MCIC Report/July 1979

MCIC-79-41

AN ANNOTATED BIBLIOGRAPHY ON SILICON NITRIDE FOR STRUCTURAL APPLICATIONS

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MCIC 79-41

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ACKNOWLEDGEMENT

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PREFACE

THIS REPORT SUPERSEDES MCIC 77-29

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 (1400 C) 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 1961-1978, 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. Department of Energy, Energy Research Abstracts (ERA)
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 persevering efforts of Mrs. Eleanor Dugan in providing many of the references and her diligent proofreading of the manuscript and the efficient contributions made by Mrs. Mary Carr and Mr. Stephen Macchi are gratefully acknowledged. The editorial and typing assistance of Mr. Willie Veasey is also gratefully acknowledged.

CONTENTS

BOOKS

1. Anderson, C. A., Bratton, R. J., Sanday, S. C., and Cohn, A., "Progress on EPRI Ceramic Rotor Blade Program", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 783-804.

   Three–component design using HPSN rotor blades is described and room temperature spin test results are given.

2. Annis, C. G., and Cargill, J. S., "Modified Double Torsion Method for Measuring Crack Velocity in NC-132 (Si_3N_4)", Fracture Mechanics of Ceramics, Vol. 4, Crack Growth and Microstructure, edited by R. C. Bradt, D.P.H. Hasselman, and F. F. Lange, Plenum Press, New York (1978), pp 737-744.

   Si_3N_4 ceramics were tested under constant crosshead displacement at 927° and 1204°. At the lower temperatures, crack prapagation is discontinuous but at 1204° it is continuous. Crack velocities (10^{-6}–10^{-1} m/cycle) increased with temperature. The stress intensity does not depend on crack length.

3. Arnon, N., Havstad, P. H., and Trela, W., "2500 F Testing-Rig Development and Ceramic Gas Turbine Components Test Results", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 317-334.

   Describes a test rig capable of testing stationary Si_3N_4 ceramic components under simulated gas turbine conditions of gas flow, pressure, and temperature up to 2500 F. Test data are included.

4. Arrol, W. J., "The Sialons - Properties and Fabrication", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 729-738.

   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.

5. Ashcroft, W., "The Tensile and Bend Strengths of Silicon Nitride and Hot-Pressed Silicon Carbide", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 245-260.

   Bend strengths in air of hot-pressed and reaction-sintered Si_3N_4 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 Si_3N_4. Tensile and bend data are compared in terms of Weibull concepts.

6. Atkinson, A., and Moulson, A. J., "Some Important Variables Affecting the Course of the Reaction Between Silicon Powder and Nitrogen", Science of Ceramics, Volume 8, British Ceramic Society, Stoke-on-Trent, England (1976), pp 111-121.

   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.

7. **Baker, R. R., Ezis, A., Hartsock, D. L., and Goodyear, M. U., "Developments in Press Bonding of Duo-Density Rotors", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 207-230.**

Approaches for making integral ceramic turbine rotors are reviewed leading to the selection of a duo-density Si_3N_4 rotor concept. Describes hot press forming a hub of fully dense Si_3N_4 while simultaneously diffusion bonding the hub to a reaction sintered Si_3N_4 blade ring. Also considers three-piece rotor concept.

8. **Bansal, G. K., and Duckworth, W. H., "Effects of Specimen Size on Ceramic Strengths", Fracture Mechanics of Ceramics, Vol. 3, Flaws and Testing, edited by R. C. Bradt, D.P.H. Hasselman, and F. F. Lange, Plenum Press, New York (1978), pp 189-204.**

Hot-pressed Si_3N_4 and other ceramics were stressed to determine the effect of varying the linear dimensions by a factor of 4 or 5. The strength decreased with increased specimen size.

9. **Barratta, F. I., Driscoll, G. W., and Katz, R. N., "The Use of Fracture Mechanics and Fractography to Define Surface Requirements for Si_3N_4", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 445-476.**

Internal or subsurface fracture initiation in hot-pressed Si_3N_4 was studied to establish critical defect sizes, fracture toughness, and failure strength. Data were used to establish surface finish criteria for various test systems.

10. **Barnby, J. T., and Taylor, R. A., "The Fracture Resistance of Reaction-Sintered Silicon Nitride", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramics Research Association, Manchester, England (1972), pp 311-328.**

The fracture toughness of reaction-bonded Si_3N_4 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 Si_3N_4. Density,Young's modulus, and plain bar bend strengths were also determined.

