperature stationary gas turbine operations.


Method of preparing Si₃N₄ bodies of almost theoretical density. Si₃N₄ powder is hot pressed with a small proportion of catalyst MgO or Mg₃N₂ at 1850 C. Physical properties of dense material indicate it should be suitable for use in making components required to operate under high stress at temperatures up to ~1200 C.


A chloroimidodisilane, Si₅N₁₀H₁₁Cl₂ is formed by the reaction of NH₄Cl with the imide Si₂(NH)₃. Its thermolysis leads to a silicon-chloronitride which is stable under vacuum up to 700 C. At high temperature the Cl is eliminated and an α-Si₃N₄ is formed.


N-O mixture was used instead of pure N to prepare Si₂O₃N₂ with very little contamination by Si₃N₄. The maximum oxynitridation was obtained at a Si-SiO₂ ratio of 6:1.


The microstructures of materials formed by sintering or hot pressing Si₃N₄ and Al₂O₃ were studied by transmission electron microscopy. It is proposed that β′-silicon aluminum oxynitride forms by a liquid phase mechanism analogous to that involved in the α/β Si₃N₄ phase transformation. The origin and crystallography of the "x-phase" is discussed.
The microstructure of fine grained (<1 μm) Si₃N₄ with an MgO additive was studied by electron microscopy at various stages in the hot-pressing process: 1) initial Si₃N₄ (~90%α) powder, 2) partially densified and partially transformed α- to β-Si₃N₄, 3) almost fully dense and fully transformed β-Si₃N₄. A solid/liquid/solid transformation mechanism is suggested.

Structure was determined on crystals obtained by sublimation. Space group is Pn a 2₁ with unit cell parameters a = 4.977, b = 5.747, c = 4.674Å; Z = 4. This ABX₂ structure is an analogue to the superstructure of sphalerite known as chalcopyrite.

Reviews the mechanical properties of commercially available Si₃N₄ and SiC and some of the more promising experimental materials. The importance of crack initiation and propagation in emphasized. The fracture mechanics and Weibull statistical approaches are summarized. Outlined are essential features of materials, manufacturing methods, microstructure, and crystal structure, followed by treatments of elastic constants and strength. Included are 171 references.

Chemical contamination of nitriding gas by O and H₂O to high concentrations does not degrade strength. Coefficient of variation in strength and "apparent" crystallite size are related to H₂O concentration in gas. Also considers formation of α- and β-Si₃N₄ and suggests that α-composition is fixed.

Creep behavior in four-point bend in air at loads to 60 MN/m² of reaction-sintered Si₃N₄ (density 2.05-2.33 g/cc) was investigated. Mechanisms considered include dislocation motion and grain boundary sliding.

Scanning electron and optical microscopy were used to study the structure of reaction-sintered Si$_3$N$_4$ at various stages during nitriding for a range of nitriding and compacting conditions. Strength was evaluated and interpreted in terms of microstructure. Fracture always occurred in a brittle manner by extension of the largest pores. Effects of prolonged annealing in air above 1000 C on structure and strength were investigated. Cristobalite was formed at 1400 C. Strength was enhanced if temperature was then maintained above 250 C. Below this temperature cracks in the oxide layer lessen the strength.


Data suggests that slow crack growth of a range of Si$_3$N$_4$ materials between 1100-1400 C may be characterized by the relation between crack velocity and stress intensity factor. Data indicate that fatigue behavior can be predicted with moderate accuracy from isothermal, static stress parameters. The application of slow crack growth data to failure predictions is described and illustrated.


Thin specimens of reaction-sintered and hot-pressed Si$_3$N$_4$ have been prepared by ion beam thinning and examined in the Harwell million-volt microscope. The reaction-sintered material consists of large grains, mostly $\beta$-Si$_3$N$_4$, in a fine-grained matrix of $\alpha$-Si$_3$N$_4$. The types of fibers observed within the pores depend on the size of the pore. The hot-pressed material consists largely of small angular grains of $\beta$-Si$_3$N$_4$ and large irregular grains. The grains of $\beta$-Si$_3$N$_4$ generally contain dislocations having a <0001> Burgers vector.


Technique for studying high-temperature crack propagation in ceramics was developed and applied to study crack propagation rate and stress intensity factor for hot-pressed Si$_3$N$_4$ to 1400 C. Data are used to develop proof testing criteria.


Kinetic behavior of Si in O, CO$_2$, N, and Ar-0.2%N was determined at 1200-1400 C by means of a thermo-balance. In O and CO$_2$ the rate laws were shown to be parabolic. In pure N erratic behavior was observed with the formation of volatile Si$_3$N$_4$. At a low pressure of N in Ar volatilization was absent and a logarithmic rate law was shown to hold.


Room-temperature shear modulus was measured for seven Si$_3$N$_4$ samples in the density range 2.37-3.18 g/cm$^3$ using the pulsed ultrasonic method. Shear modulus increased smoothly with sample density.

Elastic modulus data are given for some commercially available Si$_3$N$_4$ having densities between 2.37 and 3.18 g/cm$^3$ at temperatures from 0 to 1000°C. The density dependence of elastic constants is in approximate agreement with a theory of composite materials.


Shear moduli were obtained for hot-pressed Si$_3$N$_4$ and SiC specimens in the range 350-1000°C using a pulse-echo technique. For Si$_3$N$_4$ the shear modulus is a smoothly decreasing function of temperature in this range. Room temperature results were ~5% lower than those at 350°C.


Si$_3$N$_4$ consisting of ~85% α-Si$_3$N$_4$ and 1.95-2.85% O was prepared and annealed 2, 4, 8, and 16 hours at 1600°C converting the α-phase to β-phase which contained no O. During the process the O content decreased as N content increased. Suggest α-Si$_3$N$_4$ has composition Si$_{23}$N$_3$O.


A literature survey covering the structure, preparation, properties, and reactions of Si$_3$N$_4$ with 51 references.


Review of processing, properties, and applications of reaction-sintered and hot-pressed Si$_3$N$_4$.


Review of preparation and properties of reaction-sintered and hot-pressed Si$_3$N$_4$.


Production of hot-pressed and reaction-bonded Si$_3$N$_4$ is described. In order to study the production parameters, an induction-heated vacuum hot press was constructed, allowing production of pieces up to 300 mm diam. Possible applications as a corrosion- and abrasion resistant material with great strength even at high temperatures are discussed.


Discusses refractories made from various Si$_3$N$_4$·Cr$_2$O$_3$ compositions.

Examined porosity, refractoriness, thermal stability, impact strength, compressive strength, and thermocycling effect on the mechanical properties of hot-cast Si₃N₄-ZrO₂ ceramic samples containing 20, 40, 60, 80, 100% of Si₃N₄.


X-ray data are given for the two modifications of Si₃N₄, an oxynitride of silicon, Si₂ON, and a material prepared by the fusion of commercial Si₃N₄. The pattern for pure α-Si₃N₄ is less complex than previously reported and has been indexed on a hexagonal rather than orthorhombic cell. β-Si₃N₄ and the fused material (SiₓNᵧ) have hexagonal structures which appear to be related to that of α-Si₃N₄. The pattern of the oxynitride, although complex, can be indexed as orthorhombic.


Two methods of preparation were studied. In the first, a SiO₂-C mixture (molar ratio 1:2) was heated in a current of N₂ at 1400-1800 C to yield Si₃N₄ and SiC in 2-4% and 15-85% respectively. In the second, Si powder was heated in N₂ (at 1 atm) at 970-1600 C for times up to 25 hours, the Si₃N₄ content being determined by X-ray diffraction. Data are tabulated and plotted. The Si₃N₄ phase has no region of homogeneity.


Thick films of α-Si₃N₄ were prepared by reacting SiF₄ and NH₃ on hot carbon substrates at 1100-1550 C and pressure of 1 to 10 mm of Hg. The deposition rate varied from 1 x 10⁻⁴ to 1 x 10⁻² in/hr over the temperature range. Corrosion, electrical and thermal property data are given for the pyrolytic material thus obtained.


Presentation and discussion of isothermal section at 1760 C.


A review of phase diagrams of Si₃N₄-metal oxides systems showed that the solid solubility limits of the metal oxides depends on the size and charge of the metal elements. A misfit factor is defined which can specify these limits. When the misfit factor is small, a substantial amount of foreign atoms can be accommodated in the β-Si₃N₄ lattice, but as it becomes larger, only a small amount of foreign atoms enter the lattice.


Various grades of Si₃N₄ powder were hot pressed with additions of Y₂O₃ to 20 w/o. The effects of powder purity, percent addition, and testing temperature on resultant properties are discussed with supplemental evidence from crystallographic and Auger analyses.

Additions of 1.0-3.3 w/o \( \text{Y}_2\text{O}_3 \) to a high \( \alpha \)-phase \( \text{Si}_3\text{N}_4 \) powder hot pressed in graphite dies in a N atmosphere at 6000-7000 psi produced fully dense compacts (3.22-3.26 g/cm\(^3\) increasing with the amount of additive used) at 1750 C. Modulus of rupture at room temperature and at 1315 C was 118,000 psi 58,000-69,000 psi respectively.


Thermal diffusivity, thermal conductivity, and specific heat measurements for a range of \( \text{Si}_3\text{N}_4 \) ceramics with densities between 1990 and 3070 kg m\(^{-3}\) are presented. Conductivities vary between 7 and 36 W m\(^{-1}\) K\(^{-1}\) at 302 K, possibly due to the varying amounts of “free silicon” phase in them. In the SiC ceramics examined the “free silicon” phase reduced the thermal conductivity. Thermal diffusivity values for SiC are also presented.


Self-bonded \( \text{Si}_3\text{N}_4 \) is commercially manufactured and can be readily used to produce accurate components and has refractory and chemical properties which make it an attractive material for special refractory applications. Some are listed, but it is expected that the uses for this material will be ever-increasing.


\( \text{Si}_3\text{N}_4 \) was prepared by passing N or \( \text{NH}_3 \) over Si at 1230-1450 C or 1350 C respectively or by heating \( \text{Si(NH)}_2 \) at 1350 C. Powder diffraction studies showed \( \text{Si(NH)}_2 \) decomposition produced pure \( \alpha \)-\( \text{Si}_3\text{N}_4 \). The \( \text{Si-NH}_3 \) reaction gave chiefly \( \alpha \)- and a little \( \beta \)-\( \text{Si}_3\text{N}_4 \) and the \( \text{Si-N} \) reaction gave \( \alpha \)-\( \beta \) mixture in which the \( \alpha \)-form was favored at low temperatures. Electron microscopic studies are reported.


Mechanical properties, thermal shock and thermal fatigue characteristics of three reaction-sintered (density 1.9-2.6 g/ml) and one hot-pressed (density 3.0-3.18 g/ml) samples of \( \text{Si}_3\text{N}_4 \) differed according to composition and method of manufacture. Resistance to creep at 1000-1200 C and to thermal fatigue at 1000 C, particularly of the dense grades, can be considerably superior to that of creep-resistant alloys. The appreciable variation in performance of all grades indicates further development of the manufacturing technique is necessary.


Discussion of possible applications of \( \text{Si}_3\text{N}_4 \) in turbine blades, bearings, piston rings, cutting tools, and electronic apparatus.

Ceramics are being considered for use in high-temperature engineering, especially gas-turbine components. Unlike superalloys, ceramics offer 400-600 C increases in component temperatures without blade cooling. Glass-ceramics may be used up to ~1100 C above this temperature and up to 1400 C Si$_3$N$_4$ and SiC may be used. Properties and processing techniques for fully dense and incompletely dense Si$_3$N$_4$ and SiC are described. Design problems are examined and solutions suggested. Advantages of using ceramics are outlined and examples of a few successful applications are given.


The effect of impurities containing Fe and Al in the formation of Si$_3$N$_4$ from pure Si powders was investigated. Additions of SiC or Al$_2$O$_3$ reduced strengths in proportion to the amounts added; the $\beta$-Si$_3$N$_4$ content increased in proportion to the Al$_2$O$_3$ added. Surface grinding of reaction-bonded Si$_3$N$_4$ either reduced or did not affect its strength in the as-fired condition, but reduced the strength degradation and oxidation resulting from 250 hours exposure in air at 1250 C.


The absence of dimensional change during the nitridation consolidation of Si powder compacts during the fabrication of reaction-bonded Si$_3$N$_4$ is discussed. This facilitates the production of large, precision or joined ceramic shapes. Pressing, flame-spraying, and plastic-binder dough techniques for compaction of Si$_3$N$_4$ are described. A new and promising method of reinforcing Si$_3$N$_4$ matrices with high strength fibres is explained. A critical review of the preparation of Si$_3$N$_4$ relevant to aerospace applications is made. Also published as Report N69-34160, National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia.


High-temperature ceramics and their properties are compared to metals and alloys and their properties. Properties and use of these ceramics, including Si$_3$N$_4$, are reviewed.


Strength data for flame-sprayed and isostatically-pressed Si$_3$N$_4$ materials are given. The effects of void content and surface finish on strength are discussed and results of the influence of surface addition of SiO and H$_2$O vapor in the nitriding atmosphere are presented. A comparison is made of strength data obtained for 3-point and 4-point bend specimens with two different spans.


The development of composite materials, as fiber reinforced ceramics, having appreciable fracture toughness could be a way of obtaining meaningful improvements in the robustness of brittle material components. Only by sustained experimentation, as described, will any useful progress be made in the future.
Experiences in the use of a brittle ceramic material in engineering applications have given some hope that a means of employing such strong materials despite their brittleness will be found by designers. The ready fabricability of Si₃N₄ has provided a valuable tool in the development of a design philosophy for the use of brittle materials in high temperature engineering but many years of study will be required before a useful measure of success is obtained.

Hot-pressed Si₃N₄ and reaction-bonded SiC, the ceramics with the most potential for application in gas turbine engines, have some limitations, but the possible areas and temperature regions where they may be used are discussed. Laboratory data on the effect of oxidation exposure at temperatures up to 1400 °C are presented. Also discussed are glass-ceramics, one of which is useful to 1100 °C.

Creep of reaction-bonded Si₃N₄ (2.11-2.40 g/cm³) at 1200-1400 °C is affected by the environment. Due to internal oxidation, creep in air is more severe than in vacuo. This is not true of hot-pressed Si₃N₄. Measures to prevent the internal oxidation are proposed.

Conditions and mechanisms for growth of α-Si₃N₄ whisker crystals from a (SiO₂ + Si) mixture in a N₂ atmosphere, with the addition of H were investigated. The presence of mullite or Al₂O₃ or Fe impurities in the Si is a necessary condition for growth. The condensation of Si₃N₄ from the gas phase proceeds by a VLS mechanism. The crystallization of α-Si₃N₄ from drops and the growth of the whiskers proceed according to an axial helical dislocation mechanism.

The formation of energy-absorbing layers by leaching hot-pressed Si₃N₄ and the effect of these layers on the formation of Hertzian cracks and the remaining strength are described.

History and present state-of-the-art of German research and development in the production of hot-pressed Si$_3$N$_4$ is described especially in relation to gas turbine applications. A device for producing Si$_3$N$_4$ pieces up to 30 mm diam is described. Properties and possible applications are discussed.


Discussion of the use of ceramics, particularly Si$_3$N$_4$ and SiC, for achieving economical gas turbine operation through higher operating temperatures.


Solid solution in system reaches limit at Si$_6$-x Al$_x$ N$_8$-x O$_x$. Authors propose second phase with composition SiAlNO$_2$.


Variable-strain rate and static fatigue tests performed on hot-pressed and reaction-sintered Si$_3$N$_4$ indicated time-dependent failure in an atmosphere of H$_2$O-saturated flowing air. The effect is moisture-dependent. A model for the mechanism of stress corrosion of hot-pressed Si$_3$N$_4$ is proposed.


The enthalpy of four Si$_3$N$_4$-base materials 1) +5MgO, 2) +10MgO, 3) +5MgO + 20BN, 4) +10MgO + 20BN was measured, by the method of mixing, in a high-temperature calorimetric apparatus. Equations describing the temperature dependence and heat capacity were obtained by the least-square method.


Nitridation of Si powder in high-purity Al$_2$O$_3$ tubes was shown to enhance the formation of α-Si$_3$N$_4$. Suggest that the formation of β-Si$_3$N$_4$ is related to volatilization of impurities from muffle tubes.


Thick films of predominantly α-Si$_3$N$_4$ having a tendency to be oriented with the (001) basal plane parallel to the (111) Si surface were formed when single-crystal semiconductor grade Si was heated in a controlled purity N atmosphere. Addition of low concentrations of O or H$_2$O into the N atmosphere leads to an increase in proportion of β-Si$_3$N$_4$ formed.

Kinetics of oxidation of porous β-Si₃N₄ and Si₂ON₂ were investigated from 900-1500 C by TG, dilatometry, and X-ray analysis. Effect of pore structure on oxidation is discussed.


Compares properties of mixed materials with those of relatively pure Si₃N₄ and Si₂ON₂. The former materials are cheaper and useable under favorable service conditions.


The two forms of Si₃N₄ were studied by X-ray powder diffraction photographs taken with Fe Kα radiation. α-Si₃N₄ is hexagonal with a unit cell containing 12 Si and 16 N atoms and is assigned to space group P 31c. β-Si₃N₄ is hexagonal with a unit cell containing 6 Si and 8 N atoms and is assigned to space group P6_3/m.


Discusses design and fabrication of Si₃N₄ stator vanes. Stress analysis ignores time-dependent properties such as creep, fatigue, and corrosion-erosion but progress on the measurement of these properties is reviewed. Weibull statistics are used to relate tensile and bend strengths and high temperature (>1000 C) mechanical properties attributed to grain-boundary phases.


The work-of-fracture and yielding behavior of two grades on hot-pressed Si₃N₄ are compared in the temperature range 1000-1400 C. The correlation of strength, σₜ/σₙ ratio, and work of fracture supports the idea that the intergranular bond controls the high temperature strength behavior of hot-pressed Si₃N₄.


Slow crack-growth data were used to predict thermal fatigue life of Si₃N₄ parts in a turbine engine. Computer-predicted and experimental life were in agreement. Results suggest that minimizing grain-boundary phase will increase thermal fatigue resistance.


Presents thermal expansion data up to 1020 C obtained by X-ray diffraction methods for α- and β-Si₃N₄ and Si₂ON₂ and discusses results in relation to crystal structures. It is suggested that α- and β-Si₃N₄ are moderately- and slightly-strained crystal structures, respectively, and that this hypothesis may explain much of their behavior.

The pressure of N at which equilibrium prevails between Si$_3$N$_4$ and its elements at absolute temperatures ranging from 1606 to 1802 K was determined. This pressure is 0.27 mm at 1606 K and 5.5 mm at 1802 K. Within this temperature interval the free energy increase at one atmosphere for the reaction Si$_3$N$_4$ = 3Si + 2N$_2$ can be expressed as $\Delta F = 176,300 - 78.35T$ calories. It can be concluded that the dissociation pressure of the nitride becomes one atmosphere at about 2250 K.


Auger spectra are given for fracture surfaces of hot-pressed Si$_3$N$_4$ containing 5w/oMgO and of “sialon” containing 43w/oAl$_2$O$_3$. Results on the former material suggest an 0 rich grain-boundary phase (containing Si, Ca, and Mg) 20-30Å thick.


0 accumulation on grain boundaries in Si$_3$N$_4$ was attributed to addition of MgO or Al$_2$O$_3$.


Oxidation kinetics of powdered Si$_3$N$_4$ were studied in dry O and dry air at 1 atm pressure between 1065 and 1340 C. An automatic recording electrobalance was used to measure the weight gain as a function of time. Parabolic oxidation kinetics were observed with activation energies of 61 kcal/mol in dry O and 68 kcal/mol in dry air. The oxidation rate in dry O was approximately twice that in air. The solid oxidation product was tridymite above 1125 C and amorphous silica at 1067 C.


The crystal structure and physical, mechanical, and chemical properties of sintered Si$_3$N$_4$, and its use in crucibles, pipes, nozzles, and tiles are reviewed with 16 references.


The 1780 C isothermal section of the system was investigated by X-ray analysis of hot-pressed samples. The equilibrium relationships shown involve previously known compounds and eight newly found compounds.


Hot-pressing of Si$_3$N$_4$ powders containing various additives was characterized by X-ray diffraction and hot hardness measurements. Useful densification aids include BeO, CeO$_2$, Ce$_2$O$_3$, and La$_2$O$_3$ at the 4.5v/o level. Texture of resulting β-Si$_3$N$_4$ compacts is discussed.

Semiconductor-grade single-crystal Si disks cut parallel to the (111) plane were reacted with N, previously freed from O, at 1250-1380 °C and their weight changes recorded. The reaction layers were analyzed by electron microprobe and X-ray techniques, and examined by light and scanning electron microscopy. Even trace quantities of O were found to have a decisive effect on the reaction.


(In German)

The kinetics of the reaction of Si(>99% pure) with N were studied thermogravimetrically. Contrary to the results of earlier investigations, a linear dependence was established for the growth of the Si$_3$N$_4$ layer, both above and below the melting point of Si. The activation energy for the gas/solid reaction was found to be 156 kcal mol$^{-1}$. The purity of Si has an appreciable effect on the reaction kinetics. Traces of O have a strong inhibiting effect on the reaction as well as favoring the formation of $\alpha$-Si$_3$N$_4$.