11. **Baumgartner, H. R., "Ceramic Bearings for Turbine Applications", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 423-443.**

Rolling contact fatigue (RCF) life testing of various grades of HPSN rolling elements showed it to be superior to CVM-50 steel. The failure mechanism is spallation as in the case of bearing steels, and in contrast to other ceramics. Fatigue life is shown to be very sensitive to surface finishing techniques, and compositions. Testing of all ceramic and ceramic roller-metal race bearings is described.

12. **Baumgartner, H. R., "Evaluation of Roller Bearings Containing Hot-Pressed Silicon Nitride Rolling Elements", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 713-728.**

Rolling contact fatigue tests on hot-pressed Si_3N_4 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 Si_3N_4 rollers and the other with Si_3N_4 races and rollers - were successfully tested under accelerated conditions, i.e., 10,000 rpm and 2,500 lb load.

13. **Baumgartner, H. R., "Hot Pressed Silicon Nitride in Roller Bearing Applications", Materials on the Move, proceedings of the Sixth National SAMPE Technical Conference, Society for the Advancement of Material and Process Engineering, Azusa, California (1974), pp 439-443.**

Hot-pressed Si_3N_4 was evaluated by means of fatigue testing on elemental components and testing of full-scale prototypes of bearings. Si_3N_4 has excellent fatigue life. Two types of precision 55-mm-bore roller bearings were designed, fabricated, and successfully tested under accelerated test conditions.

14. **Baumgartner, H. R., and Wheildon, W. M., "Rolling Contact Fatigue of Hot-Pressed Silicon Nitride Versus Surface Preparation Techniques", Surface and Interfaces of Glass and Ceramics, Volume 7, Materials Science Research, edited by V. D. Frechette, W. C. LaCourse, and V. L. Burdick, Plenum Press, New York and London (1974), pp 179-193.**

Hot-pressed Si_3N_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 Si_3N_4 is critical to rolling contact fatigue life.

15. **Baumgartner, H. R., and Richerson, D. W., "Inclusion Effects on the Strength of Hot-Pressed Si_3N_4", Fracture Mechanics of Ceramics, Volume 1: Concepts, Flaws, and Fractography, edited by R. C. Bradt, D.P.H. Hasselman, and F. F. Lange, Plenum Press, New York and London (1974), pp 367-386.**

Fractographic studies of hot-pressed Si_3N_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 Si_3N_4 was significantly increased with reduction of the size and frequency of inclusions.

16. **Becker, P. F., and Halen, S. A., "Solid State Brazing of Si_3N_4", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 1077-1082.**

HPSN was brazed using ZrO_2 filler powder and the effects on the resultant mechanical properties are discussed.

17. **Bersch, C. F., "Overview of Ceramic Bearing Technology", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 397-405.**

The feasibility of using hot pressed Si_3N_4 in rolling bearing elements is being explored. Key issues are identified, test results are reviewed, and unresolved problem areas are highlighted.

18. **Billy, M., "Problems Raised in the Oxidation of Sintered Ceramics: The Case of Silicon Oxynitride", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 635-640.**

Gives results of oxidation experiments on Si_2N_2O ceramics, and discusses roles of porosity and impurities in process.

19. **Blegen, K., "Equilibria and Kinetics in the System Si-N and Si-N-O", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 223-244.**

The Gibbs free energies of formation of β-Si_3N_4 and Si_2ON_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 α- and β-Si_3N_4 were examined experimentally and it was found that the α-phase is formed by a vapor phase mechanism and the β-phase by a direct reaction of N and Si. The latter is the thermodynamically stable phase at all temperatures.

20. **Booher, C. R., Jr., "Thermal Transient Stress Analysis of an Industrial Combustion Turbine Ceramic Stator Vane and Correlation with Test Results", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 731-781.**

The first stage uncooled full-scale ceramic vane assembly and the support structure for industrial combustion turbines were tested at 2670 F for 103 peak duty transient thermal cycles. The three-piece vane made from Si_3N_4 is insulated, cushioned, and supported to minimize transient thermal stresses. The vanes were successfully tested to various cyclic conditions.

21. **Booher, C. R., Jr., and Roughgarden, J. D., "Design and Analysis of a Stationary Gas Turbine Ceramic Vane Assembly", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 79-122.**

First row stator elements for 30 MW gas turbine were designed and machined from Si_3N_4 and SiC. Discussion includes ground rules, philosophy, criteria, concepts, heat transfer, contact stresses, and thermal analyses as related to design.