Commercial hot-pressed Si$_3$N$_4$ has fatigue properties 8 times better than those of M50 CVM steel at a stress of 4175 MN/m$^2$. Desirable properties include good corrosion resistance and low coefficients of expansion and friction.


N content of Si$_3$N$_4$ was determined by decomposition in NaOH at ~320 °C and collecting NH$_3$ in a boric acid solution with the aid of steam vapor as a carrier. Solution is titrated with a standard acid solution against methyl red. A conventional gravimetric method was used to determine Si.


Crystal structure of Si$_2$N$_2$O was determined by X-ray crystallographic methods. The crystals are orthorhombic, the space group Cmc$2_1$ and the unit cell dimensions are: $a = 8.843 \pm 0.005$ Å, $b = 5.473 \pm 0.005$ Å, $c = 4.835 \pm 0.005$ Å, and there are four formula units in the cell.


Products of the reaction between Si powder and N were observed by electron microscopy to establish the morphological features relating to the kinetics. The proportionality of the reaction rate to the square root of the particle diameter was consistent with Griffiths theory. Activation energy of 156-158 kcal/mol was ascribed to N diffusion through Si$_3$N$_4$ layer.


Stable Si layers 40-100 μm thick were formed on reaction-sintered Si$_3$N$_4$ by heating 10-15 minutes at 1430-1450 °C in N. Layers were protected against oxidation to 1400 °C. Effect of O pressure on wetting is briefly discussed.
221. Inomata, Y., "Stability Relation in the System $\beta$-Silicon Nitride - $\alpha$-Silicon Nitride - Silicon Oxynitride ($Si_3N_2O$) and Their Structural Change by Heating Above 1600°C", Yogyo Kyokai Shi, 82, 522-526 (1974). (In Japanese)

Experiments were performed on heating $Si_3N_4$ and $Si_2N_2O$ samples at 1530-1730°C under 1 atm of N and the change of composition studied by X-ray diffraction. Results showed that the stable compound in the system $Si$-$N_2$ (1 atm)-$O_2$ changes in the order $\beta$-$Si_3N_4$$\rightarrow$-$Si_2N_2O$$\rightarrow$-$SiO_2$ according to the increasing partial pressure of $O_2$ and that $\alpha$-$Si_3N_4$ is unstable under the same conditions. $SiO$($g$) has an important role in the oxidation of $Si_3N_4$ and $Si_2N_2O$ at elevated temperatures.


A pellet comprising an equimolecular mixture of $Si_3N_4$ and amorphous $SiO_2$ powders was embedded in the same $SiO_2$ powders and heated for 8 hours at 1730°C in N. The stable compounds observed were $\beta$-$Si_3N_4$, $Si_2N_2O$, and $SiO_2$ but not $\alpha$-$Si_3N_4$.

223. Inomata, Y., and Inoue, Z., "Decomposition Temperature of Silicon Nitride in the System $Si_3N_4$-$C$-$N_2$ (1 atm)", Yogyo Kyokai Shi, 81, 441-444 (1973).

The decomposition temperature of $Si_3N_4$ in the system $Si_3N_4$-$C$-$N_2$ (1 atm) was determined to be 1839°C ± 14°C. A brief discussion is given regarding $\beta$-$Si_3N_4$ crystals that formed during the decomposition experiments.


Study of microstructure of hot-pressed material comprising 70 w/o $Si_3N_4$ and 30 w/o $Al_2O_3$. Structure consisted of $\beta$ or $\beta'$ grains bridged with x-phase or glass. $\beta$ to $\beta'$ transformation proceeds by solution precipitation.


Nitridation kinetics on high purity, 2 μm Si powder were linear. The observed activation energy of 158 kcal/mol and rate dependence upon square root of particle size indicate that diffusion of N through a $Si_3N_4$ product layer is rate-controlling. Reaction proceeds through repeated cracking or exfoliation of $Si_3N_4$ layer.


$\alpha$- and $\beta$-$Si_3N_4$ powders containing selected impurities and 5 w/o MgO were hot pressed to full density. Use of the former powder gave higher strength. CaO and alkaline oxides reduced high temperature strength but $Fe_2O_3$ and $Al_2O_3$ had no apparent effect.


Summarizes crystal structure, fabrication, and properties of "sialon" materials and other Si-M-O-N ceramics where M = Al, Li, Mg, Ga, or Be.

“Sialons” and other nitrogen ceramics offer better prospects for technological exploitation than $\text{Si}_3\text{N}_4$. Structures, phase relationships, and properties of these new oxynitrides are reviewed.


Announcement of development of “sialon” materials such as $\beta$-$\text{Si}_3\text{N}_4$ containing up to 60% $\text{Al}_2\text{O}_3$. Resulting $\beta$-material has the desirable properties of $\text{Si}_3\text{N}_4$ and is easier to fabricate.


Reaction-bonded $\text{Si}_3\text{N}_4$ prepared from pure (98%) Si powder was tested at room temperature and at temperatures up to 900°C after heating in air for up to 9 hours. Results show that the small increase in $K_{IC}$ is due partly to oxidation and partly to microplasticity at the crack tip. High temperature modulus of elasticity decreased with increasing temperature but the room temperature modulus increased for specimens held for long periods at high temperature. The modulus of rupture decreased with both increasing temperature and longer times at high temperature.


Etching of polished sections of reaction-sintered $\text{Si}_3\text{N}_4$ in 40% HF left material that was mainly $\beta$-$\text{Si}_3\text{N}_4$. Some hexagonal $\beta$-$\text{Si}_3\text{N}_4$ crystals had hollow cores.


Discusses the effects of solid and gas impurities on nitridation of Si.


Models of nitridation are derived from microstructural observations and it is suggested that there are at least two independent nitridation mechanisms.


The crystallization of $\beta$-$\text{Si}_3\text{N}_4$ in Si powder heated in N atmosphere at 1350-1450°C was studied. A shell of $\text{Si}_3\text{N}_4$ forms on the surface and then spikes penetrate into the Si grains. The spikes grow together into a single grain with many dislocations. The reaction rate is linear.

Of the materials currently being evaluated for gas-turbine components, hot-pressed Si₃N₄ is attractive because of its low coefficient of thermal expansion, good thermal shock resistance, and high strength at elevated temperatures. Material developments for engineering applications must include increased fracture toughness, improved oxidation and creep resistance, and improvements in high temperature strength. Si₃N₄ materials must be developed to increase the Weibull modulus ‘m’ in order to provide a more consistent material.


Use of H in nitriding gas in flow system gives strength increase similar to that obtained by using static rather than flowing N.


A “flow” nitriding system was used to study development of strength in reaction-sintered Si₃N₄. Material produced under “flow” conditions is notably weaker than that produced under “static” conditions. Low strengths obtained in nominally “static” experiments may be the result of unsuspected gas flow.


Linear relationships were found between mean strength and N weight gain for isostatically-pressed Si compacts nitrided to weight gains of <60%. For a given Si powder, the relationship depends upon the green density of the compact. A linear relationship that exists between mean strength and nitrided density is independent of green density for the compacts studied.


Extension of work reported in Entry No. 238.


Linear relationships were found between mean strength and N weight gain for Si compacts made from two fine powders. Finer particle size powders have greater potential for producing high strength material than course powders.


Liquid zones of Si were exposed to various gaseous ambients containing N and NH₃ in a floating zone apparatus. Concentration of N in Si near melting point if 10¹⁹ atoms per cm³. Si₃N₄ precipitates from supersaturated liquid during cooling.

The kinetics of interaction of NH₃ and a Si single crystal substrate were studied at 1350, 1300, 1250, 1200, and 1150 C. The isotherms of the rate of increase in film weight correspond to the equation: \( h = 10^8(k/d) \log (t+1) \), where \( k \) is the reaction rate constant \( (g/cm^2\cdot min) \), \( d \) is the density of Si₃N₄, viz. 3.18 g/cm³, \( h \) is the thickness of the Si₃N₄ film in Å, and \( t \) is the time in minutes. The energy of activation was 57.8 kcal/mole.


The crystal structure of α-Si₃N₄ was investigated by an X-ray method using a single crystal specimen prepared by CVD. The O content, 0.5 ± 0.03%, was determined by 14 MeV neutron activation analysis. α-Si₃N₄ is essentially pure and not an oxynitride.


Growth of Si₃N₄ crystals in the SiCl₄ (or SiCl₃H)-H₂-N₂ system was studied at 1000-1760 C. Whiskers of α-Si₃N₄ grew more readily on a heated W filament than on a graphite substrate. At 1500-1600 C crystals had no branches but at >1700 C there was remarkable secondary growth. Deposition on a substrate at 1400-1500 C would be suitable for the growth of fibrous Si₃N₄ crystals from the vapor phase.


Si₃N₄ produced by vapor phase reaction between SiCl₂ and NH₃ was examined by X-ray diffraction, IR spectroscopy, chemical analysis, and electron microscopy. The reaction produced amorphous products that slowly crystallized to α-Si₃N₄ with the evolution of excess N and H.


A total systems approach - design, materials processing and fabrication, materials properties, component test data, failure analysis, and NDT - is presented using a reaction-bonded Si₃N₄ nozzle (stator) of a small gas-turbine engine as an example. Emphasis is given to the design, testing, and failure analysis portion of the process and how these results are used to study the materials processing problems.


Samples containing 80% α-Si₃N₄ were annealed at 1600 C for 2-16 hours in N. Fibers, 0.1-0.2 μm, formed in the pore space at <1600 C while at 1600 C thick columnar crystals formed. The latter crystals are not associated with the β-phase. α/β transformation is attributed to loss of O.

Oxidation in air begins at 700-750 C with formation of amorphous SiO₂ and cristobalite. Formation of latter increases with temperature and Mg and Ca silicates form above 1000 C. Mg, Ca, and Fe lower oxidation resistance.


Increase of O partial pressure in preparation of Si₃N₄ by CVD gives polycrystals rather than single crystals.


Results of O content analysis and structure determination on α-single crystals indicated the α-Si₃N₄ is a polymorph of Si₃N₄ and not an oxynitride, S₁₁₅O₀₅N₁₅.


Alpha-Si₃N₄ was formed by vapor-phase reaction in the system SiO₂-C-N₂. IR absorption profile shows band at 800 cm⁻¹ identified as Si-N stretching.


Si₃N₄ was prepared on graphite susceptors by chemical vapor deposition using a mixture of SiCl₄, H, and N gases. Prismatic single crystals of α-Si₃N₄ with hexagonal morphology were obtained. Felt-like fibers, whiskers, and thin plates of Si₃N₄ were also produced. The effect of temperature and N partial pressure on the character of the deposited material was studied in detail.


Prismatic single crystals of α-Si₃N₄ were prepared on graphite susceptors by vapor-phase reaction from a SiCl₄, N, and H gaseous mixtures. The α-Si₃N₄ crystals prepared were compared with those already reported and contained less O (0.05-0.09 w/o).


Impact resistance of Si₃N₄ was improved by petalite surface layers but not by ZrO₂.


Quenching from 1350 C enhanced strength marginally.

Single crystal X-ray diffractometer data were used to refine the crystal structure of α-Si₃N₄. Bond length and site occupancy data do not indicate any O in the structure.


Review of nitride refractories and uses of Si₃N₄.


The content of O (as oxynitride) in partially oxidized Si₃N₄ and in SiC refractories with a nitride and oxynitride bond were determined by the vacuum-extraction method.


The sintering of SiC and Si₃N₄ in the presence of oxides and elements is reviewed.


A review with 19 references.


α-Si₃N₄ was synthesized by reduction of SiO₂ in a N atmosphere using various thermal treatment conditions and compositions of SiO₂ and C. Optimum reaction conditions and products obtained are described.


Sintering behavior and other properties of Si₃N₄ and AlN bodies hot pressed with additives are reported as well as rotor testing results at room temperature using model turbine-like blades. Problems in using ceramics in turbines are also reviewed.


Data on reactions of Si₃N₄ and Si₂ON₂ with acids and alkaline hydroxides. Si₂ON₂ is less stable than Si₃N₄.


Cyclic fatigue behavior of two grades of hot-pressed Si₃N₄ was investigated. Flat, cantilever type specimen (5½" x 1"), loaded by an eccentric driver rotating at 1800 rpm, were tested at temperatures up to 1300 C. Lifetime of low purity material was controlled by stress corrosion at temperatures ≤1200 C. Above that temperature plastic deformation was rate controlling for both materials.

Replica and thin foil transmission microscopy, X-ray diffraction, microprobe and Auger analyses were used to investigate the grain morphology, distribution of impurities and inclusions, phase and dislocation structures of commercial hot-pressed Si$_3$N$_4$. High concentrations of impurities, e.g., Ca, were detected at grain boundaries. Low density Si$_3$N$_4$ inclusions degraded strength. Correlations among strength, densification, and distribution of elements and phases are considered.


Alkaline oxide additions improve wetting of Si$_3$N$_4$ by MgSiO$_3$. Hot pressing of Si$_3$N$_4$ occurs via liquid-phase sintering. Alkaline impurity level should be <50-100 ppm for optimum strength.


Tensile, creep, and stress-rupture data for two commercial hot-pressed Si$_3$N$_4$ materials are presented. Strength is controlled by the grain-boundary glassy phase and deformation, at temperatures >1000 C, is controlled by grain-boundary sliding. A model based on the concept of geometrically necessary wedge cracks accounts for the observed effects of strain rate, stress, temperature environment, and impurity content. These materials are creep strain limited.


Si$_3$N$_4$ oxidizes in air at 1100-1500 C mainly with the formation of SiO$_2$ and addition of NaF contributes to formation of Si$_2$O$_2$N$_2$. In a CO atmosphere the additions of CaF$_2$ and MgO also contribute to the formation of Si$_2$O$_2$N$_2$ at 1550 C.


(In French)

The action of N on Si at high temperatures yields orthorhombic Si$_3$N$_4$, as determined by X-ray identification. Nitrides, Si$_2$N$_2$ and SiN, do not form. The Si$_3$N$_4$ is not attacked by alkaline washings but is attacked with difficulty by H$_2$SO$_4$, concentrated HF, or fused carbonates. Si and N may be determined by attack in VACUO with PbO or Na$_2$O$_2$.


Experimental observations for hot-pressed Si$_3$N$_4$ and SiC are presented to examine the crack size effect and its predicted relation to materials problems.


SiC dispersions of average particle size 5, 9, and 32 μm were used to form hot-pressed composites with Si$_3$N$_4$. Strength of the two larger particle dispersions was controlled by crack size. Strength of fine particle dispersion was controlled by both fracture energy and elastic modulus. Several of the composites appear promising as high-temperature structural materials.

High-temperature strength of commercial hot-pressed Si₃N₄ was investigated. Results indicate that strength degradation and sensitivity of high-temperature strength to stressing rate is attributed to subcritical crack growth caused by stress-enhanced grain boundary sliding at the crack front. The susceptibility to crack growth increases with increasing impurity content (i.e., Ca) and increasing temperature. The viscosity of the boundary phase greatly influences the high-temperature mechanical behavior.


A fracture mechanics approach was used to study the hot-pressing behavior and mechanical properties of Si₃N₄. High strength of material fabricated from high α-Si₃N₄ powder relates to high fracture energy, the latter being attributed to the presence of elongated grains.


Hot-pressing technique using a powder vehicle as a pressure transmitting medium is described. A 70% dense reaction-sintered Si₃N₄ turbine blade was densified to 98% of theoretical. Pressure transfer and effect of surface geometry on shape are discussed.


An attempt was made to densify the porous reaction-sintered Si₃N₄ by means of infiltration which only succeeded with so-called de-oxidation alloys which react with Si₃N₄. The phases, structures, and mechanical properties of the best of these composites are reported.


Atmospheric pressure sampling and mass spectrometry were used to analyze the vapor constituents of the oxidation over Si₃N₄ compacts at 1000, 1200, and 1400°C. The gases observed were NO and N, no SiO was detected. The oxidation of Si₃N₄ yields SiO₂ and NO followed by the dissociation of NO into N and O.


Vapor species generated from the oxidation of Si₂ON₂ were examined by mass spectrometric and atmospheric pressure sampling techniques. The oxidation yields NO and N but not SiO. The process is similar to the oxidation of Si₃N₄ in which NO is a major product which subsequently dissociates.


The nitridation of Si was examined by analyzing the atmosphere with a mass spectrometer. SiO vapor was found throughout the entire temperature range in the order of 10⁻³ of the volume of the nitriding agent. Controversial results obtained in previous investigations are explained in terms of the SiO vapor and the O partial pressure of the system. The effects of H and H₂O on nitridation are also discussed.
Fiber reinforcement of Si$_3$N$_4$ is a possible solution to the brittleness problem which limits the use of ceramic materials in engineering. Mechanical property data presented for Si$_3$N$_4$/SiC fiber composites show the capability of increasing the fracture toughness of Si$_3$N$_4$ by fiber additions.

Development, manufacture, properties, and applications of Si$_3$N$_4$ are reviewed.

Review of the fabrication processes and engineering properties of reaction-sintered Si$_3$N$_4$.

The oxidation resistance of Si$_2$N$_2$O powders was studied at 16-135 torr and $>$1100 C. Two successive processes, interfacial (activation energy 43 kcal/mol) and diffusional (activation energy 36 kcal/mol), control the kinetics of the oxidation reaction. The reaction rate is almost independent of O pressure except initially when O absorption is the main process.

A fully instrumented experimental hot-pressing system is described in which the temperature and pressure application are reproducibly controlled and the densification of powder is continuously recorded. The equipment has been used to study the effects of process variables on the densification of all $\alpha$-Si$_3$N$_4$ pressed at 1700-1750 C. Effects of some variables were examined with respect to modulus of rupture measured at room temperature. Time at temperature has a pronounced effect - some electron micrograph evidence is given.

Addition of H to the nitriding atmosphere altered the grain structure and grain-boundary composition of Si$_3$N$_4$, improving both the room-temperature and high-temperature physical properties.

X-ray data show $\alpha$-Si$_3$N$_4$ unit cell of P31c symmetry ($a = b = 7.765$, $c = 5.622$ Å) contains four formula units. Structure was refined to R = 8.6% for non-zero data. The sequence of the planes containing Si atoms is ABCD.

Young's modulus for Si$_3$N$_4$ ceramic fibers was determined by flexural vibration technique. Removal of surface silica changed E values from 1.52-2.21 to 2.51-2.98 dynes/cm$^2$. 

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Investigated were effects of heat treatment, atmosphere, and particle character on sintering. $\mathrm{Al}_2\mathrm{O}_3$ and $\mathrm{MgO}$ promote densification. High densities can be obtained and a liquid phase sintering mechanism is proposed.


$\alpha$-$\mathrm{Si}_3\mathrm{N}_4$ solid solution was formed by nitriding Si powder with $\mathrm{AlN}$ and/or $\mathrm{Al}_2\mathrm{O}_3$ in a N-H atmosphere at 1200-1400 $\degree\mathrm{C}$. Lattice spacings and intensities are given for $\alpha$-$\mathrm{Si}_3\mathrm{N}_4$ and for the new solid solution.


A ceramic/plastic forming route, warm molding, has been developed and used for the fabrication of reaction-bonded $\mathrm{Si}_3\mathrm{N}_4$. This technique makes it possible to fabricate complex shaped ceramic components at medium production rates, with high density, high fracture strength, and good as-fired surface finishes.


Additions of ~2.5 at/o rare-earth oxides as $\mathrm{Ce}_2\mathrm{O}_3$, $\mathrm{CeO}_2$, $\mathrm{CeH}_3$, and especially $\mathrm{CeN}$ yield $\mathrm{Si}_3\mathrm{N}_4$ with high density (98-99.9% theoretical) and improved thermomechanical properties. Data are included on microstructure, oxidation, and high-temperature creep.


Very high-purity, fine-particle-size, amorphous $\mathrm{Si}_3\mathrm{N}_4$ powders were produced by thermal decomposition of $\mathrm{Si(NH}_2)\_2$ in vacuum. The powder gradually transformed to $\alpha$-$\mathrm{Si}_3\mathrm{N}_4$ at temperatures $\leq$1450 $\degree\mathrm{C}$, and to $\beta$-$\mathrm{Si}_3\mathrm{N}_4$ at higher temperatures. Hot-pressing parameters, chemical etching, and dielectric property measurements are discussed.


Double-torsion technique was used to study slow crack growth in $\mathrm{Si}_3\mathrm{N}_4$. Stress intensity data are given for several environments at temperatures near ambient.


Review of status of ceramic materials with potential for turbine applications. $\mathrm{Si}_3\mathrm{N}_4$ and SiC have good high-temperature properties and show promise for low cost forming techniques. Development of design technology for these materials is discussed.

The reaction products formed by the reaction of metals and alloys with Si-based ceramics in air at temperatures ~1000°C after 100 hours were silicides, silicates, and carbides. The severity of the interaction depended on temperature and the ease of migration of free Si from the ceramic part to the metallic phase. These reactions may be deleterious in applications in which the ceramics and metals are in contact for extended periods at high temperature.


Weight losses of up to 20% were found on Si₃N₄ powders milled in Al₂O₃ and heated in N at 1450°C. Kinetics and thermodynamics of possible decomposition reactions are discussed.


The kinetics of the reaction of Si powder compacts and N to form Si₃N₄ were investigated thermogravimetrically from 1300-1450°C. The results indicate that trace amounts of O inhibit the rate of nitridation by forming a thin protective layer of SiO₂, whereas Fe impurities catalytically accelerate the rate of reaction by liquid-phase formation. Complicating factors that account for difficulties in interpreting the reaction kinetics and for the poor agreement among previous investigations are discussed.