22. **Bourne,W. C., and Tressler, R. E., "Alteration of Flaw Sizes and K_{Ic}'s of Si_3N_4 Ceramics by Molten Salt Exposure", Fracture Mechanics of Ceramics, Vol. 3, Flaws and Testing, edited by R. C. Bradt, D.P.H. Hasselman, and F. F. Lange, Plenum Press, New York (1978), pp 113-124.**

Experiments on molten salt exposure effects on the strength limiting parameters for hot-pressed and reaction sintered Si_3N_4 ceramics have shown that for relatively short exposure times the critical flaw sizes are substantially increased and the K_{Ic} values of the surface region are measurably reduced in the case of the hot-pressed material. The K_{Ic} values for the sintered material are not much affected by the molten salt. It is concluded that mechanical properties of Si_3N_4 can be significantly degraded by exposure to such environments.

23. **Boyer, S. M., Sang, D., and Moulson, A. J., "The Effects of Iron on the Nitridation of Silicon", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 297-304.**

Suggests Fe enhances rate of Si-N reaction by devitrifying SiO_2 layer invariably present on Si, enhancing "active" oxidation. Shows that effect exists with Fe at ppm level.

24. **Bratton, R. J., Anderson, C. A., and Lange, F. F., "Hot-Pressed Si_3N_4 Developments", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 805-825.**

Review of developments at Westinghouse during the previous five years, on understanding and improvement of the high temperature properties of HPSN.

25. **Bratton, R. J., and Holden, A. N., "Ceramics in Gas Turbines for Electric Power Generation", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 37-60.**

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

26. **Bratton, R. J., and Miller, D. G., "Brittle Material Design, High Temperature Gas Turbine – Stationary Turbine Project Summary", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978) pp 689-730.**

Review of highlights of work conducted by Westinghouse from July 1971 to June 1976. The desired objective was achieved with the result that the ceramic design concepts developed have proven feasible for large industrial gas turbines.

27. **Brennan, J. J., "Improving the Impact Properties of Silicon Nitride", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 521-528.**

Impact strength of HPSN was improved by surface layers of iron titanate and silica-zircon. Also studied was degradation of impact resistance and strength of HPSN after high temperature oxidation.

28. **Brennan, J. J., "Increasing the Impact Strength of Si_3N_4 Through Fibre Reinforcement", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 123-134.**

The use of Ta wire reinforcements increased the Charpy impact strength of hot-pressed Si_3N_4 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-Si_3N_4 composite system also exhibited a threshold energy, below which no damage occurs upon impact, that is considerably higher than that of the unreinforced Si_3N_4.

29. **Brook, R. J., Carruthers, T. G., Bowen, L. J., and Weston, R. J., "Mass Transport in the Hot Pressing of a Silicon Nitride", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 383-390.**

Suggests that both hot pressing and α/β transformation are controlled by diffusion through grain boundary phase. Transformation is not considered essential to densification. Conclusions are based on experimental data on hot pressing of Si_3N_4-MgO mixtures.

30. Brown, R. L., Godfrey, D. J., Lindley, M. W., and May, E.R.W., "Advances in the Technology of Silicon Nitride Ceramics", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 345-360.

Discussion of progress in reaction-bonded Si_3N_4 in three areas: (1) the achievement of high strength (300 MN/m^2) in Si_3N_4 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 Si_3N_4, (3) the production of a mouldable form of Si powder compact by the use of polymeric additives.

31. Burke, J. J., Gorum, A. E., and Katz, R. N., eds., Ceramics for High Performance Applications, Proceedings of the 2nd Army Materials Technology Conference, Hyannis, Massachusetts, 13-16 November 1973, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974).

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.

32. Burke, J. J., Lenoe, E. M., and Katz, R. N., eds., Ceramics for High Performance Applications – II, Proceedings of the Fifth Army Materials Technology Conference, Newport, R. I., March 21-25, 1977. Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978).

Collection of 58 papers of international scope, emphasizing heat engine applications. Pertinent papers are annotated in this bibliography with each entry under the name of the specific author.

33. Cabannes, F., and Charpentier, A., "Creep Measurement of Sialon Sintered Without Additive", Science of Ceramics, Volume 9, British Ceramic Society, Stoke-on-Trent, England (1977), pp 510-518.

High temperature compressive creep of hot-pressed sialon materials without additives and rich in Al_2O_3 was studied. Creep activation energy was 158 ± 15 kcal/mol. High creep rate was due to the ultrafineness of the grains (0.2-0.5 u.).

34. Calvert, G. S., and Carruthers, W. D., "Ceramic Blade Attachments", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 839-860.

The turbine rotor with hot-pressed Si_3N_4 blades attached to the superalloy disk with a Pt interlayer of plastic forging was hot spin tested in vacuum at 2250 F and 45,000 rpm for 50 hours. The fully bladed (30) rotor survived.