It is shown that O impurities at levels considerably <10 ppm can significantly retard the rate of nitridation of Si powder compacts. Outgassing and the use of a suitable getter enhance the rate of nitridation.


The effect of O partial pressure on the amount of Si nitrided was small but with decreasing O pressure the amount of β-phase increased and the α-phase decreased.


Si₃N₄ was hot pressed with 5% MgO at 1450-1900°C under N pressure. Maximum density obtained was 95% of the theoretical value. The sintering process was inferred to be liquid-phase divided into two processes: rearrangement and solution precipitation. Rearrangement contributed ~10% and solution precipitation the remaining 17% of densification.


Density of 95% of theoretical was obtained by gas-pressure sintering of Si₃N₄ with 5% MgO at 10 atm N and 1800°C. Densification was attributed to rearrangement at <1500°C and solution precipitation at higher temperature.

α-Si₃N₄ had a lower oxidation resistance than β-Si₃N₄ and the activation energies for each phase were similar. The results fitted a parabolic rate law and O diffusion in cristobalite was inferred to be the rate determining process.


Structurally pure α-Si₃N₄ was obtained by the thermal decomposition, at temperatures up to 650 C, of Si(NH)₂ prepared by bubbling NH₃ into cooled SiCl₄. From a thermodynamic point of view the incorporation of O into Si₃N₄ is inevitable and the reasons are shown.


Si₃N₄ powder containing 5% MgO was sintered to >90% of theoretical density at 1700 C in N at 10 atmospheres.


Discussion regarding agreement of Wills’ data with theory of isomorphous replacements of ions in oxynitride structures. (See Entry Nos. 398 and 399)


The viscosity of the grain-boundary amorphous phase in commercial hot-pressed Si₃N₄ was measured by an internal friction technique. The viscosity in the region of the glass transition (850-900 C) was ~5 x 10¹⁵ p/cm² of the grain boundary, with an apparent activation energy of 163 kcal mol⁻¹.


High-temperature reaction of SiO₂ and N in the presence of C was used to prepare Si₃N₄. Formation of Si₃N₄ started at 1300 C and was complete by 1550 C without any formation of liquid Si. The highest yield was attained when the mole ratio C/SiO₂ = 2.6.


Measurements were made by ultrasonic technique of the normal modulus of elasticity of α-Si₃N₄ whiskers of three crystallographic orientations: E₅ K<0001> = 47,930, E₅ K<1212> = 38,530, and E₅ K<2421> = 49,750 kg/mm².

Short communication on investigations of \( \alpha \)- and \( \beta \)-Si\(_3\)N\(_4\) by X-ray and electron diffraction. Diffraction patterns were indexed and lattice parameters determined.


Alpha- and beta-Si\(_3\)N\(_4\) coexist in different proportions depending on nitriding conditions. In general, \( \alpha \)-Si\(_3\)N\(_4\) formed on the surface of the piece during nitriding, and \( \beta \)-Si\(_3\)N\(_4\) formed in the center. Temperatures below 1200 C and above 1300 C promoted the growth of \( \alpha \)-Si\(_3\)N\(_4\) and \( \beta \)-Si\(_3\)N\(_4\) respectively. The finer the particle size and the lower the purity of the Si powder, the more \( \alpha \)-Si\(_3\)N\(_4\) formation is favored. Articles of \( \alpha \)-\( \beta \)-Si\(_3\)N\(_4\) powders were pressed under the same conditions and sintered in N at 1400-1800 C for three hours. Porosities and mechanical strength were measured in relation to sintering temperature and pressing pressure.


Pyrolytic Si\(_3\)N\(_4\) was deposited on graphite substrates, using a mixture of SiCl\(_4\), NH\(_3\), and H\(_2\). The effect of deposition conditions on some properties of the deposited products and the dependence of formation of amorphous or crystalline deposits on deposition temperature and total pressure were investigated. The surface and cross-sectional structures showed growth cones and oriented crystals which are strongly dependent on the deposition conditions. No segregation of N or Si at the cone boundaries was found.


CVD Si\(_3\)N\(_4\) (pyrolytic Si\(_3\)N\(_4\)) has been prepared from a SiCl\(_4\) + NH\(_3\)/H\(_2\) system at 1100-1500 C under total pressures of 5 to 300 torr. The densities of the crystalline deposits are 3.15 to 3.18 g cm\(^{-3}\) and almost independent of the deposition conditions, while the densities of amorphous deposits depend strongly on the deposition conditions, having a minimum value of 2.60 g cm\(^{-3}\) at 1200 C and 40 torr. The deposition rate of the Py-Si\(_3\)N\(_4\) obeys a linear law and has activation energies of formation 30 to 33 and 53 kcal mol\(^{-1}\) for the amorphous and crystalline deposits respectively.


Review of manufacturing methods, properties, and applications of Si\(_3\)N\(_4\). Structural, refractory, electrical insulating, abrasive, and coating applications are considered.


The microstructure of \( \beta \)-Si\(_3\)N\(_4\) produced by hot pressing 93% \( \alpha \)-Si\(_3\)N\(_4\) powder with 5 w/o MgO was examined by replica and thin foil techniques. The \( \beta \)-Si\(_3\)N\(_4\) exhibited preferred orientation and evidence was found for the presence of an amorphous phase.
Creep testing was carried out at 1227 C and 77 MN/m² and at 1370 C and 77 MN/m² on commercial hot-pressed Si₃N₄ materials and a range of hot-pressed sialon research materials. Data on the modulus of rupture strength at room temperature, 1200 C, and 1370 C and on oxidation resistance at 1370 C are included.

Recrystallization processes in a Si₃N₄-base material containing Si₃N₄, 5% MgO hot pressed at 1600-1700 C were studied by metallurgical and electron microscopy. Results showed the grain size decreased as a result of hot pressing.

X-ray diffraction studies of sintered powdered mixtures were used to show that AlN is in a substitutional solid solution in Si₃N₄-AlN-Al₂O₃ system and that the solubility limit is mainly determined by vacancy density.

Solid solution in the system was of the type Si₃N₄₅₅. (Al₂O₃-Ga₂O₃). A tentative phase diagram is given.

Studies were made on sintered Si₃N₄ with MgO added and hot pressed at 1730 C. At low concentrations of MgO only β-Si₃N₄ was observed, as MgO concentrations increased MgSiN₂ was formed, and, later, 2MgO·SiO₂. Solubility limit of MgO in β-Si₃N₄ is estimated to be 30% at 1730 C. Enhanced sintering of β-Si₃N₄ with MgO is attributed to diffusion of Si vacancies.

X-ray diffraction analysis and electron probe microanalysis showed the presence of a new phase in mixtures of Si₃N₄, α-Al₂O₃, and Li₂CO₃ powders compacted at 1750 C. The new phase is a solid solution comprising Si₃N₄-Al₂O₃ or Si₃N₄-Li₂O-Al₂O₃.

The general design philosophy and methods used in the design of ceramic turbine stators and rotors are discussed. Test results on Si₃N₄ components are presented.

A method for the determination of N in Si$_3$N$_4$ in which the nitride is dissolved in a mixture of HF contained in a closed vessel lined with PTFE. The NH$_3$ formed after dissolution at 150°C overnight (at least seven hours) is steam distilled from an alkaline solution and determined by titration. The coefficient of variation is ~1.0%.


Review of preparation and properties of reaction-bonded Si$_3$N$_4$. Duplex structure is described. Properties discussed include density, bend strength, creep, hardness, thermal expansion, elastic modulus, and oxidation resistance.


Si$_3$N$_4$ is presented as one of the new, hard, inorganic nonmetallic materials as having possible engineering applications. Si$_3$N$_4$ responds to normal manufacturing processes and possesses good thermal shock resistance. It is available in the form of (1) theoretical density material with transverse rupture strength of the order of 100,000 psi, (2) porous, permeable and non-permeable bodies, (3) whisker wool. Production routes and design considerations are explained. A compact chart reviewing the properties and suppliers of Si$_3$N$_4$ is provided.


Recent experience in production methods, physical properties, and current experimental applications of reaction-bonded Si$_3$N$_4$ bodies are described. Applications are aimed at establishment of an appropriate design philosophy to exploit the unusual properties obtained in this material.


Describes experiments to establish the conditions under which α- and β-Si$_3$N$_4$ may be produced independently or in varying proportions. Suggests a method for varying the properties of Si$_3$N$_4$ by incorporating a dispersion or continuous network of other elements and compounds.


The equilibrium pressure of N gas over pure Si metal and Si$_3$N$_4$ was measured in temperature range 1400-1700°C. From the experimental data, the standard free energies and enthalpies of formation of α-Si$_3$N$_4$ have been calculated as functions of temperature over this range. Specific heat, molar enthalpy, molar entropy, standard enthalpy of formation, and standard free energy of formation are estimated for the temperature range 298-1400°C.


Effects of surface removal and annealing on flaws in and stress intensity factors of hot-pressed Si$_3$N$_4$.\[50]

Surface flaws of controlled size and shape were produced in high-strength hot-pressed Si₃N₄ with a Knoop microhardness indenter. Fracture was initiated at a singly suitably oriented flaw on the tensile surface of a four-point bend specimen. The stress required to propagate the controlled flaw was used to calculate stress-intensity factor, KIc. Effects of annealing and slow crack growth at high temperatures are also discussed.


The room temperature mixed-mode fracture of commercial hot-pressed Si₃N₄ was examined using controlled surface flaws in four-point bending. Catastrophic fracture paths were non-coplanar with the initial flaw plane, and stress intensity factor ratio KI/IKIc was <1 for fracture in modes II and III. A non-coplanar maximum strain-energy release rate fracture criterion best described mixed-mode fracture.


Rheological properties of Si₃N₄ slips were examined as functions of solid-phase content and pH. Drying shrinkage of slip-cast articles was <3%.


The preparation of Si₃N₄ by heating pressed, extruded, or slip-cast Si powder in N and by other methods is described. The effects of temperature, atmosphere, and impurities on the rate of nitriding are considered: (1) the temperature must not be raised too quickly, (2) the presence of O can reduce the nitriding rate, (3) Fe₂O₃ and CaF₂ catalyze the reaction. The structures of the Si₃N₄ and of the fibers sometimes formed on nitriding Si are described.


Preparation of Phase-I and Phase-II nitrides of Si and Ge are described. Phase-I can be indexed as orthorhombic and Phase-II as rhombohedral.


The intergranular amorphous phase in Si₃N₄ hot pressed with 7% MgO was identified, by Auger electron spectroscopy, as a glass having the estimated composition (0.40 ± 0.03)CaO · (0.75 ± 0.10)MgO · 2SiO₂. The rapid decrease in strength at temperatures >1000 C is attributed to the decrease in viscosity of this glass phase.


Pure α-Si₃N₄ was prepared by CVD and analyzed for O content. Five determinations showed (0.30% ± 0.005%) O with a standard deviation of 1.00%. The indexed X-ray pattern showed only α lines. Treatment at 1800 C and 275 psig N in a pressure furnace for several hours produced no conversion to β-Si₃N₄. It is concluded that α-Si₃N₄ is a stable, high temperature phase that does not require O for structural stability.

Preparation and properties of Si$_3$N$_4$ are described. The reaction-sintering technique to produce articles of Si$_3$N$_4$ is treated in detail, followed by a review of the mechanical and physical properties of the material. Si$_3$N$_4$ can be used for high temperature applications. A review of the possible applications is given.


Si$_3$N$_4$ samples, surface ground to various depths, were measured using a technique developed for accurately determining the relative abrasive wear resistance. Resistance was lowered for a distance approximately equal to the depth of the cut, suggesting that care must be taken in the final finish operations to remove the surface damage introduced by earlier stages.


A new material having excellent thermal shock and oxidation resistance and adequate creep strength at 1200 C was produced as a result of a search for stator blade materials for use in gas turbines at 1200 C. The best material was found to be Si$_3$N$_4$ stiffened with a fine dispersion of SiC. Reviewed are production methods, properties, and field trials in experimental gas turbines.


ESCA is used to characterize Si$_3$N$_4$ surface oxidation. Oxidation at high temperature yields oxynitride films with gradients in composition.


Of many materials examined for potential aircraft gas turbine engine components only Si$_3$N$_4$ and SiC exhibited the physical and mechanical properties above 1423 K to make them contenders for high temperature applications. An experimental glass-ceramic may be useful below that temperature.


ZrO$_2$, ZrN, ZrC, and Zircon are effective aids in densification of Si$_3$N$_4$ by hot pressing to produce material with bend strength as high as 137 ksi.


The addition of 3.0 w/o ZrO$_2$ - monoclinic or stabilized cubic form - improved the density (99% theoretical), creep, and oxidation resistance of hot-pressed Si$_3$N$_4$.  

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$Si_3N_4$ specimens with controlled impurity levels were prepared by hot pressing and tested for flexural strength at 1375 C. Decreasing the metallic impurities increased flexural strength. High temperature properties of two specimens of different purities were compared.


Discusses advances in the use of refractory ceramic materials based on $Si_3N_4$ for high temperature applications.


Time-to-failure data are given for hot-pressed $Si_3N_4$ in combustion gases at 1173 and 1223 K. Na, Mg, and V additions to fuel don’t affect failure times but failure in gas is more rapid than in air. Failure time is shorter at the higher temperature and room temperature fracture toughness can be increased by exposure to hot gas.


X-ray powder diffraction patterns of $\alpha$- and $\beta$-$Si_3N_4$ and $Ge_3N_4$ were separated and indexed. The structures of the $\beta$-nitrides are of the phenacite type ($BeSiC_4$). The structure proposed for the $\alpha$-nitrides is related to that of phenacite, one layer of phenacite type alternating with a similar but differently oriented layer in a hexagonal cell.


Equilibrium measurements are reported on the approximate ratios of pressures of $O$ to $N$, $10^{-15}$ at 1400-1500 C, required for the existence of $Si_2N_2O$ under equilibrium conditions at elevated temperatures.


Evaporation of $Si_3N_4$ was studied by the Langmuir and Knudsen methods in the temperature range 1688-1773 K. The compound dissociates into Si (solid or liquid depending on the temperature) and N. The rate of evaporation depends on the area of the effusion orifice. The equilibrium pressure of N above $Si_3N_4$, the evaporation coefficient, and the standard heat of formation were determined.


Summarizes known physical, mechanical and chemical properties of $Si_3N_4$ and compares them with properties of several ceramics and other materials in common use. It is shown how the combination of certain properties in $Si_3N_4$ make it an ideal material for six general types of applications.


Discussion of the effect of various binders on sintering of $Si_3N_4$. 

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Comparison of two methods of preparing strong and dense Si$_3$N$_4$ articles. In one, blanks from powdered Si were formed and then nitrided producing only thin-walled articles. In the second, powders were formed and the blanks sintered producing thin- and thick-walled articles without inclusions of fused non-nitrided Si.


Mixed Al$_2$O$_3$-Si$_3$N$_4$ materials were made by cold pressing and sintering in a N atmosphere at various temperatures to 1650 C. Mullite formation claimed to activate sintering. Maximum observed bend strengths were ~6 kg/mm$^2$ (8.5 psi) and strengths decreased with increasing Al content.


The mechanical properties of materials in the MgO-Si$_3$N$_4$ system are dependent on composition, temperature, sintering time, and testing temperature. The optimum sintering temperature is 1600-1630 C. Strength is related to bulk density.


Study of the effects of temperature, composition of green powder, and gaseous medium on the structure and properties of materials of the Si$_3$N$_4$-SiC system. Products sintered under optimum conditions have improved mechanical properties due to the formation of a bond of Si$_3$N$_4$ that penetrates into the pores at high temperatures.


Reaction of W and Ta with Bn, AlN, and Si$_3$N$_4$ were studied in Ar to 2100 C. W reacted with Si$_3$N$_4$ to form W$_3$Si$_2$. Ta formed TaN and TaSi$_2$.


Si$_3$N$_4$ and SiC materials obtained by pyrolytic deposition are more resistant than sintered materials to corrosion in hot air and CH$_4$ combustion products containing various salts. Resistance is generally due to vitreous layer on ceramic surface.

A simple, accelerated service-simulation test was used to compare hot-pressed Si₃N₄ with other materials, under heavily loaded, lubricated, un lubricated, and elevated temperature rolling contact. The Si₃N₄ was the best commercially available wear resistant material tested under un lubricated ambient temperature conditions, but was not effective under heavily loaded lubricated conditions. Use of a solid lubricant at elevated temperature eliminated wear.


Using a simple, accelerated service simulation test Si₃N₄ was compared with En 31 ball bearing steel, high speed tool steels and WC under conditions of heavily loaded, lubricated, un lubricated, and elevated temperature rolling contact. Low density, porous, heterogeneous reaction-bonded Si₃N₄ did not appear to be a suitable rolling material. Hot-pressed Si₃N₄ under lubricated test conditions was not as effective as En 31 and high speed tool steels and under un lubricated conditions was inferior to WC.


Acoustic fatigue occurred in thermally shocked TiB₂ and Al₂O₃, but not in hot-pressed Si₃N₄.


The internal structure of reaction-sintered Si₃N₄, after oxidation at 1000 C and 1400 C was examined by high voltage electron microscopy. A sheath region of amorphous SiO₂ around internal pores was formed after oxidation at both temperatures. The effects of oxidation on strength are discussed.


Na attacked grain boundaries at 550 C and Li caused extensive cracking at 400 C.


Oxidation rate of hot-pressed Si₃N₄ in O is slightly increased by addition of H₂O in temperature range 1200-1400 C. Nature of products and oxidation reactions are briefly discussed.


The “passive” oxidation behavior of Si₃N₄ hot pressed with 1 w/o MgO was studied at 1000-1400 C. The oxidation followed the classical parabolic behavior with an apparent activation energy of 375 kJmol⁻¹. The oxide film consists predominately of MgSiO₃, in which various impurity elements, Ca, Fe, Al, etc., concentrate. The rate controlling mechanism appears to be the outward diffusion of Mg ions and impurity cations from the grain boundary glass phase through the oxide film.

Binder was paraffin - 10% beeswax. Bend strength of slip-cast specimens was greater than that of pressed and sintered ones.


Effects of various catalyst additions on the nitriding of Si were studied experimentally. Selected additions were used to synthesize materials of compositions close to α-Si3N4 and β-Si3N4 respectively. Properties discussed include microstructure, lattice parameters, density, and thermal expansion.


Wetting angle decreased with decreases in total pressure and N partial pressure, but wetting mechanisms are poorly understood.


Reflectivities of Si3N4 and Si2ON2 were 12.2% and 8.8% respectively. Differences in reflectivity between reaction-bonded α- and β-Si3N4 are so small that they could not be distinguished. Microhardness data show Si3N4 to be slightly harder than Si2ON2.


Si3N4 powder containing 5% MgO was sintered at 1650 C to 90% of theoretical density. High temperature mechanical properties, oxidation behavior, and room temperature dielectric properties are discussed.


The densification behavior of Si3N4 containing MgO was studied. Initially the MgO forms a liquid phase which wets and allows atomic transfer of Si3N4. Evidence of a second phase between grain boundaries was obtained. Transformation from α- to β-Si3N4 is unnecessary for densification.


Liquid phase sintering and bulk decomposition are countervailing processes in the sintering of Si3N4 powder with 5 w/o MgO at 1500-1750 C. High densities can be achieved for long times at low temperatures or short times at high temperatures. Pore growth due to decomposition is said to limit shrinkage.


Oxidation of Si3N4 powder was investigated at various O partial pressures at temperatures from 1050 to 1300 C. Oxidation rate depended on O pressure during induction period. Rate during latter stages was diffusion controlled. Activation energy (35 kcal mol e-1) agreed with that for diffusion of O in SiO2.

Experimental values were obtained for mechanical properties of Si3N4 over a range of densities. Analyses of results for fracture strength in bending and Young’s modulus show that reaction-sintered Si3N4 behaves as a normal porous ceramic body. All useful properties are attributed to the bulk material itself rather than to any effects of the reaction-sintered microstructure.


A.C. and D.C. conductivities of Si3N4 and Si-Al-O-N compositions were measured between 400 and 1000 C. The materials were p-type below 900 C and n-type above 900 C. Electrical properties are consistent with presence of glassy phase.


Highest final weight gains and densities were obtained when Si-Al compacts with homogeneous microstructure were nitrided in O-enriched atmospheres. X-ray diffraction analysis showed a β'-Si-Al-O-N solid solution. Obtaining this phase depends upon adjusting O content after N pressure of the reaction atmosphere has been set.


Describes hot pressing and sintering of Si3N4 and SiC and discusses advantages and limitations of each process.


Experimental results obtained with hot-pressed Si3N4 and SiC at temperatures up to 1500 C are presented. The variations in high temperature strength as a function of impurity content, strain rate, and grain size are discussed. Reaction-sintered Si3N4 and SiC are also discussed.


Contaminant ion penetration can be substantial, and, in the case of Na, could affect mechanical properties.


Multiphase scales comprising mainly α-cristabolite and enstatite are oxidation products of commercial hot-pressed Si3N4. Large increase in rate at >1450 C is attributed to melting of scale. No O pressure dependence was found at 1400 C.

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Si$_3$N$_4$ and Y$_2$O$_3$ powder mixtures were hot pressed at 1750, 1800, and 1850 C. Reaction products were identified and a proposed phase diagram is presented.


The effects of fabrication on the high temperature strength of hot-pressed Si$_3$N$_4$ containing 5 w/o Y$_2$O$_3$ were studied. Materials containing crystalline Si$_3$N$_4$ . Y$_2$O$_3$ at grain boundaries had better high temperature strength than ones containing the same boundary composition in the glassy form.


Si$_3$N$_4$ has been prepared by heating pure Si in purified N at 1450 C. X-ray studies showed the presence of two nitrides and a method was devised for separating them. These nitrides differ in crystal structure, but have the same composition corresponding to Si$_3$N$_4$. Chemical tests were performed on finely divided Si$_3$N$_4$ prepared at or above 1450 C. Various alloys, Si content varying, were nitrided under different conditions and the X-ray diffraction patterns of the nitrides extracted were found to agree with that of α-Si$_3$N$_4$.


The steady-state creep behavior of reaction-bonded Si$_3$N$_4$ was examined in four-point bending with stresses ranging from 10,000 to 20,000 psi at 1200-1400 C. Creep rates were proportional to the 1.4 power of the stress. Microstructural examination indicated that the rate-controlling mechanism of creep is grain-boundary sliding.


High temperature creep tests (1200-1400 C) on hot-pressed Si$_3$N$_4$ showed the stress exponent of creep rate was ~1.7 and the activation energy for creep was determined to be 140 kcal mol$^{-1}$. Creep is ascribed to grain-boundary sliding.


Evidence for solid solution of AlN in β-Si$_3$N$_4$. Product at highest heat treatment temperature (1400 C) comprised β-Si$_3$N$_4$ phase, AlN, and an unidentified phase.


Refractory bodies were prepared from volcanic ash and 20-50 w/o powdered Al by sintering in a N atmosphere at 400 kg/cm$^2$ and 1400 C for 5 hours. α-Si$_3$N$_4$ whiskers were formed on the sintered bodies. Products included α-Al$_2$O$_3$ and β-Si$_3$N$_4$. 

Technique for production of foamed Si$_3$N$_4$, with controlled microstructure, using the rigid polyurethane foam route. Si$_3$N$_4$ foams with good compressive strength and porosities in the range of 90-60% have been fabricated. The fabrication, microstructure, and physical properties are presented.


Ceramic components, as hot-pressed Si$_3$N$_4$, would allow the jet engine to operate at $>$300 degrees higher and thereby markedly reduce fuel consumption. These ceramics could even make the gas turbine a practical proposition for the motor car, allowing it to be produced and operated about as cheaply as a conventional petrol engine.


Review of the status of Ford’s ceramic gas turbine program. (See entry nos. 489-498). Properties, costs, and required design considerations for ceramics are highlighted.


Si$_3$N$_4$ offers rain erosion resistance and thermal shock resistance in aerodynamic heating to velocities as high as Mach 7. Reaction-sintered Si$_3$N$_4$ is preferred for radomes and fabrication and dielectric data are given.


Review of the discovery, preparation, and properties of Si$_2$ON$_2$. Specific heat, thermal conductivity, thermal expansion, modulus of rupture, modulus of elasticity, Knoop hardness, and electrical resistivity were measured. Oxidation studies showed oxidation resistance superior to SiC and Si$_3$N$_4$ at temperatures as high as 1750 C.


Si$_3$N$_4$ compacts of near theoretical density can be produced without significant conversion to $\beta$- form by hot pressing $\alpha$-Si$_3$N$_4$ powders containing additives, chiefly 5 w/o MgO at 1500-1700 C and at pressures of 1 to 5 x 10$^3$ psi. MgO breaks down the amorphous SiO$_2$ layer which inhibits the deformation mechanism of the $\alpha$-crystallites.


Wetting of Si$_3$N$_4$ by liquid Si and binary Si alloys containing Cu, Fe, and B were determined by the sessile drop method. All contact angles measured were $<$90 degrees. Hot-pressed Si$_3$N$_4$ is easily wet by Si.

\( \beta' \)-sialon powders may be prepared in small amounts (0.2 g) by reaction of NH\(_3\) or NH\(_3\)-H mixtures with kaolin.

398. Wills, R. R., "Reaction of Si\(_3\)N\(_4\) with Al\(_2\)O\(_3\) and Y\(_2\)O\(_3\)\(^{•}\)\), J. Amer. Ceram. Soc., 58, 335 (1975).

Report of new phase 5Y\(_2\)O\(_3\) : Si\(_3\)N\(_4\) : Al\(_2\)O\(_3\) : Y\(_2\)O\(_3\) is an effective aid for sintering "sialon".


Role of Y\(_2\)O\(_3\) in hot pressing of Si\(_3\)N\(_4\) is to form low-melting Si\(_3\)N\(_4\) : 3Y\(_2\)O\(_3\) which further reacts to form more refractory compound Si\(_3\)N\(_4\) : Y\(_2\)O\(_3\). Diffraction data are given for both compounds.


Oxidation at 1000 C of various Y-Si-O-N compositions produced weight gains and volume changes. Suggestions are given to minimize oxidation problems in Y\(_2\)O\(_3\)-based hot-pressed Si\(_3\)N\(_4\).


Examination of compositions in the system Si\(_3\)N\(_4\) : Y\(_2\)O\(_3\) : SiO\(_2\) using sintered samples revealed the existence of two regions of melting and three Si\(_3\)N\(_4\) : Y\(_2\)O\(_3\) phases. Two ternary phases and one binary phase were observed. It is suggested that Y\(_2\)O\(_3\) promotes a liquid-phase sintering process which incorporates dissolution and precipitation of Si\(_3\)N\(_4\) at the solid-liquid interface.


Fracture was initiated at flaw, introduced by Knoop hardness indentation on bend specimen and K\(_{IC}\) was calculated from stress to propagate flaw catastrophically. Vacuum annealing and heating above 1200 C reduced K\(_{IC}\) 25%. This effect is ascribed to O and effects of oxidation are discussed.


Silicon lanthanide oxynitrides are prepared by the reaction between Si\(_3\)N\(_4\) and oxides of the lanthanide series. The oxides formed compounds of the type Si\(_3\)N\(_4\) : R\(_2\)O\(_3\) and R\(_4\)Si\(_2\)O\(_7\)N\(_2\) (R = lanthanide). Unit cells of these compounds are similar, and their structures are discussed in terms of those of known minerals.


Reviews previous work on the preparation and properties of Si\(_3\)N\(_4\).

Attempts to obtain a single-phase Si$_3$N$_4$ ceramic containing 5% MgO in the system Si$_3$N$_4$·Al$_2$O$_3$ were unsuccessful. The physical and mechanical properties of the materials and phases of the Si$_3$N$_4$·Al$_2$O$_3$ system were studied.


Suggests presence of N vacancies in Fe-doped Si$_3$N$_4$.


Si$_2$ON$_2$ is stable in an inert atmosphere at temperatures up to 1300 C but above this temperature (especially $>$1550 C), it rapidly volatilizes. Under these conditions the decomposition product is Si$_3$N$_4$. Decomposition in other atmospheres, particularly those containing O, is also discussed.

Technique for obtaining high-temperature fracture toughness of ceramic materials, as Si$_3$N$_4$, is described. A free-falling ball was dropped onto a ceramic specimen and the fracture toughness was determined by taking the product of the weight of the ball and the height from which the ball dropped when fracture occurred. Results are given versus temperature for hot-pressed Si$_3$N$_4$.


Si$_3$N$_4$ was synthesized at 1050-1500 C. The structure of the products was studied by X-ray diffraction, IR atomic spectroscopy, chemical analysis, and electron microscopy.


Recrystallized SiC made by a casting process and reaction-bonded Si$_3$N$_4$ shaped by a simple machining process before firing, offer not only high-temperature materials capable of living in the gas turbine environment, but also at an intricacy of shape consistent with combustor, shroud, and associated high-temperature component needs. The low expansion coefficient, thermal shock resistance, and 2900 F capability make Si$_3$N$_4$ a material of real merit. Properties, potential applications, and design capabilities are discussed.


Significant increases in strength at 1400 C were observed as the MgO/SiO$_2$ ratio was increased to 3:4. Observations are discussed with regard to possible changes in chemistry of grain boundary phase.


A review of materials development programs showing that hot-pressed Si$_3$N$_4$ and SiC are consistent engineering materials for gas turbine vanes. General machining parameters, including diamond wheel specifications are discussed.


After 27 different surface finishing procedures, strength, surface finish, and rolling contact fatigue life were determined for two grades of hot-pressed Si$_3$N$_4$. Rolling contact fatigue lives of Si$_3$N$_4$ with selected smoother finishes tested at 800 ksi Hertz stress were an order of magnitude longer than those obtained on the M50 bearing steel controls and more than twice as long as the best results previously obtained on Si$_3$N$_4$. 62
Six hot-pressed Si$_3$N$_4$ materials of varying composition were prepared, characterized, and evaluated in rolling contact fatigue (RCF). All equalled or exceeded the fatigue life of M50 steel at 325 lb load. A stress corrosion mechanism is used to explain the time-dependent fatigue behavior and life differences are attributed to differences in slow crack growth rates. Ten precision bearings containing Si$_3$N$_4$ rollers and steel races were designed, fabricated, and tested.

Hot-pressed Si$_3$N$_4$ evaluated as bearing material. Reports rolling contact fatigue tests of Si$_3$N$_4$ rods, and design, fabrication, and testing of full-scale roller bearings.

The incorporation of Ta wire increased the Charpy impact strength of hot-pressed Si$_3$N$_4$ from 0.5 to 14.8 ft/lbs. Specimens containing 50-mil wire retained impact strength to 1300 C. Data are also given on ballistic-impact, thermal-shock and thermal-aging resistance.

Hot-pressed Si$_3$N$_4$ matrix composites containing 5-15 w/o Y$_2$O$_3$ and reinforced with Ta wire exhibited excellent thermal fatigue and thermal shock properties, as well as impact resistance. Ta-reinforced material was as good as or better than the unreinforced material in creep at 1300 C. Component vanes and wedge shapes of both Si$_3$N$_4$ and the Ta-reinforced materials have been formed with minimal finish grinding using the “pseudo-isostatic” hot pressing technique.

Ta wire reinforcement in hot-pressed Si$_3$N$_4$-15 w/o Y$_2$O$_3$. Room- and high-temperature properties of matrix and reinforced materials were superior to those of other materials tested.

Charpy impact strength of Si$_3$N$_4$ reinforced with W was increased at elevated temperature but not at room temperature. With Ta wire reinforcements, Charpy impact strength increased at room temperature and the mode of failure was affected so that interfacial splitting along with ductile fiber elongation occurred, resulting in very small fragments of matrix breaking off upon impact.

Technique is described and results are presented on determination by neutron activation analysis of O in hot-pressed and reaction-sintered Si$_3$N$_4$.


Bend and tension tests were performed at room temperature on a commercial Si$_3$N$_4$ material. Using the two-parameter Weibull analyses for a material governed by volumetric flaw distribution, tensile properties of the specimen were determined and compared. Results indicated that the bend test tends to predict fracture stresses ~8% higher than those obtained in actual tension tests.


Fibrous materials such as SiC whiskers were added to SiC and Si$_3$N$_4$ and the resulting composites were consolidated by hot pressing. Addition of the SiC whiskers increases the impact strength of the SiC from 0.55 in/lbs (0.062 J) to 1.6 in/lbs (0.18 J) at room temperature and from 0.64 in/lbs (0.07 J) to 1.35 in/lbs (0.153 J) at 2400 F and the Si$_3$N$_4$ from 1.05 in/lbs (0.119 J) to 1.33 in/lbs (0.15 J) at room temperature and from 1.31 in/lbs (0.15 J) to 1.68 in/lbs (0.19 J) at 2400 F. Si$_3$N$_4$ has a higher impact strength than SiC. The thermal stability and shock resistance of the composites were determined under simulated gas turbine stator vane environments at 2400 F. The presence of whiskers did not seriously affect either characteristic.


Study of the processing characteristics and physical properties of Si$_3$N$_4$ ceramic bodies with duplex microstructure formed by "in situ" vapor reaction between Si powder compacts and N.


Discusses design, processing, and testing of Si$_3$N$_4$ components for gas turbines.


The beneficial impact in future energy demands, multiple fuel potential, and lessened dependence on foreign materials are sufficient motivation to initiate the recommended programs.

(Si, Al)N Alloys were deposited by reactive ion plating from Si and Al evaporation and NH₃ or NH₃ + 1% SiH₄ gas mixtures. Deposits had large columnar grains composed of smaller grains. At temperatures from 100-300°C there were no observable changes in morphology. Adhesion of deposits to a variety of surfaces was good.


An improved crack velocity monitoring procedure able to cope with irregular crack initiation and crack acceleration in ceramics was developed and used to obtain Kic measurements for Si₃N₄ and other ceramic materials.


Specimens were prepared of Si-Al-O-N compositions to permit evaluation of chemical, physical, and mechanical properties. Several different processing techniques were used on various precursor materials. Moduli of rupture and elasticity measurements were made and strength values were lower than expected from literature data.


Basic studies on the suitability of Si₃N₄ binders as a rolling bearing material with emphasis on interactive behavior with lubricating fluids are reported. The wettabilities of six lubricants on a Si₃N₄ surface were measured. Lubricant film thickness and traction force were measured with an optical elastohydrodynamic apparatus.


Wettability, lubricant film thickness, rolling/sliding traction coefficients, sliding friction coefficients, abrasive wear coefficient, and rolling contact fatigue of Si₃N₄ suggest that it possesses satisfactory ability to be lubricated by conventional lubricants, as well as good mechanical strength and fatigue resistance properties.


Life of M50 steel bearings with Si₃N₄ balls is controlled by life of currently available Si₃N₄ balls. Bearing behavior is illustrated and described.


Importance of understanding surface damage effects is emphasized. Rolling contact fatigue tests were done between Si₃N₄ and steel. Variables included lubricant viscosity, surface finish, type of contact (line or point), and hardness of steel rollers. Concludes that Si₃N₄ rolling elements can improve fatigue life of very high-speed bearings.

Mechanical properties, oxidation, and hot corrosion of Si$_3$N$_4$ and SiC are presented for comparison with those of superalloys. The hot-pressed ceramics are shown to have superior strength and environmental resistance but are lacking in impact strength. Reaction-sintered Si$_3$N$_4$ is shown to be a low-cost, low-strength material.


Review of the mechanical properties and design data of ceramic components, including reaction-sintered and hot-pressed Si$_3$N$_4$ and SiC with emphasis on the materials science considerations. General recommendations for future are made.


An ultrasonic nondestructive evaluation (UNDE) technique was developed to detect small defects in gas-turbine quality SiC and Si$_3$N$_4$. Conventional mechanical tests were also performed to verify defect sizes and to correlate material strength with UNDE results.


Concentrations of Si$_2$ON$_2$ cristabolite, and $\beta$-Si$_3$N$_4$ were determined over cross sections of reaction-bonded (2.20 g/cc) Si$_3$N$_4$ specimens creep tested at different rates under oxidizing conditions. Internal oxidation degrades creep resistance.

437. “Engineering Property Data on Selected Ceramics. Volume I, Nitrides”, Metals and Ceramics Information Center, Battelle's Columbus Laboratories, Columbus, Ohio, Report No. MCIC-HB-07-Vol. I (March 1976), section 5.3.3. (AD-A023 773)

Property data including physical, thermal, mechanical, and other properties for hot-pressed and reaction-sintered Si$_3$N$_4$, silicon oxynitrides and sialons are presented in detail.


Si$_3$N$_4$ samples were dissolved in teflon-lined acid digestion bombs using a mixture of HF and HNO$_3$. The Si was removed as the volatile fluoride and the samples were analyzed by a solution-spectrographic method. Results and standard deviations for Al, Fe, Ti, Cr, Mn, Mg, and Ca are reported and compared with values obtained by spectrophotometric methods.


Design procedure based on Weibull statistics.

Review of Ford’s ceramic gas turbine program.


Citations of research (1964-1975) on ceramic fracture in relation to fabrication, microstructures, mechanical properties, and composition. Reports include ceramic use in rocket components, gas turbines, nuclear reactors, and structural parts. Pertinent reports are annotated in this bibliography with each entry under the name of the specific author.


Y2O3 is an effective densification aid to Si3N4. Significant increases in strength and stress-rupture properties have been demonstrated for the Si3N4-Y2O3 system at temperatures of 2400-2500 F, as compared to the Si3N4-MgO system. Additional work is needed to assess the performance of the Y2O3 material in the gas turbine environment.


A method was developed for the rapid determination by X-ray diffraction analysis of weight fractions of phases in mixtures of α-Si3N4, β-Si3N4, and Si. The heights of several peaks of each phase were averaged to minimize preferred orientation effects. Extinction effects were negligible except for the Si phase. The measured composition of a known standard was within 1-2% of its actual composition.


The CuKα and CuKα X-ray diffracted integrated intensities from α- and β-Si3N4 powders were computed using the known atomic position parameters. Also listed are 2θ, d-spacing, structure factor and multiplicity values. The computed intensities agree with those determined experimentally.


Grinding forces were determined for four aluminas and hot-pressed Si3N4. Relative wear rates were determined for all materials and conditions. Wear is related linearly to Young’s modulus. Ceramic grinding temperature is 1477 C for Si3N4.
Hot-pressed \( \text{Si}_3\text{N}_4 \) was evaluated for application as a high-temperature gas bearing material. The results of a start-stop and a continuous-run thrust washer test in terms of coefficient of friction and mode of wear are reported. Properly prepared surfaces should give a coefficient of friction of 0.1. The extent and type of wear appear to depend on the congruency of the mating surfaces. A compilation of the properties of \( \text{Si}_3\text{N}_4 \) is provided in the Appendix.

A review of the variety of \( \text{Si}_3\text{N}_4 \) and SiC materials and their performance and economics.

Measurements of the rate of oxidation and of creep in air of CVD \( \text{Si}_3\text{N}_4 \) at \( \sim \)1500 °C are reported. Attempts to prepare pure, dense \( \text{Si}_3\text{N}_4 \) bodies by hot-pressing powder at ultra-high pressures were partially successful. Work on the sintering of covalently bonded solids, \( \beta\)-SiC, Si, \( \alpha\)-Si\(_3\)N\(_4\), AlN, is presented.

In the method described, the sample, encapsulated in a platinum tube, is reacted with C, first at 1300 and then at 2100 °C, the CO formed at each temperature being removed in a stream of high-purity He. After oxidation of the CO with Cu\(_2\)O the CO\(_2\) is frozen out in a multiloop trap and finally measured in an open-well capillary manometer. The two heating temperatures distinguish between “free” or adsorbed O and combined O.

Hot-pressed \( \text{Si}_3\text{N}_4 \) was leached with HF and subjected to impact at low velocities by a WC sphere. The remaining strength of the leached specimens after impact was substantially greater than those that were not leached. The leached layers prevented formation of Hertz cracks in the underlying material.

\( \text{Al}_2\text{O}_3 \), \( \text{Si}_3\text{N}_4 \), and SiC specimens were fractured at various loading rates and temperatures and the fracture surfaces studied by optical and scanning electron microscopy. Fracture origins were located and the flaws at the fracture origins identified, characterized, and classified. Applications of results to ceramic processing, designing with brittle materials, and theory of fracture are discussed.

Time-dependent failure of hot-pressed and reaction-sintered Si$_3$N$_4$ in the temperature range from 0-900°C was studied. The tests were carried out in air saturated at room temperature with H$_2$O in order to identify the temperature range where static fatigue phenomena are important and also to identify the moisture-related stress corrosion process. Reaction-sintered Si$_3$N$_4$ did not exhibit strain rate dependence of strength in the temperature range tested. Delayed failure of hot-pressed Si$_3$N$_4$ is moisture related.


Time-dependent failure of commercial Si$_3$N$_4$ materials in the temperature range ambient to 900°C was studied using variable strain rate and static load tests in four-point bending. Room-temperature strength decrease for hot-pressed Si$_3$N$_4$ was found to be moisture dependent and more marked in the presence of acids. Reaction-sintered Si$_3$N$_4$ showed static fatigue, but its strength was independent of strain rate. Proposed theory attributes static fatigue to ion exchange in glass grain-boundary phase.


Si$_3$N$_4$ was obtained by firing pressed specimens of Si and SiC in a N atmosphere. Data presented include the dependence of weight gain, density, and compressive strength on the SiC content of the material.


Study of the formation of reaction-bonded Si$_3$N$_4$ radomes from slip-cast Si. Costs are compared with SiO$_2$ and fabrication procedures are described. Also included are transmission and pattern degradation results on small radomes. Densities ranged from 2.0-2.6 g/cm$^3$, but acceptable electrical properties are difficult to obtain at higher densities.


Eleven reaction-sintered Si$_3$N$_4$ radomes were prepared by slip casting Si blanks and reaction sintering in N. Items investigated were repeatability of electrical transmission characteristics, methods of sealing pores, attachment systems, and preparation of a radome for rain erosion sled testing.


Reaction-bonded Si$_3$N$_4$, containing up to 1% Fe and fabricated by injection molding was studied as a candidate radome material. Fabrication equipment and techniques and test techniques for thermal, mechanical, and electrical evaluation are described. Results suggest a direct relationship between final sintered density and dielectric properties.