35. Campos-Loriz, D., and Riley, F. L., "Factors Affecting the Formation of the α- and β- Phases of Silicon Nitride in the Nitridation of Silicon Powders", Science of Ceramics, Vol. 9, British Ceramic Society, Stoke-on-Trent, England (1977), pp 38-45.

In the early stages of nitriding of Si the formation rate depends on the powder surface area and phase transformation occurs at solid surfaces. Metallic impurities (as Fe), liquid phase/growth sites, and the presence of low O_2 partial pressure and efficient O_2 gelter enhance the β-Si_3N_4 formation.

36. Canteloup, J., and Mocellin, A., "Synthesis of Ultrafine Nitrides and Oxynitrides in R. F. Plasma", Special Ceramics, Volume 6, proceedings of the 6th Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 9-11 July 1974, edited by P. Popper, British Ceramic Research Association, Manchester, England (1975), pp 209-222.

Si and Al powders were nitrided with NH_3 to produce ultrafine AlN, Si_3N_4, and Si-Al-O-N powders. Equipment design and powder characteristics are discussed.

37. Chin, J., and Elsner, N. B., "Preparation of Silicon-Aluminum-Nitrogen Compounds by Reactive Ion Plating", Proceedings of the Conference on Chemical Vapor Deposition, Fifth International Conference, 1975, edited by J. M. Blocher, Jr., H. E. Hintermann, and L. H. Hall, The Electrochemical Society, Princeton, New Jersey (1975), pp 241-257.

(Si, Al) N alloys were deposited by reactive ion plating from Si and Al evaporation and NH_3 or NH_3 + 1% SiH_4 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.

38. Chiu, Y. P., and Dalal, H., "Lubricant Interaction with Silicon Nitride in Rolling Contact Applications", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 589-608.

Fabrication response of Si_3N_4 is similar to that of M50 tool steel presently used for aircraft engine bearings. Si_3N_4 can be satisfactorily lubricated by hydrocarbon and ester-base lubricants at temperatures to 260 C.

39. Clarke, D. R., "Direct Observation of Lattice Planes at Grain Boundaries in Silicon Nitride", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 433-440.

Electron photomicrographs obtained by lattice imaging suggest that grain boundaries in HPSN do not comprise a glass phase as often had been assumed.

40. Clarke, D. R., and Shaw, T. M., "Polytypism in Magnesium Sialon", Processing of Crystalline Ceramics, edited by H. Palmour III, R. F., Davis, and T. M. Hare, Plenum Press, New York and London (1978) pp 589-596.

The morphology and crystallography of the 12H and 21R polytypes in a Mg "sialon" were investigated by high resolution electron microscopy. Intergrowths of polytypes occur introducing mismatch strains and it is concluded that careful process control will be necessary to avoid that situation.

41. Clarke, D. R., and Thomas, G., "Lattice Imaging of Grain Boundaries in Ceramics", Proceedings of the 35th Annual Meeting of the Electron Microscopy Society of America, Boston, Mass., 1977, edited by G. W. Bailey, Claitor's Publishing Division, Baton Rouge (1977), pp 114-115.

Includes information on grain boundaries in HPSN prepared with MgO addition.

42. Clarke, D. R., and Thomas, G., "The Structure of Grain Boundaries in Silicon Nitride Based Alloys", Processing of Crystalline Ceramics, edited by H. Palmour III, R. F. Davis, and T. M. Hare, Plenum Press, New York and London (1978), pp 627-639.

Grain boundaries were examined in HPSN (fluxed with both MgO and Y_2O_3) and a magnesium "Sialon" by high resolution electron microscopy including lattice fringe imaging. Room temperature observations indicate that glassy phase is nonwetting and thus cannot form a continuous film. Grain boundary composition is discussed.

43. Coe, R. F., Lumby, R. J., and Pawson, M. F., "Some Properties and Applications of Hot-Pressed Silicon Nitride", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 361-376.

The properties and applications of hot-pressed Si_3N_4 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.

44. Dalal, H. M. "Machining of Ceramics for Bearing Applications", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 407-422.

Severe degradation in fatigue life can be caused by surface flaws generated during abrasive machinery of Si_3N_4. Under the conditions chosen, diamond is preferable to SiC for abrasive machining of Si_3N_4 in terms of rate of material removal and surface roughness.

45. Davidge, R. W., "Economic and Energetic Considerations for Nitrogen Ceramics", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 653-657.

Attempts to estimate production costs for Si_3N_4 for comparison with nickel alloy turbine materials, concludes RBSN would be competitive on volume, but not on weight basis.