Turbine vane platforms were fabricated from hot-pressed Si$_3$N$_4$ and tested at elevated temperature in a cascade of transpiration-cooled turbine vanes representative of advanced engine concepts. There was no damage after steady-state endurance testing for 10 hours at >2000 C.


Preliminary estimates of enthalpies of formation of α- and β-Si$_3$N$_4$ by combustion in fluorine were determined from calorimetric measurements.


The structural development of Si$_3$N$_4$, hot pressed from a high α-phase powder with MgO additions, was observed using scanning electron microscopy. The extent of the concurrent densification processes, α→β tranformation, and development of mechanical properties was determined as a function of time, temperature, and MgO content. Full densification occurred prior to the completion of the α→β transformation. Maximum strength was independent of time and temperature once full density was achieved. Relationship between α/β transformation and fibrous microstructure is discussed.


Selected impurities as Al$_2$O$_3$, CaO, Fe$_2$O$_3$, Li$_2$CO$_3$, and Na$_2$CO$_3$ were added to relatively pure β-Si$_3$N$_4$ powders and subsequently hot pressed to full density using 5 w/o MgO as the pressing additive. None of the impurities affected room temperature strength and only CaO affected high-temperature strength. High-purity, high-α-Si$_3$N$_4$ powder was produced, but no details are given.


Reduction in high-temperature strength and creep resistance of commercial hot-pressed Si$_3$N$_4$ is shown to be associated with impurities. Selected impurities including oxides and carbonates were added to α- and β-Si$_3$N$_4$ starting powders that were hot pressed to full density using 5 w/o MgO as the pressing additive. The Si$_3$N$_4$ hot pressed from the α-powder exhibited higher strengths at both 25 and 1400 C. Room-temperature mechanical properties were uneffected by the impurity additions.


A model gas dynamic laser (GDL) nozzle array was fabricated from hot-pressed Si$_3$N$_4$ components and tested under thermal cycling air flow conditions to 1150 K. Excellent dimensional stability was shown by the center nozzle of the three-nozzle assembly and examination revealed no degradation of the materials.

\[ \alpha-Si_3N_4 \] fibers were successfully grown in graphite crucibles by a new method using silicates and Si as sources of Si and using C, Al, and Si as reducing agents. A build-up of coatings on the solid raw material particles hindered the evolution of Si or SiO vapor and thereby slowed down further formation of \( Si_3N_4 \) fibers.


Expected compounds were not found. Suggests addition of AlN to \( Si_3N_4 \) would eliminate glassy phase which decreases high-temperature strength.


Compressive surface layers were formed on \( Si_3N_4 \) by quenching and/or carburizing. In some cases impact resistance and/or flexural strength were increased.


The strength degradation of hot-pressed \( Si_3N_4 \) and \( SiC \) due to impacts by spheres at low velocities was determined. Results showed that the impact force necessary to form Hertz cracks in \( Si_3N_4 \) was \(~4 \) times that for \( SiC \). The cracks were characterized and the dimensions compared with calculated values.


The impact resistance of both room temperature and elevated temperature of \( Si_3N_4 \) and \( SiC \) ceramics was improved by the formation of energy absorbing surface layers. Low modulus layers were formed by using: (1) materials that microcrack as a result of thermal expansion anisotropy, (2) phases differing in thermal expansion, (3) materials that have phase transformations, and (4) vitreous coatings.


The effects of the additions of Al4.2 and 9.0 a/o in Si powders used to prepare reaction-sintered \( Si_3N_4 \) were investigated. The Al nitrided preferentially to form AlN. Bend strength and \( \alpha-Si_3N_4 \) content were reduced by the additions.

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Quasi-equilibrium diagram is presented for Si-Al-O-N compounds at 1800 C in 1 atm of N. X-ray diffraction spectra for several phases are given and the reaction and sintering processes are discussed. Theoretical densities are calculated from lattice parameter data on solid solutions.

Presents current property data for both dense Si$_3$N$_4$ and SiC that are required to calculate thermal stresses: strength, modulus of elasticity, Poisson’s ratio, thermal expansion, thermal conductivity, and specific heat.

Mechanical properties of Si$_3$N$_4$ are reviewed from the standpoint of related fabrication parameters and compositional content. Microstructure of dense Si$_3$N$_4$ is governed by the phase relation of the constituents in the starting powder and these phase relations, in turn, govern the mechanical behavior.

Si$_3$N$_4$-Al$_2$O$_3$ (<50 w/o) mixtures were hot pressed and sintered at temperatures up to 1650 C. Additions of MgO increased sintering kinetics. Thermal expansion, densification, and flexural strength were studied.

Surface damage was introduced into flexural-strength specimens of dense Si$_3$N$_4$ and SiC using spherical steel indenters and the specimens were then fractured in four-point loading. Si$_3$N$_4$ required ~ four times the indenter load as SiC to introduce surface damage. After surface damage was introduced fracture due to subsequent external loading initiated from a portion of the sub-surface cone crack.

Phase equilibria studies at 1400-1750 C have established three important tie lines in the Si$_3$N$_4$-SiO$_2$-MgO system: (1) Si$_3$N$_4$-MgO, (2) Si$_3$N$_4$-Mg$_2$SiO$_4$, (3) Si$_2$N$_2$O-Mg$_2$SiO$_4$. Maximum strengths were obtained at 1400 C for MgO/SiO$_2$ molar ratios that approach zero and infinity. Oxidation of these materials is discussed.

Si₃N₄-SiC composite system was investigated to relate microstructure to strength-controlling factors: fracture energy, elastic modulus, and crack size. Composites formed by hot pressing included three different SiC dispersions (5 μm, 9 μm, and 32 μm) at several different volume fractions. Strength behavior of material containing two larger-size dispersions was controlled by crack size. Strength of 5 μm material was controlled by fracture energy and elastic modulus. Strength measurements at 1400 C and thermal conductivity measurements show that some composites are superior to hot-pressed Si₃N₄.


Hot-pressed Si₃N₄ and SiC are emphasized as strong, high-temperature ceramics that can withstand thermal cycling without failure and therefore be used in high-temperature structural applications. The relations between fabrication parameters, microstructure, and strength are presented for both materials and other structural considerations such as thermal shock, impact, and oxidation are reviewed. Current trends for obtaining improved and new materials are discussed.


Composite powders were hot pressed to determine the phase relations within the Si₃N₄-SiO₂-Y₂O₃ pseudo-ternary system. Study of the four quarternary compounds identified showed they were unstable under oxidizing conditions. On the other hand, compositions within the Si₃N₄-Si₂N₂O-Y₂Si₂O₇ compatibility triangle were extremely oxidation resistant.


The strength of hot-pressed Si₃N₄ is dependent on the starting powder, the method used to prepare the powder for hot pressing, and the orientation of the crack plane relative to the hot-pressing direction. The material’s elongated grain morphology is hypothesized to be responsible for its high fracture energy and directional properties. Study revealed that no single hot-pressing model adequately describes the hot-pressing behavior of Si₃N₄. The feasibility of hot pressing complex shapes using the powder vehicle technique was demonstrated. Dielectric properties were measured.


Phase equilibria were studied in the system Si₃N₄-AlN-Al₂O₃-SiO₂. At temperatures above ~1750 C a broad two-phase field of liquids is in equilibrium with β'-SiAION solid solutions. Studies were undertaken to exploit this two-phase field to effect a homogeneous transient liquid-phase sintering of β'-compositions.

Final report of five-year contract with earlier annual reports listed in the Appendix. Slow crack growth does not occur in hot-pressed Si₃N₄ at room temperature, precluding use of proof testing to predict lifetime. Strain energy release rate remains constant with increase in loading rate. Also discussed is fracture toughness of various materials including Si₃N₄.


Compares various life computation procedures wherein realistic properties variability is treated. Predicted behavior of Si₃N₄ is studied and adequacy of estimating procedures is discussed.


The introduction of the gas turbine engine into automotive transport will depend, in part, on the achievement of an efficient working cycle, that is, the operation of the turbine at inlet temperatures in excess of 1500 K. Of the candidate ceramic materials, Si₃N₄ is the most attractive because of its low expansion coefficient, good thermal shock resistance, and high strength at these temperatures. Fabrication and processing techniques for the production of Si₃N₄ are sufficiently advanced to enable material costs predictions to be made.


Method of manufacturing refractory parts from a Si₂ON₂ base powder with a refractory metal oxide additive (~5% Al, Y, Mg, Be oxide).


Method of manufacturing a heat-resistant, thermal-shock resistant, and high-strength Si₃N₄ material using various metal oxides, as MgO and Al₂O₃, and sintering at 1600-1800 C to form a spinel second phase.


Ceramic materials are suggested as a means of achieving lower cost and higher inlet temperature in small gas turbine engines. Si₃N₄, SiC, and Li-Al-Si oxides are identified as promising materials for high-temperature turbine engine components.

Review of Ford's ceramic gas turbine program. (See entry nos. 489-498)


Review of design, fabrication, and thermal testing of Si$_3$N$_4$ components. Also includes results on high-temperature testing of stators and reviews spin-testing techniques.


In the vehicular gas turbine project, ceramic turbine components of improvised design were fabricated and engine testing was started. During the first contract reporting period, Si$_3$N$_4$ turbine stators of the new design have shown considerably improved durability in testing to date. New design Si$_3$N$_4$ nose cones were fabricated by injection molding. Design studies on ceramic turbine rotors have shown that computed operating stresses can be withstood by dense SiC and dense Si$_3$N$_4$. Development programs were started to fabricate rotors in these materials.

Work on the stationary turbine project has concentrated on materials evaluation and initial design of ceramic stator vanes. Maximum calculated vane stresses were reduced 40% by decreasing the stator vane chord. The strength of hot-pressed Si$_3$N$_4$, one of the candidate materials, has been significantly improved. A variety of microstructural details of this material have been identified. Physical property data were obtained on hot-pressed Si$_3$N$_4$.


In the vehicular turbine project, the improved second generation (Design B) stationary ceramic components made of reaction-bonded Si$_3$N$_4$ have undergone initial engine tests successfully. A computer program has been developed to determine heat transfer in the rotor, attachment, and shaft assembly. A design study was completed for the attachment of the rotor to the shaft. A complete integral rotor has been fabricated by CVD of SiC, although material quality needs improvement. An etching technique has been developed permitting microstructure study of any form of Si$_3$N$_4$, and significant determinations were made of ceramic material properties.

In the stationary turbine project, a first generation 3-piece vane assembly was designed and analyzed. A complete set of Si$_3$N$_4$ airfoil vanes was fabricated. Engineering properties of Si$_3$N$_4$ and SiC have been characterized. A better understanding of the effects of microstructure on properties of hot-pressed Si$_3$N$_4$ was obtained. Data was obtained on static oxidation kinetics and corrosion-erosion behavior.
In the vehicular turbine project, steady state and transient stresses were determined for a monolithic turbine rotor of hot-pressed $\text{Si}_3\text{N}_4$. A new rotor concept, using both hot-pressed and reaction-sintered $\text{Si}_3\text{N}_4$, has been analyzed for steady-state stresses; work on bonding the two materials appears promising. Improvements in CVD $\text{SiC}$ rotors include the forming of hoops of sufficient thickness and the production of material of considerably improved purity. Blade cracking of the first stage ceramic stator was duplicated on a thermal test rig, leading to improved durability through a change in the blade design. Some fabrication variables of reaction-sintered $\text{Si}_3\text{N}_4$ were studied, which indicate methods for material improvement.

In the stationary turbine project, a model of the 3-piece stator vane assembly demonstrated that design integrity was maintained when differential motion exceeded design limits fivefold. The 3-dimensional finite element stress and heat transfer analytical program has been applied to rotor blades, and preliminary results are presented. Statistical data treatment has been applied to hot-pressed $\text{Si}_3\text{N}_4$ and additional property data plus corrosion testing results are presented for hot-pressed $\text{SiC}$. It was found necessary to design and construct a new static rig, delaying testing under turbine conditions until August.

In the vehicular turbine project, a more refined heat transfer and stress analysis was performed for the monolithic hot-pressed $\text{Si}_3\text{N}_4$ rotor. Methods of fabricating duo-density $\text{Si}_3\text{N}_4$ rotors were evaluated, with several rotors being made; the best of these failed at 50,500 rpm during spin testing. Revised design stators demonstrated improved durability, although cracking has not been completely eliminated. Creep resistance of reaction-sintered $\text{Si}_3\text{N}_4$ has been considerably improved by decreasing Ca-containing impurities. The strength of reaction-sintered $\text{Si}_3\text{N}_4$ has been increased by the use of small amounts of H added to the N atmosphere.

In the stationary turbine project, stress and heat transfer analyses were completed for the stator vane assembly system. The 3-dimensional stress analysis program has been expanded to include steady state and transient heat transfer capability. Installation of the static test rig for evaluating stator vanes under turbine conditions has been completed. Additional information about the properties of hot-pressed $\text{Si}_3\text{N}_4$ and $\text{SiC}$ has been determined, and the microstructure of hot-pressed $\text{SiC}$ was studied in detail.

In the vehicular turbine project, Weibull theory was utilized to predict failure probabilities of monolithic hot-pressed $\text{Si}_3\text{N}_4$ turbine rotors, including the effects of varying disk contours. Good agreement with theory resulted from strength testing of $\text{Si}_3\text{N}_4$ bars and disks. Processing parameters were established for the fabrication of multi-density rotors, and a number of prototype rotors were spin tested. Thermal response of stator vanes during engine operation was determined directly using a quartz window in a stator test rig. Improvements in properties were made for both injection molded and slip cast reaction-sintered $\text{Si}_3\text{N}_4$.

In the stationary turbine project, a major objective was achieved when the first static rig test of hot-pressed $\text{Si}_3\text{N}_4$ stator vanes was completed at temperatures up to 2200 F. Although some vanes failed due to out-of-tolerance final machining of critical interfaces, it was encouraging that two vanes which were subjected to the highest temperatures and most severe transient effects were not damaged. Additional information was also generated on the properties and corrosion resistance of hot-pressed $\text{Si}_3\text{N}_4$. 
In the vehicular turbine project, 3-dimensional stress analysis programs are being developed and applied to turbine rotors and stators. Improvements have been made in the fabrication of duo-density Si$_3$N$_4$ rotors. A major objective was reached with the completion of a 50-hour cyclic engine test of ceramic hot-flow path components. A SiC combustor tube was tested in a combustor rig for 50 hours, including 6 hours at an outlet temperature of 2500 F. Non-destructive evaluation techniques have been applied to the fabrication of ceramic components resulting in the elimination of defective parts at an early stage in processing.

In the stationary turbine project, considerable design effort was expended on the modification of the rotating test turbine for the high-temperature testing to meet program objectives. The static test rig was rebuilt for 2500 F peak temperature operation, and 5 cycles were run to 2300 F to establish control parameters. Damage to the new ceramic duct section and to the mixer caused testing to be stopped. The Si$_3$N$_4$ and SiC stator vane assemblies being tested were apparently undamaged. A rotor blade configuration was analyzed by the 3-dimensional stress analysis program and the results are presented.
In the vehicular turbine project, design work was completed and tooling ordered for a revised Design D Si$_3$N$_4$ duo-density turbine rotor using radially stacked airfoil sections which reduced blade stresses by 16%. Press bonding of duo-density rotors continues to show excellent bonding between the hot-pressed hub and the reaction-sintered blade ring when hub-forming and bonding are accomplished in the same operation. Two hot-pressed Si$_3$N$_4$ hubs were successfully tested through ten cycles to 1950 F and 35,000 rpm in the turbine rotor test rig with no observable deterioration in the curvic coupling rotor-to-shaft attachment. Stators of 2.55 g/cm$^3$ density Si$_3$N$_4$ were injection molded which were free from flaws as determined visually and by X-ray radiography. Further development of 2.7 g/cm$^3$ density (84.5% T.D.) injection molded silicon nitride resulted in improved moldability; test samples nitrided in an atmosphere of 4% H$_2$/96% N$_2$ had an average modulus of rupture of 43.2 ksi. This material will be used for molding of engine components.

In the stationary turbine project, a decision was made to de-emphasize the 30 Mw size turbine demonstration of ceramic stator vanes and to focus available efforts on static rig testing. The static rig was rebuilt following catastrophic failure, and incorporates a new metal combustor with additional air cooling as well as other improvements. Tensile testing of Si$_3$N$_4$ continues, with the development of a method of powder support for the specimens which considerably improved alignment. Long-term static oxidation testing of hot-pressed Si$_3$N$_4$ resulted in strength degradation, due to the formation of MgSiC which chemically attacks the Si$_3$N$_4$. Hot-pressed Si$_3$N$_4$ made with yttria additives was found to have poor oxidation resistance at 1800 F, although oxidation resistance was good when measured at higher temperatures.

The demonstration of uncooled brittle materials in structural applications at 2500 F is the objective of this program. Ford Motor Company, the contractor, will utilize a small vehicular gas turbine while Westinghouse, the subcontractor, will use a large stationary gas turbine. Both companies had in-house research programs in this area prior to this contract.

A significant achievement in the vehicular turbine project was the successful engine test, 175 hours at 1930 F, of a Si$_3$N$_4$ stator. Two stator vanes survived 1000 cycles to 2500-2600 F plus 3720 cycles to 2900 F in the thermal shock rig. A poor quality partially bladed duo-density Si$_3$N$_4$ turbine rotor was tested for two hours with excursions to 1920 F and 33,600 rpm before failure. Two ceramic rotors with short blades were successfully proof spun to 64,000 rpm, cold, as part of a program to test ceramic rotors with phased increases in blade height. One of seven hot-pressed rotor hubs, spun to determine material strength, achieved 111,800 rpm before failure.

Reduction of the MgO content increased the hot strength of the hot-pressed Si$_3$N$_4$ rotor hub material. Improvements in the nitriding cycle and injection molding process produced 2.7 g/cm$^3$ test bars with a characteristic four-point bend strength of 44.3 ksi with a Weibull slope of 6.8. A stress rupture test on 2.7 g/cm$^3$ injection molded material was suspended without failure after 1159 hours at 2300-2400 F and stresses in four-point bending of up to 35 ksi.

The goal of the stationary turbine project is to demonstrate ceramic stator vanes operating at a maximum temperature of 2500 F for 100 cycles simulating peaking service conditions. The original goal to accomplish this in an advanced gas turbine engine was revised to complete the demonstration in a static test rig. Sixty cycles have been completed in the static test rig with the total time at temperature (2500 F) approaching three hours and three of the original eight vanes remain crack free.
In the stationary gas turbine project at Westinghouse, the test of ceramic stator vanes in a static rig for 100 cycles up to temperatures of 2500°F has been completed.

A significant achievement, in the vehicular turbine project at Ford, was the test of a partially bladed duo-density silicon nitride turbine rotor in an experimental high temperature gas turbine engine up to a speed of 52,800 rpm and turbine inlet temperature of 2650°F before failure on a subsequent run. Two rotors, with blades of 10% length, were successfully tested for 45 minutes at 32,000 rpm and 2000°F turbine inlet temperature. Cold spin test results of nine hot-pressed Si3N4 rotor hubs correlated well with analytical predictions based on Weibull MOR data from 140 test bars cut from five additional hubs. Testing of the stationary components continued with a “Refel” SiC combustor tube successfully accumulating over 200 hours in the steady-state test rig, equivalent to the prescribed 200-hour engine duty cycle goal. Twenty-six hours and 40 minutes of this testing was at a turbine inlet temperature of 2500°F. A reaction-bonded SiC stator accumulated 147 hours of operation at 1930°F and remains crack free. Testing of stationary components at turbine inlet temperatures up to 2500°F continued with over nine hours of test time accumulated without failures.

An important fabrication development to make duo-density turbine rotors in three pieces was conceived and demonstrated a significant reduction of applied loads during hot-press bonding generally eliminating blade and rim cracking.

Modulus of Rupture tests were conducted on hot-pressed Si3N4 to investigate the effects of surface finish, post machining heat treatments and process variations. Bending stress rupture tests on 15 specimens resulted in no time dependent failures for this material up to 2200°F. Twelve of the tests were suspended, without failure, after 200 plus hours at stresses of 20-30 ksi and temperatures of 1900-2200°F. The key to uniform microstructure, fine porosity, and associated high strengths is the control of localized nitriding exotherms so that no silicon melt out occurs.


An inert gas fusion technique using an impulse heating furnace at 2600-2700°C and a gas-solid chromatographic method of gas measurement is described for the simultaneous determination of O and N in nitrides of Si, Ti, Zr, and the carbides of Ti and W. A single determination of O and N requires ~10 minutes.


The reaction-sintering process for the fabrication of Si3N4 was investigated over the temperature range from 1150-1450°C. The effects of Fe and O impurities and of particle size were determined. The kinetics of the reaction between pure (99.99%) Si powder compacts and N were parabolic.

Unreacted Si at levels >0.5-0.6 w/o seriously degrade the dielectric properties of reaction-sintered Si₃N₄. The use of fine particle size Si and various oxide additives were both effective in reducing unreacted Si. Two independent measurements of dielectric properties were in good agreement. The properties appear adequate for radome applications up to 1000 C.


Dielectric properties of various reaction-sintered and hot-pressed Si₃N₄ specimens were measured at 10 GHz at room temperature, 1000 F, and 2000 F. Dielectric constant values ranged from 5.5 to 9.3, and tangent loss values from 0.001 to 0.16. The major detrimental impurity was identified as residual unreacted Si.


Results of a survey to determine what, if any, ceramic engine development using Si₃N₄ was being pursued in the Soviet Union. There is evidence of a strong capability for basic research, but no evidence of a program to evaluate Si₃N₄ in gas turbine engines or ceramic components of any kind.


A region of rapid densification, coincident with the transformation of amorphous to α-Si₃N₄ during hot pressing at 1490 C, has been seen in highly pure material made from Si(NH)₄ by the liquid NH₃ route. A tentative explanation of the phase relationships of α- and β-Si₃N₄ is presented based on conflicting σ and π orbital overlap requirements in multiply bonded Si and N.


Reactive hot pressing of Si(NH)₄ produced Si₃N₄ of up to 85% theoretical density. The presence of β-Si₃N₄ in the product indicated low O activity during the process.


The degree and nature of (p-d) pi-bonding in various Si₃N₄ compounds was studied. On the basis of relative bond lengths and angular relationships and assuming that both α- and β-Si₃N₄ compounds are pure, it is predicted that the β-form is more stable, only by a very small amount. Some implications of Si-Al-O-N bonding are reviewed.

Relevant material properties of prototype hot-pressed Si₃N₄ and SiC vanes were determined. Primary limitations revealed were a propensity for sudden thermal fatigue crack propagation and low impact damage resistance.


Direct measurements of decomposition temperature of Si₃N₄ were performed in the highly pure Si₃N₄-C-N₂ system at 1 atm. The decomposition temperature obtained, 1839 C ± 14 C, is the lowest yet reported. Briefly describes β-Si₃N₄ single crystals that were obtained.


Characteristics of the Si₃N₄-Al₂O₃ system sintered materials are discussed. Oxidation resistance of the Al₂O₃ additive in the sintered Si₃N₄ was analyzed. Chemical reactions and processes used to produce the sintered material are described. Tables of the physical and mechanical properties are presented.


Various aspects of the design technology being developed for ceramic materials within the framework of the Ford/ARPA contract are outlined. (See entry nos. 489-498). Analytical and statistical design tools and design methodology are discussed in detail. Correlation of analytical strength predictions with controlled tests of simplified structures is presented in support of statistical theories, and use of statistical analysis in rotor design is discussed.


Hot-pressed Si₃N₄ was evaluated as a rolling element bearing material at 55 C using the five-ball fatigue tester. Fatigue life was equal to typical bearing steels and much greater than that of other ceramics and cermets.


Hot-pressed Si₃N₄ balls were tested under rolling contact conditions in the five-ball fatigue tester and fatigue lives compared with those for typical bearing steels, AISI 52100 and AISI M-50. Extrapolation of experimental results indicated that the Si₃N₄ fatigue life was comparable to or exceeded that of the steels and was considerably greater than the other ceramics or cermets tested.
Hot-pressed Si$_3$N$_4$ was evaluated as a rolling-element bearing material in a five-ball fatigue tester at 800,000 psi and a race temperature of 55 C. Fatigue spalls in Si$_3$N$_4$ resembled those in typical bearing steels. The 10% fatigue life of Si$_3$N$_4$ was $\sim$1/8 to 1/5 that of typical bearing steels (52100 and M-50) and the load capacity was $\sim$1/3 but considerably higher than previously tested ceramic materials.

Fatigue life of hot-pressed Si$_3$N$_4$ approaches that of AISI 52100 steel. The usefulness of Si$_3$N$_4$ balls in contact with steel races is limited. There has been some success in using Si$_3$N$_4$ for both balls and races.

Compressive surface layers were formed on hot-pressed SiC by quenching and on hot-pressed Si$_3$N$_4$ by carburizing treatments. Impact resistance of SiC at 2400 F was improved and some improvement of Si$_3$N$_4$ was noted under the same conditions.

Mass spectrometric study of the Si-N vapor system showed the presence of the binary species Si$_2$N, having a heat of formation of 83 ± 4 kcal/mol. No ternary Si-N-O or Si-C-N species were found. The vaporization behavior of Si$_3$N$_4$ was found to be quite complex.

A 35 mm bore angular contact ball bearing having M50 tool steel races and hot-pressed Si$_3$N$_4$ balls was tested at speeds to 75,500 rpm. The bearing ran smoothly throughout 32 hours of accumulated time. Heat generation was 10-20% less than that of a comparable bearing with steel balls and the Si$_3$N$_4$ bearing required 30% less axial load at the inception of ball skid.

Initial experiments on press forging Si$_3$N$_4$ are reported.

Fabrication and microstructure control studies were conducted on SiC, Si3N4, and composites based on the compounds. Charpy impact tests to 2400 F showed coated Si3N4 and Si3N4 derived from α-Si3N4 powder, and other materials had promising strengths. Improved 2000 °F–100 hours strengths were obtained by increasing the grain size (to at least 5 μm), the density, and possibly the phase purity of Si3N4. At 2400 F where a grain-boundary phase controls strength these parameters became less important.


Emphasizes work on Al2O3 but reports on forging of Si3N4. Densities were >98% with strengths near those for hot-pressed material.


A detailed and systematic study of the processing parameters on microstructure and the effect of well characterized microstructural morphology on the bulk properties of reaction-bonded Si3N4 is presented. Desirable and undesirable microconstituents were investigated.


Evaluation of friction and wear properties showed that Si3N4 yielded more wear debris than B4C. Surface preparation for gas bearings was studied in depth.


Specimens of 23 oxidation resistant, nonmetallic materials, including Si3N4 (two very high density and one 20% porous) were systematically exposed in a high gas velocity burner in a gas turbine engine. Exposure to Mach 1 and Mach 0.5 hot gas streams resulted in specimen temperatures of 1204 C (2200 F). Si3N4 and SiC exhibited the most promising behavior surviving all exposures including Mach 1 for 120 cycles (10 hours).


Summarizes testing programs at NASA Lewis Research Center on 23 ceramics. SiC and Si3N4 were identified as outstanding in resistance to oxidation and thermal stress and were chosen for further testing in simulated vane shape geometry. Certain SiC and Si3N4 materials were superior to others based on several criteria including weight and dimensional changes, metallography, fluorescent penetration analysis, X-ray diffraction analysis, and failure mode.

Considers ceramic materials including reaction-sintered and hot-pressed $\text{Si}_3\text{N}_4$ for seal materials. Suggests stabilized $\text{ZrO}_2$ and hot-pressed $\text{SiC}$ are the best candidates.


Expanded ring tests were performed on specimens machined from hot-pressed $\text{Si}_3\text{N}_4$ in 30% RH air at 70 F ± 2 F. Results indicated there was no significant variation of mean fracture strength for specimens tested at stress rates between $1.5 \times 10^2$ psi/sec and $5 \times 10^5$ psi/sec.


Electron diffraction data are presented for both $\alpha$- and $\beta$- phases of $\text{Si}_3\text{N}_4$. Interplanar spacings and angles, relative spot intensities, and two beam extinction distances were computed and a range of typical diffraction patterns were prepared for both phases. Unambiguous identification of the structures by this method is possible only under certain conditions.


Assesses materials including hot-pressed $\text{Si}_3\text{N}_4$ as encapsulants for $\text{PuO}_2$ ceramic fuel. Materials limitations include impact resistance, weight, and difficulties in fabrication.


Corrosion behavior of hot-pressed $\text{Si}_3\text{N}_4$ and $\text{SiC}$ in the temperature range 1800-2500 F is discussed. Static oxidation and dynamic corrosion tests were performed. The oxidation of both $\text{Si}_3\text{N}_4$ and $\text{SiC}$ followed parabolic rate laws during initial stages of oxidation with the formation of stable $\text{SiO}_2$ layers on their surfaces.


Oxidation and corrosion-erosion behavior of high-strength hot-pressed $\text{Si}_3\text{N}_4$ and $\text{SiC}$ in gas turbine environments up to 1370 C is reviewed and discussed. The oxidation behavior is governed by the impurities and various additives present. Both materials resist deterioration by high concentrations of Na, V, and S. The excellent corrosion resistance is due to the formation of protective surface layers of silica and/or silicates.

The objectives of this study were to evaluate the advances in the uses of ceramics, including Si₃N₄, as engineering load carrying structural materials and to make recommendations for support of future developments, particularly for the U. S. Department of Defense and the National Aeronautics and Space Administration, and generally for the nation as a whole.


Rolling contact fatigue machines were used to test elemental fatigue of bearings made with Si₃N₄ rolling elements and M50 CVM steel or Si₃N₄ races. The bearings were tested at speeds <500,000 DN (bore diam times rpm) under heavy loads to give accelerated test conditions and showed promise.


Si₃N₄ containing 5 w/o MgO can be densified to 90% of theoretical without application of pressure if the proper time/temperature schedule is followed. Shrinkage is consistent with liquid-phase sintering. Above 1650 C decomposition reduces densification.


Optimum turbine wheel geometry was calculated for two materials—hot-pressed Si₃N₄ and densified SiC. Minimum failure probability was determined by coupling the mathematical program technique with finite element and finite differences methods. Results indicate an improvement in material quality is necessary.


High strength combined with good oxidation and thermal shock resistance make hot-pressed Si₃N₄ a most promising candidate for advanced gas turbine hot components. This form of Si₃N₄ has flexural strengths of 110,000 psi at room temperature and 60,000 psi at 1200 C. A recent experimental version of the system exhibited strengths as high as 145,000 psi at room temperature and 100,000 psi at 1200 C.


Included are results on the oxidation behavior of SiC, Si₃N₄, and Si at high temperatures. Oxidation kinetics and resulting oxide microstructures were sensitive to impurities in the matrix. Activation energies for oxidation ranged from 28 kcal/mol for Si to 122 kcal/mol for hot-pressed Si₃N₄.


Rolling contact fatigue studies compared hot-pressed Si₃N₄ with M-50 steel. Si₃N₄ was superior by at least an order of magnitude. Surface finish affects fatigue life of Si₃N₄ and skidding may degrade its surface durability.
Ceramic-solid-lubricant material test program was conducted to select materials and lubricants for a plain spherical bearing design. Best performance, at stress levels to 7500 psi, was obtained with an $Al_2O_3$ rider sliding against a $Si_3N_4$ plate lubricated with $MoS_2$.

A friction and wear screening program was conducted using $Si_3N_4$ rider specimens in contact with various ceramic coatings on Ti. Test results indicated that the ceramic airframe bearing shows promise for future application, but that additional development was required.

A friction and wear screening investigation of ceramic coatings, lubricants, and lubricant reservoir designs were conducted for an 1100 F bearing application. An improved lubricant reservoir ceramic bearing design was developed using a hot-pressed $Si_3N_4$ ball sliding against an $Al_2O_3$ coating on Ti.

Charpy impact testing at 2415 F established the effectiveness of higher purity $Si_3N_4$ powder sources in reducing the scatter measurements and in improving the short-time bend strengths as well as bend stress rupture properties. Additions of stabilized $ZrO_2$ enhanced the low and high temperature bend strengths for all grades of $Si_3N_4$ powder.

The problems involved in the hot pressing of $Si_3N_4$ are reviewed with special reference to the manufacturing technique and to the thermodynamic and kinetic aspects of the sintering process. Probable mechanisms of densification and the effect of additives and impurities on the process are discussed. Areas of future research are suggested.

Hot-pressed $Si_3N_4$ and BN were two of the materials evaluated for rain erosion resistance. The $Si_3N_4$ exhibited no erosion for expanded periods of time at supersonic speeds.
SJ3N4 was investigated for applications in structural elements in high-temperature, air-cooled reactors. Thermal stress parameters and high temperature (at least 2700 F) strength of Si3N4 were superior to those of alumina and beryllia. Of the properties of Si3N4 that are significant for radome applications, the electrical properties are least known.

Screen rolling contact fatigue tests were conducted on high strength Si3N4, SiC, and Al2O3. Si3N4 with conventional lubricants showed excellent life, greater than M-50 steel, at comparable loads. Friction and wear properties were nearly the same for steel-steel and steel-Si3N4 combinations.

Attempt to remove SiO2 from Si3N4 powder by thermal treatment and compensating remaining O with Mg and Al nitride additives. Mg nitride aided densification while Al2O3 had to be added to the AlN composition to densify it. Materials hot pressed from these compositions showed no improvement in impact strength compared to existing materials, but their high temperature mechanical properties were improved.

Stable isotopes Si29 and N15 will be used as tracers to simultaneously obtain self-diffusion coefficients in Si3N4 materials including α-Si3N4, β-Si3N4, “sialons”, etc.

Program to develop techniques for simultaneous measurement of Si and N self-diffusion in Si3N4. Both α- and β-Si3N4 and a variety of “sialons” were examined and characterized. Specimens selected for measurement were a dense high purity α- and a dense commercial grade β-Si3N4.

The vaporization of Si3N4 was studied to determine the gaseous products and the composition of the remaining phase. The gas phase above Si3N4 consisted mainly of N, but Si (at mass 28) was also detected. It was found that the Si3N4/Si ratio did not change after a certain time, apparently due to the formation of a constant boiling composition that could be S.52N.48.
Stirred-ball-mill-blended Si$_3$N$_4$ and Al$_2$O$_3$ powders were pressure sintered to investigate the mechanism of solid solution formation and densification in the Si$_3$N$_4$-Al$_2$O$_3$ system. The compaction behavior of the powdered blends during pressure sintering was determined by observing the density of the powder compact as a function of time and temperature.

Describes methods of obtaining powder of approximate composition Si$_2$ON. These include heating Si in O-N gas mixture, nitriding Na silicate or H$_3$BO$_3$ bonded Si pellets, heating Si$_3$N$_4$ in O, etc.


Method of producing porous Si$_3$N$_4$ comprising of mixing finely divided Si having an oxidic silicon film with aqueous HF insufficient to dissolve all of the Si, to form a stable foam which is dried and heated in a N atmosphere at 1100-1500 C to convert it to Si$_3$N$_4$.


A method of making a shaped body designed to withstand high temperatures and to resist creep and thermal shock at such temperatures. A powdered mixture consisting of Si and 5-10% by weight of finely divided SiC, particle size 400 B.S., evenly distributed in the Si is compacted into the required shape. Mixture is fired in an atmosphere of N initially at a temperature below the melting point of Si for a sufficient time to produce a rigid network of Si$_3$N$_4$. Shape is then fired at a temperature above the melting point of Si to complete the nitriding of the remaining uncombined Si.


A method of producing Si$_3$N$_4$ fibers by reacting at an elevated temperature (about 1400 C) gaseous N with a silica material and a reducing agent, consisting of graphite or lampblack.


Si$_2$ON$_2$ is produced by heating a mixture of silica and Si in a controlled, N and O containing, atmosphere with an alkaline earth oxide as a promoter, in the amount up to 5% by weight. The reactant mixture may be molded to shape and then fired, or loose reacted powder may be hot pressed to make refractory bodies having a high degree of chemical and thermal stability.


Glaze comprising 5 w/o Al$_2$O$_3$, 93 w/o SiO$_2$, and 2 w/o Fe$_2$O$_3$ is fired at 1300-1500 C in O.


High yields of Si$_3$N$_4$ whiskers, having high tensile strength and substantially uncontaminated by other crystalline phases, are produced by heating Si/SiO$_2$ mixture to form a Si-containing vapor, reacting this vapor with N at about 1400 C in the presence of C and H, whereby Si$_3$N$_4$ whiskers are deposited on substrates adjacent to the gaseous reaction zone.

A vapor phase deposition method for producing a-Si$_3$N$_4$ whiskers comprising the reaction of Si in alumina or refractory boats with N-Ar mixtures at temperatures between 1350 and 1600 C.


Method of reducing the tendency of Si$_3$N$_4$ bodies to fracture when subjected to thermal shocks by exposing them to Li$_2$O vapor for 3-200 hours at 500-1500 C.


A process for preparing manufactured articles of Si$_3$N$_4$, comprising admixing Si$_3$N$_4$ powder of at least 90% purity and a fineness of less than 0.075 mm with less than 25% by weight of the mixture of a binder selected from the group consisting of boric acid, boric anhydride, and boron phosphate. The mixture is cold compacted under a pressure between 0.5 and 5 t/cm$^2$ and the resulting material is sintered in a N atmosphere selected from the group consisting of N, NH$_3$, and air at a temperature between 850 and 1250 C.


Si$_3$N$_4$ is manufactured by mixing finely divided Si with finely divided Si$_3$N$_4$ and then heating resultant mixture in a non-oxidizing atmosphere containing N. Normally, finely divided Si is used alone, but it was found that the addition of some Si$_3$N$_4$ leads to a reduction in operating time which is considerably greater than the reduction which would be expected because some of the mixture is already constituted by Si$_3$N$_4$.


Method of producing a Si$_3$N$_4$ article by forming a Si powder compact, sintering the compact in a N-free atmosphere, machining the Si compact to a required accuracy, and subsequently nitriding it in the temperature range from 1180-1450 C.


Si$_3$N$_4$ ceramics made by nitriding mixtures of Si and B or BN and oxidizing product by heating in air at 1050-1350 C to form glassy protective layer. For example, a 95:5 Si-B mixture is nitried at temperatures up to 1450 C, ground and oxidized 2 hours at 1350 C to yield oxidation-resistant material. (Also issued as German Patent 2,152,066)

Method of forming Si$_3$N$_4$ components by hot milling and then shaping a dough-like material comprising Si powder and a suitable organic chemical binder consisting of 34-40% butyl methyl methacrylate and 60-65% trichloroethylene and subsequently subjecting the form to a nitriding treatment.


Si$_3$N$_4$ composites made by hot pressing a powdered mixture containing Si$_3$N$_4$ (>90% α-phase) and 1.25-5% MgO flux onto Si$_3$N$_4$. Two Si$_3$N$_4$ pieces were joined by spreading a layer of the mixture between them and hot pressing at 1650 C to give a bond with modulus of rupture 84 kg/mm$^2$. (Also issued as German Patent 2,135,648)


Method of increasing the strength of a porous Si$_3$N$_4$ artifact by subjecting it to controlled oxidation in air at 1000 C. Room temperature strength is increased from 220 to 280 MN m$^{-2}$. (Also issued as British Patent 1,312,688)


High strength hot-pressed Si$_3$N$_4$ by use of ~5 w/o phosphates, phosphides, arsenates, arsenides or nitrides of Al or Ga as sintering aids.


Fabrication of high strength, high density Si$_3$N$_4$ by adding 1.0-3.5 w/o yttrium compound [Y$_2$O$_3$, Y(NO$_3$)$_3$, YCl$_3$] to Si$_3$N$_4$ powder and pressing at 1750-1850 C and 6000-7000 psi pressure.


Parts were joined by oxide glasses of compositions: (1) 63 w/o Mn oxide, 38 w/o SiO$_2$, and (2) 50 w/o Mn oxide, 39 w/o SiO$_2$, and 11 w/o Al$_2$O$_3$.


Combination of AlN and/or Si$_3$N$_4$ with powders of an oxide of La, Ce, Sc, Y, and/or YAG and with powders or whiskers of SiC, BN, and/or C were mixed and sintered to obtain heat resistant and strengthened composite materials.

A method of manufacturing a composite in which Si₃N₄ powder is mixed with C fibers coated with a layer of SiC (0.1-2.0 μm thick) to prevent reaction between the fibers and Si₃N₄ and a layer of Si₃C (1 μm thick) to aid bonding of the fibers to the Si₃N₄ matrix and mixture is then hot pressed. The composites have good cross-breaking strength. (Also issued as British Patent 1,305,910)


Method of producing a Si₃N₄ product containing a complex metal silicate having the general formula Ro · Al₂O₃ · SiO₂ (Ro being the metal oxide). The flexural strength at 20 C is >100,000 psi and at 1375 C is >45,000 psi and the density between 3.1 and 3.3 g/cc.


Compacts containing MgO or Mg silicate fluxes and binders are nitrided at 1200 C in 90 v/o N-10 v/o H to give α-Si₃N₄ of density 2.1 g/cm³. Resulting compacts are hot pressed to final density of 3.2 g/cm³ in graphite dies at 1750 C. (Also issued as British Patent 1,340,696)


Method of manufacturing Si₃N₄ compacts, >80% α-phase from powdered Si (~10 μ grain size) containing 1.4-2.5% reactive O and 5% α-Si₃N₄. (Also issued as British Patent 2,132,152 and German Patent 2,147,513)


Method of forming a complex article as a rotor for a gas turbine engine in which the best characteristics of hot-pressed Si₃N₄ and slip-case Si₃N₄ materials are brought together. The structure is bonded together by a strong and uniform bond at the junction between the different materials.


Si₃N₄ is proposed by an exothermic reaction in which powdered Si is spread on trays in a closed, electrically heated reaction chamber fed with N, Ar, and NH₃. The flow rate of N is governed by the pressure in the chamber and is used as a means for controlling the operation. The periodic on and off cycling of the Ar provides high yields of Si₃N₄ and prevents runaway reaction rates.


Method of producing Si₃N₄ from the reaction of rice hulls and N, either singly or in combination with a catalyst comprising Fe, at 1100-1350 C.

Method of forming a glass joint between $\text{Si}_3\text{N}_4$ parts by inserting a powdered glass (30-60 w/o $\text{SiO}_2$, 11-57 w/o MgO, and up to 32 w/o $\text{Al}_2\text{O}_3$) between the parts and heating the pressed parts in an inert atmosphere. (Also issued as British Patent 1,374,817)


Method of forming a complex article as rotor for a gas turbine engine in which the best characteristics of hot-pressed $\text{Si}_3\text{N}_4$ and an injection molded $\text{Si}_3\text{N}_4$ material are brought together. The structure is bonded together by a strong and uniform bond at the junction between the different materials.


Method of preparing a triple density $\text{Si}_3\text{N}_4$ in which the first element is formed by hot pressing a mixture of 95-99.5 w/o $\text{Si}_3\text{N}_4$ particles and 0.5 to 5.0 w/o MgO; the second element is formed by injection molding Si metal particles and a thermoplastic resin carrier and subsequently burning out the carrier; the third element is formed slip casting in contact with the second element and then nitriding together.


Method of preparing a triple density $\text{Si}_3\text{N}_4$ in which the first element is formed by hot pressing a mixture of 95-99.5 w/o $\text{Si}_3\text{N}_4$ particles and 0.5 to 5.0 w/o MgO; the second element is formed by injection molding Si metal particles and a thermoplastic resin carrier and subsequently burning out the carrier; the third element is independently cast and sintered in an inert atmosphere, bonded to the second element with slip and then the second and third elements are nitried together.


Method of producing a $\text{Si}_3\text{N}_4$ containing finely dispersed SiC or SiAlON$_2$ having high strength at room and elevated temperatures and controlled low electrical resistivity. The transverse rupture strength at 20 C is $>100,000$ psi as measured by a four-point test, and at 1375 C, $>40,000$ psi as measured by a three-point test.


Method of preparing a $\text{Si}_3\text{N}_4$ article with a fine matrix of apertures by stacking intervening layers of composite plastics in preformed sheets made of a powder refractory and a thermosetting binder, as poly (vinyl butyral), which bond the sheets together at the ribs or walls of the preformed material. The stack is heated to cure the binder and burn off sheet material and then fired to form the sintered article.

Method of preventing reaction between Si$_3$N$_4$ and graphite during hot pressing. The powder compact is coated with Al$_2$O$_3$ and the mold with BN. (Also issued as German Patent 2,316,348)


Method of preparing an impact-resistant fiber-reinforced ceramic from a number of continuous Ta wires preferentially oriented and embedded in a hot-pressed Si$_3$N$_4$ matrix which approaches theoretical density.


A method of producing heat-, oxidation-, and abrasion-resistant Si$_3$N$_4$ ceramics of low thermal expansion by hot pressing mixtures containing Si$_3$N$_4$ 10-80\% m/o, Al$_2$O$_3$ 10-90\% m/o and optionally AlN 2-70\% m/o at 1650-2000 C in a nonoxidizing atmosphere. (Also issued as German Patent 2,262,785)


Turbine rotor comprising high-density (hot-pressed) hub and low-density (sintered) blades that may be fabricated from Si$_3$N$_4$.


A hot-pressed Si$_3$N$_4$ composite body with its outer layers locked in compressive stress is formed with surface layers of Si$_3$N$_4$ having a predetermined thermal expansion coefficient and an internal layer made up of a mixture of Si$_3$N$_4$ and SiC which has a thermal expansion coefficient less than that of the outer layer.


Method of producing a ceramic article for use in gas turbine engine environment comprised of a matrix of hot-pressed Si$_3$N$_4$ with reinforcing filaments of W embedded in it.


A method of preparing an improved flowmolding composition for molding Si powder shapes. The composition includes a granular material (65-77 v/o) and a deflocculant (0.1-1.0 v/o) and the remainder of volume being a 90/10 ratio by weight mixture of a 135 F melting paraffin wax and a 195 F microcrystalline wax.

Formation of high α-Si₃N₄ powder from Si powder by using various measures to control exothermic reaction and to avoid formation of β-Si₃N₄.


Method of forming a pressureless sintered Si₃N₄ based ceramic, having improved mechanical and chemical properties, by the addition of two metal oxides that form a spinel.


Method of preparing dense, thermal resistant Si₃N₄ ceramics by mixing Si₃N₄, Al₂O₃, and MgO and sintering in a N atmosphere under ambient pressure at 1400-1750 C.


Method of improving the electrical conductivity of a Si₃N₄ body by heating at 1350-1550 C, high enough to partially decompose the Si₃N₄ but below Si evaporation temperature, in an atmosphere of Ar or H which is inert to Si. The Si₃N₄ material is used as a resistance heater. (Also issued as British Patent 1,397,070)


Method of producing high purity α-Si₃N₄ powder by thermal decomposition of product of reaction of SiCl₄ with excess NH₃ gas in benzene or hexane at 0 C.


Preparation of Si-Al-O-N compositions by sintering with C and N mixtures of clay, rice hulls, and Al source.


The oxidation resistance of a Si₃N₄ article is increased by preheating to 2500-2750 F, inserting the Si₃N₄ article into the preheated furnace, and maintaining it in the furnace for a period sufficient to develop an oxidation resistant surface on the article.

Method of fabricating Si₃N₄ bodies by mixing Si₃N₄ powder with an oxide, hydride, or nitride of yttrium or an element of the lanthanide series and hot pressing for 30-60 minutes at 1600-1700 C.


Method of preparing an amorphous Si₃N₄ composition from 95-99.9% amorphous Si₃N₄ and 0.1-5.0% C. Composition is useful in the preparation of dense sialon.


Hot-pressed Si₃N₄ containing 1-25 w/o ZrC, ZrN, ZrSiO₄, or a mixture of these.


Hot-pressed Si-Al-O-N material formed from mixture of powdered Si₃N₄, AlN, Al₂O₃, and SiO₂.


A method of making a shaped body of self-bonded Si₃N₄ designed to withstand high temperature and to resist creep and thermal shock. Powdered Si is compacted in a block which is fired in an atmosphere of N at a temperature below the melting point of Si for a period of at least one hour to produce a self-supporting, readily-machinable block. The block is worked to the required finished shape and the shaped body is fired in an atmosphere of N to effect complete nitriding of the Si.


A method of making a shaped body designed to withstand high temperatures and to resist creep and thermal shock at such temperatures consisting of a self-bonded Si₃N₄. Powdered silicon is compacted in the required shape and fired in an atmosphere of N initially between 1250 and 1350 C for a sufficient time to produce partial nitriding. Nitriding is completed by continuing the firing in N at 1700 C to produce a material high in β-Si₃N₄.


Method of forming a refractory body of Si₃N₄ fibers and a continuous polycrystalline phase by first forming fibers by a reaction between Si vapor and NH₃ at temperatures between 1300 and 1500 C. Nitride fibers produced are mixed with chromium carbide, B, and Si and heated to a temperature at which the constituents form a polycrystalline mixture of chromium boride, silicon carbide, and Si₃N₄ fibers.

A method of forming a Si$_3$N$_4$ ceramic including the step of mixing 0.1% to 25% by weight of a fluxing agent in powder form with powdered Si$_3$N$_4$ and then pressure sintering the mixture to convert the Si$_3$N$_4$ into a ceramic form.


A method of producing whiskers of Si$_3$N$_4$ comprising heating Si powder to produce Si vapor and mixing this vapor with a stream of N gas in such a manner that the resultant reaction to produce whiskers of Si$_3$N$_4$ occurs in a zone displaced from the Si from which the vapor is produced.


A method of making a Si$_3$N$_4$ product, comprising heating in a non-oxidizing atmosphere containing N and H (5-25% by volume) a quantity of powdered Si to a temperature not exceeding 1300 C so as to form powdered α-Si$_3$N$_4$, mixing the Si$_3$N$_4$ thus formed with MgO and MgCO$_3$, and subsequently pressing the resultant mixture to a predetermined shape at a temperature not exceeding 1650 C to produce a solid body.


Si powder flame-sprayed onto a preheated metal form coated with H$_2$O soluble release agent such as NaCl. After light machining the shaped compact is removed from the form and treated with N or NH$_3$ at high temperature to convert it to Si$_3$N$_4$.


A process for producing Si$_3$N$_4$ articles wherein a compact of Si powder is first sintered at temperatures between 800 and 1400 C in a protective atmosphere free from N and subsequently nitrided at 1350 C for 16 hours and at 1450 C for 20 hours.


A method of production of reaction-bonded Si$_3$N$_4$ ceramic matrix composite materials comprising depositing Si powder by flame-spray means onto a reinforcement material which is in the form of a fiber or fibers and heating the matrix in a nitriding atmosphere to convert Si to Si$_3$N$_4$.

612. Lumby, R. J., “Method of Manufacturing Silicon Nitride Powder”, British Patent 1,206,468 (September 23, 1970), assigned to Joseph Lucas (Industries), Ltd.

A method of manufacturing Si$_3$N$_4$ powder comprising mixing Si powder with Si$_3$N$_4$ powder and then heating the resultant mixture in a non-oxidizing atmosphere containing N.

Method of preparing disklike matrices of Si$_3$N$_4$ used in rotary regenerative heat exchangers from a homogeneous mixture of Si powder, a binder (vinyl butyral), and a plasticizer (debutyl phthalate) shaped and cured at 300-400 C before nitriding at 1350-1450 C in N. For shaping, corrugated and uncorrugated sheet of mixture is wound spirally into shape of the matrix.


Method of manufacturing Si$_3$N$_4$ product with improved strength at high temperature by mixing Si$_3$N$_4$ powder with a <10 w/o flux of Zn or Zn compound, grinding the mixture to 1 µm particle size and pressure sintering the mixture at 1740 C and 4000 psi in graphite dies.


α-Si$_3$N$_4$ is produced by the reaction of Si with N at 1180-1500 C in the presence of O(0.3-1.8 w/o of Si) and an inert gas such as Ar. A dispersant (0.1-50 w/o) such as Al$_2$O$_3$, MgO or Si$_3$N$_4$ may be mixed with the Si powder. Mixture is heated to 1180 C in N-Ar, then air is admitted and the temperature raised to 1195 C during 1 hour. Mixture is then heated in N-Ar while the temperature is raised at 15 C/hour Si is converted to Si$_3$N$_4$.


Method of forming Si$_3$N$_4$ consisting of compressing a mixture of 1-70% fugitive binder, 1-65% china and/or ball clay (or 1-63% mullite) and Si powder sufficient to yield predominately Si$_3$N$_4$ after nitriding. The clay components do not interfere with the final properties of the Si$_3$N$_4$ material.


Method of preparing a Si$_3$N$_4$ product comprising flame spraying Si and spraying inert fibrous material, such as asbestos, onto a mandrel, and then heating the Si and fibrous material in a N atmosphere.


A method of manufacturing a composite in which Si$_3$N$_4$ powder is mixed with C fibers coated with a layer of SiC (0.1-2.0 µm thick) to prevent reaction between the fibers and Si$_3$N$_4$ and a layer of Si$_3$N$_4$ (1 µm thick) to aid bonding of the fibers to the Si$_3$N$_4$ matrix and mixture is then hot pressed. The composites have good cross-breaking strength.


A method of manufacturing a Si$_3$N$_4$ - C fiber composite similar to that described by Coe and Lumby in British Patent 1,305,910 (February 7, 1973).

A bearing for shafts and like rotatable members in which the bearing surface is formed by a Si₃N₄ collar which is divided into a number of spaced segments and which is self-sustaining until self-generated gas pressures are produced.


Method of producing bodies of dense or porous self-bonded Si₃N₄ containing free Si are brazed using an alloy of Si (Cr or Ti) >5 a/o % Si, having thermal expansion characteristics substantially matching those of Si₃N₄.


Method of forming composite material comprising sintering mixtures of at least 85% of first component which is Al₄C₃, SiC, Si₃N₄, B₄C, or BN with oxides of Group IIIa or oxides of the lanthanide series. Examples of oxides used are Sc₂O₃, Y₂O₃, La₂O₃, or Ce₂O₃. Flexural strengths as high as 42.1 kg/mm² were obtained by sintering Si₃N₄-Sc₂O₃ mixtures in N.


Method of anchoring Si₃N₄ gas turbine blades to a metal member by inserting a part of the metal spindle into a cavity formed in Si₃N₄ blade and inductively heating to cause deformation of the metal within the cavity to prevent its withdrawal.


Manufacture of α-Si₃N₄ powder by careful control of nitriding temperature. Another claim deals with nitriding mixture of Si₃N₄ and Si powders.

626. “Process for Producing a Mixture of Silicon Oxynitride and Silicon Carbide”, British Patent 1,317,011 (May 16, 1973), assigned to Danfoss A/S.

Process for producing a composition containing SiC and Si₂ON₂ free of SiO₂ by heating Si in a CO-N atmosphere with an O partial pressure of <10⁻¹⁶ atmospheres at 1200-1600 C.


Protective Al₂O₃ coatings on Si₃N₄ formed by the decomposition of surface coating [preferably Al(NO₃)₃] or by CVD of AlCl₃ followed by hydrolysis.

Method of producing Si$_3$N$_4$ tape, etc., by forming Si powder preform with polymer.


Designs for Si$_3$N$_4$ bearings for rotating shafts.


Method of producing a pair of interconnected Si$_3$N$_4$ parts by applying a mixture of $\alpha$-Si$_3$N$_4$ and 1-5 w/o MgO and hot pressing at 1400-1750 C.


Watch case comprising various hard materials including dense Si$_3$N$_4$.


Hot molding of hot-pressed Si$_3$N$_4$ using graphite or vitreous carbon dies with or without BN coating as a release agent.


Method of producing shaped bodies of Si$_2$ON$_2$ by firing, in a N atmosphere, a preshaped mixture of Si and SiO$_2$, a portion of the latter comprising colloidal silica powder of particle size $\leq$0.5 $\mu$.


Coating formed by plasma arc depositing Si into a compressor blade-shaped former coated with NaCl release agent, removing and nitriding the Si layer, and attaching the Si$_3$N$_4$ sheath formed to the blade by adhesive.


Production of Si$_2$ON$_2$ by nitridation of mixtures of Si and SiO$_2$. Control of exothermic reaction is critical.

Si is plasma arc sprayed onto former coated with NaCl to form both flat and corrugated sheets. Sheets are stacked and nitrided to form heat exchanger.


Method of forming shapes, e.g., turbine wheels, by sequentially hot pressing individual segments.


A method of making Li-SiN composition by reacting SiN with Li either in vapor or molten form in an atmosphere free of O and N. An inert gas atmosphere as Ar may be used.


Method of preparing SiN products as turbine blades and propellers in which SiN powders and 1% MgO flux were ground, passed through a sieve of 400 BS, and mixed with an aqueous binder, containing 2% methyl cellulose, to give a paste containing 23.5% H2O. Paste was pressed at 2.46 kg/mm² to the shape of a propeller and hot pressed 30 minutes at 2.11 kg/mm² at 1700 C to a density of 3.2 g/cm³. (Also issued as German Patent 2,156,592)


Preparation of compounds by electric-arc evaporation of metals or alloys into reactive gas comprising N, O, or other mixtures.


Method of manufacturing a turbine guide vane by hot pressing SiN-MgO mixtures. (Also issued as German Patent 2,302,202)


Method of forming several articles simultaneously in one mold.


A heat-resistant and strengthened composite material is formed by molding a finely powdered SiN, an oxide of Y, Sc, La, or Ce, and Al2O3 together with a volatile binding material into a shaped mass and sintering or hot pressing in a nonoxidizing atmosphere at 1400-1900 C.

Method of preparing $\text{Si}_3\text{N}_4$ articles requiring a minimum of machining by hot pressing spaced charges of $\text{Si}_3\text{N}_4$ powder and a fluxing agent to give a block of partially shaped articles with adjacent articles joined by a web. The remaining faces of each article are formed by a cutting tool which removes the webs.


$\text{Si}_3\text{N}_3$ powder with MgO added is hot pressed in a graphite mold with vaporizable cores of MgO + C + $\text{NH}_4\text{OH}$ + flour at 1800 C and ~1100 psi pressure. The cores are vaporized and formed body is in the form of a heat exchanger matrix of $\text{Si}_3\text{N}_4$.


Method of making Si powder shapes for nitriding by blow molding, etc., a mixture of Si powder and plasticizer.


Method of forming a glass joint between $\text{Si}_3\text{N}_4$ parts by inserting a powdered glass containing Si and Mn oxides (30-60 w/o $\text{SiO}_2$, 11-57 w/o MnO and up to 32 w/o $\text{Al}_2\text{O}_3$) between the parts and heating the pressed parts in an inert atmosphere.


Method of molding shapes such as heat exchanger matrices using resin vehicle.


Method of producing $\text{Si}_3\text{N}_4$ or $\text{Si}_3\text{N}_4$ and BN having protective coatings of fluxed borosilicate glass which comprise ≥1 w/o of the object and 1-20 w/o of $\text{B}_2\text{O}_3$.


Method of increasing strength of part by injecting powder/thermoplastic mixture into desired region.

Hot-pressed materials comprising Si₃N₄ as one component, a second component consisting of at least one oxide of La, Ce, Sc, Y, and/or Y₃Al₅O₁₂, and a third component consisting of SiC and/or BN and/or C.


Oxidation-resistant surface coatings applied on hot-pressed Si₃N₄ by heating, RF sputtering, or by vapor deposition.


High temperature journal bearing with Si₃N₄ elements.

657. Sorrall, A. J., “Method of Brazing Ceramic Articles to One Another”, British Patent 1,387,478 (March 19, 1975), assigned to British Leyland Truck and Bus Division Ltd.

Joining porous Si₃N₄ pieces with braze obtained from decomposition of Mo salt, e.g., ammonium molybdate.


Bearing design with Si₃N₄ liner.


Hot-pressed materials comprising 10-80 m/o Si₃N₄ and 20-90 m/o Al₂O₃ or 10-80 Si₃N₄, 10-90 Al₂O₃ and <70 m/o AlN.


The process includes producing a silazine compound by reacting NH₃ with at least one C, containing halogeno-silane at up to 200 degrees. Solutions that are produced can be used to form fibers, thin films, etc., that are subsequently heated in N to form products comprising homogeneous mixtures of SiC and Si₃N₄.


Hot pressing to high density of reaction-sintered Si₃N₄ infiltrated with MgO.
662. Wilks, R. S., and Worrall, J., “Improvements In or Relating to the Manufacture of Artefacts”, British Patent 1,396,773 (June 4, 1975), assigned to Advanced Materials Engineering, Ltd.

Reaction-sintered Si₃N₄ heat-exchanger disks using a binder which minimizes oxide formation.

663. Verbeek, W., “Production of Shaped Articles of Homogeneous Mixtures of Silicon Carbide and Nitride”, British Patent 1,396,830 (June 4, 1975), assigned to Bayer A.G.

Fibers, filaments, flakes, powders, films, coatings, and foams comprising SiC and Si₃N₄ are formed via silazane compounds that are decomposed to form moldable resins.

664. “A Method for the Production of Mouldings of Great Hardness which Contains Silicon Nitride and/or Silicon Oxynitride”, British Patent 1,396,916 (June 11, 1975), assigned to Annawerk GmbH.

High hardness bodies of Si₃N₄ and/or Si₂ON₂ were prepared by reacting a silicon halide with an excess of NH₃, removing the ammonium halide by heating, mixing remaining powder with 5-8 w/o MgO, and hot pressing the mixture at 1300-1800 °C.


Si₃N₄ catalyst support bonded to refractory component by glass.


Method of making dense (3.2 g cm⁻³) Si₃N₄ points for tools. (Also issued as German Patent 2,301,426)


Preparation of Si₃N₄-bare ceramics having high strength and good corrosion resistance by mixing 60-92 m/o finely powdered Si₃N₄ and metal oxides of MgO, ZnO, or NiO with Cr₂O₃, Y₂O₃, TiO₂, Al₂O₃, or SnO₂ and sintering in an inert atmosphere at 1600-1800 °C for 2-3 hours.


High-density, hot-pressed Si₃N₄ with Mg silicate second phase.


Si₃N₄ foam produced by nitriding Si foam. Latter powder is mixed with foamable resin to give preform.

Reaction-sintered Si₃N₄ made by nitriding Si-powder compact containing 1-5% B or B compound. Additive reduces exothermic-reaction effects and promotes uniform nitridation.


High α-Si₃N₄ powder was prepared by heating a bed containing Si powder in N₂ at a temperature low enough to prevent formation of β-Si₃N₄.


Shapes made by molding Si-epoxy resin mixture.


Coating of Si₃N₄ preform with Al₂O₃ to minimize interaction with graphite die and to form product having dense surface layer of Si-Al oxynitride.


Joining of Si₃N₄ pieces by nitriding Si layer between them.


Group IIa metal is heated with Si to make preform which is nitrided. Additive increases rate of nitridation.


Method of preparing a Si₃N₄-ceramic support for an automobile exhaust treatment catalyst having a high specified surface area and capable of being coated with a catalyst without an intermediate surface layer.


Method of treating reaction-bonded Si₃N₄ with SiH₄ and NH₃ at >1000 C to produce Si₃N₄ in the body, thus improving physical and chemical properties.

Si compact is coated with Si slurry, coating is partially nitrided and machined, and complete structure is nitrided to form precision part.


Method of manufacturing refractory ceramic products, particularly Si$_3$N$_4$ containing ~1% MgO by sintering in a die with simultaneous application of heat and pressure. As the temperature is increased, a pyrometric signal controls a hydraulic valve, so increased pressure is supplied. In the temperature range 750-1700 °C, the pressure is 750-4000 psi.


Method of hot pressing shapes from mixtures of powdered Si$_3$N$_4$, MgO, and binder. Dimensional ratio of part remains unchanged during pressing. Suggests turbine blades be made this way.


Structural units are made from Si powder by pressing, sintering, or partly nitriding, followed by coating with a low-viscosity mixture of 1.0% aqueous NH$_4$ alginate and Si powder of <40 μm diameter, then pressed together under low pressure and dried at ~100 °C. Sintering at 1350-1450 °C in a N$_2$ atmosphere gives a homogeneous Si$_3$N$_4$ ceramic substance. The transverse breaking strength at the joint at room temperature is ~42 kg/cm$^2$ (600 psi).


A seal made from Si$_3$N$_4$ hot pressed with MgO.


Method of manufacturing Si$_3$N$_4$ products as sheets with a modulus of rupture of ~21-24 kg/mm$^2$, by mixing powdered Si (3 μm grain size) polymeric dispersion, as acrylic latex (Acronal 4D) in H$_2$O, shaping the product before or after removal of a dispersing agent, decomposing the polymer, and nitriding the residue.


Preparation of crack-free Si$_2$ON$_2$ molds by nitriding compacted mixtures of Si, SiO$_2$, and CaO.

Compacts of high strength were manufactured from powdered Si₃N₄ containing >10% β-phase by adding 10% clinoenstatite and (or) forsterite or MgO and SiO₂ in stoichiometric amounts for their formation. Composite compacts were made by pressing the powdered Si₃N₄-MgO-SiO₂ mixture onto a Si₃N₄ substrate or by pressing Si₃N₄ elements connected with a Si₃N₄-MgO-SiO₂ paste. Si₃N₄ of 75 μ average particle size containing 80% β-phase and 10% clinoenstatite were ground to 1 μm average particle size and compacted at 1750 C and 2.81 kg/mm² to give elements of theoretical density 3.2 g/cm³ and modulus of rupture 56-84 kg/mm² at room temperature, which are comparable to those from α-phase powder.


German Patent 2,147,513 (March 30, 1972). (See U. S. Patent 3,839,541, Entry No. 575)


Hot pressing of α-phase powders of Si₃N₄ or Si nitride oxide obtained from thermal decomposition of SiCl₄-NH₃ reaction products. 5% addition of MgO was used to produce dense Si₂ON₂.


German Patent 2,156,592 (May 25, 1972). (See British Patent 1,357,099, Entry No. 641)

Smith, D. W., and Lumby, R. J., “Hot-Pressing of Silicon Nitride Parts”, German Patent 2,236,585 (February 8, 1973), assigned to Joseph Lucas (Industries), Ltd.

Method of making shaped parts of Si₃N₄, for example conic sections, by hot pressing in shaped BN molds.


Method of improving the bending strength of hot-pressed Si₃N₄ and Si₃N₄-Si₂ON₂ by annealing 2-40 hours at 1380-1700 C in vacuo or under N or Ar.


Formation of Si, Al, O, N compounds by hot pressing Al₂O₃-Si₃N₄ mixtures in graphite dies with BN protective coatings. Specimen pressed at 3.9 kg mm⁻² for 1 hour at 1700 C and then heated ¾ hour at 2000 C was single phase.
697. German Patent 2,301,426 (July 26, 1973). (See British Patent 1,405,171, Entry No. 677)


Hot pressing of Si$_3$N$_4$ with MgCO$_3$ additive.


Formation of Si$_3$N$_4$ by reaction sintering Si powder compact in an atmosphere of N-NH$_3$. Si particle size was 2 $\mu$m, average, and 10 $\mu$m, maximum. Heating was done for 24 hours in 100 C steps from 1200-1450 C.


Si$_3$N$_4$ parts were soaked in an aqueous solution of (NH$_4$)$_6$Mo$_7$O$_{24} \cdot 4$H$_2$O, dried and heat treated to yield Mo coatings. Parts were joined by putting additional coatings of Ag or Ni on surfaces and then heating in a reducing atmosphere.


Hot pressing of Si$_3$N$_4$ plates in dies using embedded heaters.


A porous Si$_3$N$_4$ part is impregnated with H$_2$CrO$_4$, heated to 677 C, and cooled. The cycle is repeated 13 times to produce a Cr oxide-containing body with Rockwell 15N hardness of 94-97.


Method of preparing dense Si$_3$N$_4$ shapes, especially turbine blades, by shaping powdered starting material with plasticizers and isostatically hot pressing at $\geq$1500 C.


Method of preparing primarily $\alpha$-Si$_3$N$_4$ powder by treating Si particles in a fluidized bed with a gas mixture (90% N-10% H) at temperatures $\leq$1300-1400 C. The supply of N is adjusted by the valves controlling the parts that admit the reacting mix.

Molded bodies of hot-pressed dense Si₃N₄ and/or Si₇ON₂ containing SiC were prepared by firing a mixture Si powder and C in a N atmosphere at 1100-1450 C, pulverizing and hot pressing with an oxide pressing aid, as MgO.


Reaction-sintered Si₃N₄ bending test specimen (porosity 28%) was infiltrated with Me polysilicate in vacuo at room temperature, dried, and annealed at 1050 C resulting in 5.5% weight gain, decrease in porosity, and ~9% increase in cold bending strength.


Si₃N₄ is hot pressed using glassy additives that are subsequently converted to glass ceramics by recrystallization anneal at 800 C.


Hot-pressing of Si₃N₄ powder and Al₂O₃, MgO, Cr₂O₃, Y₂O₃, ZnO, NiO, TiO₂, and SnO₂.


Method of preparing Si₃N₄ ceramics of approximate theoretical density by compacting Si powder, reaction sintering in N for ~12 hours at 1200-1350 C, and compacting in a BN-coated graphite mold at 1600-1850 C and 2.35 kg/mm² after impregnating with 1-5 v/o MgO as flux. Additions of MgO, SiC, BN, graphite and Fe improved the high temperature, bearing, wear, and impact properties.


Cr oxide surface coatings on porous Si₃N₄ decrease porosity and increase hardness and oxidation resistance.


Materials comprising Si₃N₄ or Al-Si oxynitride and SiC sintered with MgO sintering aid.


Parts comprising hot-pressed and reaction-sintered Si₃N₄.

Production of parts by injection molding.


Method of producing Si$_3$N$_4$ articles by injection molding a mixture of Si powder and a thermoplastic material, heating to burn out the plastic and further heating in a N atmosphere to form the nitride.


Slip casting of Si with control of particle size, solid content, and pH of slip. The latter contains Si, Fe$_2$O$_3$, and monoethanolamine in H$_2$O.


Injection-molded and sintered Si powder preform is coated with Si slip before nitriding.


Method of making parts of a gas-turbine rotor by mixing 60-6 v/o powdered Si (particle size 10-15 μ) with a thermoplastic resin, injection molding, burning out the resin at 350 C, and nitriding to produce Si$_3$N$_4$.


Method of marking Si$_3$N$_4$ by applying a mixture consisting of one or more metal oxides and/or a starting material capable of forming such oxides, a liquid vehicle (as H$_2$O) and a binder, and calcining the coated nitride.


Hot pressing of Si$_3$N$_4$ with CeO$_2$ additive.


Hot pressing of Si$_3$N$_4$ with Group IIIa metal oxide additives, specifically Y$_2$O$_3$.


Method of reducing the gas permeability of porous Si$_3$N$_4$ moldings by partially or completely filling the open pores with components that form cordierite or a borosilicate glass in the pores.

Method of making a Si₃N₄ refractory by sintering Si₃N₄-TiO₂ powder mixtures in N or oxidizing atmospheres at 1400 C.


Method of preparing Si₃N₄ of various porosities by spark isostatic pressing of Si powder with stoichiometric amounts of N introduced into the press. Use of pure N produces a nitride with zero porosity and the porosity is controlled by adding He to N. When a mixture of O and N was used a nitride-oxide composite was formed.


Sintered Si₃N₄ refractories containing SiO₂ and various sintering aids such as CaSiO₃, Al₂O₃ cement, bentonite, and amorphous SiO₂.


Fibrous composites made by mixing nitrides or carbides of Al, Si, or B with 15 m/o R₂O₃ (R = Y, Sc, Ta, or Ce) and sintering in N atmosphere at temperatures to 1700 C.


Diatomaceous earth (96% SiO₂) is mixed with C and nitrided to yield Si₃N₄, SiC, and Si₂ON₂.


Powder containing at least one component selected from AlN, Al₄C₃, Si₃N₄, SiC, B₄C, and BN and at least one component selected from ThO₂, PaO₂, UO₂, BeO, SiO₂, and TiB₂ ~1-15 m/o was sintered in a nonoxidizing atmosphere to produce a fibrous structure.


Powder containing at least one component selected from AlN, Al₄C₃, SiC, Si₃N₄, B₄C, and BN (96-99% w/o) and at least one component selected from Y₂O₃, ThO₂, Sc₂O₃, La₂O₃, and Ce₂O₃ (0.1-4.0 w/o) was hot pressed in a nonoxidizing atmosphere.


Powder mixture of 40-90 m/o AlN, 2-40 m/o SiO₂, and 0-30 m/o Si₃N₄ is hot pressed at 1650-2000 C to give dense material resistant to corrosion by molten glass at 1400 C.

Powder mixture of 15-90 m/o Si$_3$N$_4$, 10-60 m/o Ga$_2$O$_3$, and 0-68 m/o AlN is heated with or without pressure at 1650-2000 C to give dense body with expansion coefficient of 2.50 x 10$^{-6}$ C.


Sintered ceramic formed by heating with or without pressure at 1650-2000 C powder mixture comprising 45-90 m/o Si$_3$N$_4$, 9-55 m/o GeO$_2$, and 0-20 m/o AlN.


Method of preparing refractory composite materials with high strength by sintering Si$_3$N$_4$ >80 w/o and Al$_2$O$_3$ 0.1-20 w/o at 1500-1800 C for 10-240 minutes in a nonoxidizing atmosphere. The composites are used for turbine parts and wear-resistant tools.


Method of preparing Si$_3$N$_4$ whiskers is described in which Si is reacted with gas mixture containing N$_2$ and/or NH$_3$ together with Cl and/or HCl at 860 C. The conversion rate was 78.2% and the whiskers were 0.01-1.0 µm diameter and 1.0-18 mm long with a tensile strength of 1400 kg/mm$^2$.


Amorphous SiO$_2$ with absorbed F (acid fluoride or fluorosilicate) was mixed with carbonaceous matter and heated at 1300-1500 C in a N atmosphere to produce Si$_3$N$_4$.


Method of preparing a Cr-dispersed Si$_3$N$_4$ sintered material from CrN, Si, and Si$_3$N$_4$ by controlled heat treatment.


Hot-pressed body comprising 25-40 m/o AlN, 10-30 m/o SiO$_2$, and balance Si$_3$N$_4$ had low porosity and good abrasion resistance.


Method of compacting powdered Si$_3$N$_4$:TiO$_2$:Ti and paraffin at 2000 kg/cm$^2$ and heating to 1700 C in H to produce a Si$_3$N$_4$ cermet with high strength and toughness. Other metal-oxide combinations may also be used.
Oxidant-resistant, high strength ceramic products consisting of Si$_3$N$_4$ and TiN were produced by mixing powder Si$_3$N$_4$, AlN, and TiO$_2$, molding, and sintering in an nonoxidizing atmosphere at 1650-1800 C or by hot pressing at 1700 C.

Al-Si-Al$_2$N$_3$-Si$_3$N$_4$-system composites were made by adding 0-10% Cu or Mg, presintering, heating in N at 900 C, and hot forging.

A mixture containing 80 w/o powder α-Si$_3$N$_4$, 10 w/o Y$_2$O$_3$, 10 w/o Al$_2$O$_3$ with 5% stearic acid as a binder was molded and sintered in a N atmosphere at 1700 C for 2 hours to obtain a refractory composite.

Sintered products containing 60-90 m/o Si$_3$N$_4$ and the balance MgO, ZnO, and/or NiO and Al$_2$O$_3$, and Cr$_2$O$_3$, Y$_2$O$_3$, and/or TiO$_2$ in spinal state and having diameter $\geq$3.10 g/cm$^3$ high abrasion resistance, and useful for cutting tool materials for hypereutectic Al-Si alloys.

Pressure infiltration of Al into porous Si$_3$N$_4$ compact.

Si$_3$N$_4$ hot pressed/sintered material containing SiO$_2$, Al$_2$O$_3$, TiO$_2$, and optionally oxides of Li, Be, Mg, Ca, Sr, Cd, Ba, Mn, Fe, Co, and Ni.

Use of fluxes, e.g., aqueous solution of NaCl and NaF, to improve wetting and infiltration of porous Si$_3$N$_4$ with metals, e.g., Al alloy. Bend strength of material impregnated with latter alloy was 400 M Pa.

Si₃N₄ fibers prepared by heating Si or Si compound with catalyst and reducing compound at 1300-1500 C in N. Catalyst may be elements or compounds of Ti, Zr, etc., and reducing compound C, graphite, or coke.


Title reactants yield SiO which is reduced to Si which reacts with N to form predominately α-Si₃N₄ whiskers at 1200-1350 C, and β-Si₃N₄ whiskers at ~1450 C.


Method of preparing a Si₃N₄ refractory by mixing 95 w/o Si₃N₄ with 5 w/o clay, to be used in steel ingot manufacture and in a furnace for melting metals.


Fibers of Si₂ON₂, 5-15 μm diameter times 5-200 μm long were obtained by adding a heavy metal (as Fe, Mn, or Cu), or its salt, to a mixture of Si and SiO₂ and heating at ≤1420 C in N or a H containing N gas stream.


Si₃N₄ is mixed with 0.1-10% Group IIIB and IVB metal oxides followed by hot pressing to obtain super hard composites, with Vickers hardness 1500-1600.


A mixture of Si, Al, Al₂O₃, and Fe₂O₃ was fired under N at 1350 C. Resulting powder was formed into crucible and sintered at 1600 C to give a product with 7% porosity. Al was unsuccessfully melted in crucible. Patent also includes other refractory compositions.


Hot-pressed material comprising Si₃N₄, SiO₂, and Y₂O₃. AlN may also be added.


Si₃N₄, AlN, SiO₂ mixture that may be sintered or hot pressed. Data are given for hot-pressed material.
Si₃N₄ (60-95 parts) was mixed with Al₂O₃-SiO₂-alkaline earth metal oxide mixture (5-40 parts), shaped and sintered at 1580 °C to obtain a Si₃N₄-based porcelain product having high strength, small thermal expansion coefficient, and good electrical insulating properties.

A 100 μm Si layer was formed on porous Si₃N₄ by heating in contact with Si powder in N for 15 minutes at 1450 °C.

High-strength sintered Si₃N₄ products by mixing raw Si₃N₄ with Group IIA and VI metal oxides and hot pressing in the presence of AlN, e.g., compact is coated with 5 mm AlN and pressed at 1750 °C.

Reaction-sintered Si₃N₄ containing various oxides such as TiO₂, etc.

Method of preparing α-Si₃N₄ from a mixture of pure SiO₂ and C in a mole ratio 1:5, at 1300-1400 °C in an atmosphere of N or NH₃ and then oxidizing the excess C at 550-700 °C.

Method of preparing dense Si₃N₄ by mixing SiO₂ with Fe₂O₃ and C and heating in a N atmosphere.

Method of forming a Cr-dispersed Si₃N₄ by sintering Si, Cr, and Si₃N₄ at 1500 °C in N and heating at 1800 °C in N to yield dispersed Cr phase.

Powdered Si containing O as SiO₂ or Si₂ON₂ and C or SiC was heated to 1200-1420 °C in a N atmosphere to convert metallic Si to α-Si₃N₄.

Powdered Si and MgO were mixed and heated at 1250-1450 C in a N-H atmosphere to obtain α-Si₃N₄.


Si or ferrosilicon powder is mixed with additives including Al₂O₃, Y₂O₃, Ce₂O₃, and La₂O₃, compacted, and nitrided.


The method of producing shaped articles by pressing a mixture based on Si₃N₄ and oxides as Al₂O₃ and MgO with subsequent nitriding. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 48 (35) 87-88 (1971)]


Method of preparing Si₃N₄ during reprocessing of Fe containing >3% Si by blowing N through the vat is changed to produce Si₃N₄ as one of the reduction products by blowing N through at the beginning of melting and collecting Si₃N₄ formed in dust collectors or electrostatic precipitators. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (7), 106 (1972)]


A method of preparing a refractory material containing 50-90% Si₃N₄ and 10-50% dispersed α-Al₂O₃ with increased thermal stability and mechanical resistance. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (9), 66 (1972)]


Method of producing a material containing Si₃N₄ 30-89, SiC 1-60, and Al₂O₃ or MgO 10-15 m/o % having increased chemical and erosion resistance and mechanical strength. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (23), 97 (1972)]


Method of producing a ceramic material containing Si₃N₄ 80-85 w/o and Cr₂O₃ 15-20 w/o having increased mechanical strength and thermal stability. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (28), 67 (1972)]

Method of producing a refractory material with increased thermal stability and impact strength containing Si$_3$N$_4$ 80-85 and β-Al$_2$O$_3$ crystals 15-20 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 49 (30), 54 (1972)]


Method of preparing a refractory material containing Si$_3$N$_4$ 30-99, BN 0.5-50, and SiC fibers 0.5-20 m/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (15), 42 (1973)]


Method of preparing an electroinsulating refractory material containing Si$_3$N$_4$ 30-70 and TiO$_2$ 30-70 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (15), 42 (1973)]


Method of preparing a refractory material with increased mechanical strength, thermal stability, and erosion resistance containing Si$_3$N$_4$ 40-98, SiC 1-45, and SiC fibers 1-15 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (15), 42 (1973)]


A material of superior impact strength was produced from Si$_3$N$_4$ powder containing 15-20 w/o Si$_3$N$_4$ whiskers. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (21), 81 (1973)]


Method of producing a refractory material containing Si$_3$N$_4$ 62-89.5 w/o, mullite crystal whiskers 2-29.5 w/o, and AlN 8-35.5 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (27), 57 (1973)]


Addition of 20-79 m/o Al$_2$O$_3$ to material comprising 10-69 m/o BN and 10-69 m/o Si$_3$N$_4$. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (29), 85 (1973)]


Method of increasing the density, mechanical strength, chemical resistance, and erosion resistance of a refractory material containing Si$_3$N$_4$ 62-89.5 w/o and BN 8-35.5 w/o by adding mullite crystal whiskers 2-29.5 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (29), 86 (1973)]

Method of producing an impact resistant refractory material containing Si$_3$N$_4$ 80-85 w/o and Al$_2$O$_3$ whiskers 15-20 w/o. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (30), 70 (1973)]


Al$_2$O$_3$ (9.5-49 w/o) was added to composition containing Si$_3$N$_4$ (50-89.5 w/o) and TiO$_2$ (0.5-1.0 w/o) to increase density, mechanical strength, erosion, and chemical resistance. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 50 (48), 66 (1973)]


Method of increasing the mechanical strength, erosion, and heat resistance of Si$_3$N$_4$ refractory by adding mullite crystal whiskers (4.5-9.5 w/o) as well as MgO (4.5-15.0 w/o). [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 51 (13), 87-88 (1974)]


Refractory composition containing 63-96 w/o Si$_3$N$_4$, 3.5-33 w/o Al$_2$O$_3$, and 0.5-4.0 w/o SiO$_2$ for manufacturing of electrical insulating blanks. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 51 (18), 54 (1974)]


Refractory containing an intermediate layer of SiC to increase the adhesion of Si$_3$N$_4$ to graphite and its stability in corrosive media. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 51 (37), 59 (1974)]


Mullite crystal whiskers (4.5-9.5%) and Al$_2$O$_3$ (4.5-15%) were added to Si$_3$N$_4$ to produce a refractory having increased strength, erosion resistance, and heat resistance. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 51 (41), 42 (1974)]


Si$_3$N$_4$ with improved physicochemical properties was prepared by pressing blanks from powdered Si and sintering in N$_2$ at 40-60 atm. at 1700-1800 °C. [From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 53 (23), 27 (1976)]


Method of preparing turbine parts for use above 700 °C consisting of a core of Si$_3$N$_4$ or Si$_2$ON$_2$ encased with a heat-resistant gas-impermeable alloy or refractory metal silicide.

Includes ambient and high temperature data on fracture energy of Si₃N₄. Fracture energy was dependent upon microstructure, but it did not correlate with fracture strength.


Oxidation of hot-pressed Si₃N₄ was studied at 600-1450 C. Oxidation products include SiO₂ and Mg and Ca silicates. Wear Behavior and effects of oxidation on wear are also described. A novel surface parameter relating friction and wear characteristics is proposed and experimental methods are described.


Kinetics of the reaction between Si and N were studied. Gas access shown to control nitridation in some cases. Effects of time, temperature, gas composition, surface area of powder, and solid phase impurities are also discussed. Reaction rate under certain conditions may be controlled by diffusion of N through a protective layer of β-Si₃N₄.


Different morphologies of α- and β-Si₃N₄ examined by scanning electron, transmission electron, and optical microscopes were correlated with the processing conditions. Mechanisms are proposed for formation of most of the observed microconstituents. Models explaining the bonding in both the α- and β-phases are proposed.


Products of high temperature oxidation (to 1450 C) of hot-pressed Si₃N₄ were studied by X-ray diffraction and scanning electron microscopy. Products observed included amorphous SiO₂, cristobalite, and Mg silicates.
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