46. Davidge, R. W., "Mechanical Properties of Reaction Bonded Silicon Nitride", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 541-559.

A review of the structure and properties of RBSN with 19 references. Summarizes properties and state-of-the-art.

47. Davidge, R. W., Evans, A. G., Gilling, D., and Wilyman, P. R., "Oxidation of Reaction-Sintered Silicon Nitride and Effects on Strength", Special Ceramics, Volume 5, proceedings of the 5th International Symposium on Special Ceramics held by the BCRA, Stoke-on-Trent, England, 14-16 July 1970, edited by P. Popper, British Ceramic Research Association, Manchester, England (1972), pp 329-344.

Specimens of reaction-sintered Si_3N_4 (α/β ratio ~50/50), density 2.53 x 10^3 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.

48. Engel, W., Gugel, E., and Thuemmler, F., "Fluage du niture de silicium aux Temperatures elevées", Science of Ceramics, Volume 7, Societé Francaise de Ceramique, Paris (1973), pp 415-416.(Abstract)

Four-point bending apparatus was used to study creep of hot-pressed and reaction-sintered Si_3N_4 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 Si_3N_4 occurs by grain boundary sliding.

49. Engel. W., Lange, E., and Müller, N., "Injection Molded and Duo Density Silicon Nitride", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 527-538.

Injection molding of RBSN is described. Densities $\geqslant$2.5 g/cm^3 were obtained. Important fabrication parameters are discussed. The hot-press bonding process to produce RBSN/HPSN parts is described, and thermal expansion data were obtained for both materials.

50. Evans, A. G., "High-Temperature Slow Crack Growth in Ceramic Materials", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 373-396.

High-temperature slow crack growth processes in several ceramic systems, including Si_3N_4 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.

51. Evans, A. G., and Sharp, J. V., "Transmission Electron Microscopy of Silicon Nitride", Electron Microscopy and Structure of Materials, proceedings of the 5th International Materials Symposium held at University of California, Berkeley, 13-17 September 1971, edited by Gareth Thomas, University of California Press, Berkeley (1972), pp 1141-1154.

Thin films of reaction-sintered Si_3N_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 β-Si_3N_4 in a fine-grained matrix of α-Si_3N_4 and pores which usually contain fibers. The fibers have the α-Si_3N_4 structure often with an amorphous layer. The deformed material contained some heavily dislocated grains of β-Si_3N_4. Most dislocations have a Burgers vector $<0001>$ and the remainder a vector of $\sim <11\bar{2}3>$. The observation of dislocation activity in the vicinity of cracks indicated that dislocation motion near the cracks contributes to the fracture surface energy.

52. Ezis, A., "The Fabrication and Properties of a Slip-Cast Silicon Nitride", Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 207-222.

Preparation of slip comprising Si powder suspended in H_2O 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_3N_4.

53. **Fate, W. A., "Pulsed Ultrasonic Measurements in Ceramic Materials at High Temperatures", Ceramics for High Peformance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1974), pp 687-696.**

Experimental methods for MHz frequency, pulsed ultrasonic measurements at high temperatures are reviewed. Elastic property data are presented for Si_3N_4, SiC, and a Li-Al-Si glass ceramic.

54. **Freiman, S. W., Mecholsky, J. J., McDonough, W. J., and Rice, R. W., "Effect of Oxidation on the Room Temperature Strength of Hot-Pressed Si_3N_4-MgO and Si_3N_4-ZrO_2", Ceramics for High Performance Applications — II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 1069-1076.**

Strength decreased up to 65% for Si_3N_4 hot pressed with an MgO additive that was oxidized at 1000-1380 C for up to 400 hours. Much smaller decreases were measured for an experimental material in which 2 w/o ZrO_2 was used as the additive.

55. **Freiman, S. W., Williams, A., Mecholsky, J. J., and Rice, R. W., "Fracture of Silicon Nitride (Si_3N_4) and Silicon Carbide", Ceramic Microstructures, 1976, edited by R. M. Fulrath and J. A. Pask, Boulder, Colo.: Westview Press (1977), pp 824-834.**

Measured fracture energies of HPSN vary from 26 to >100 J/m^2 but strengths do not follow the same trend. Measurements on as-received and oxidized material are discussed on basis of fracture surface analysis.

56. **Gatti, A., and Noone, M. J., "Ceramics in the Si-Al-O-N System Fabricated by Conventional Powder Processing and Sintering Techniques", Processing of Crystalline Ceramics, edited by H. Palmour III, R. F. Davis, and T. M. Hare, Plenum Press, New York and London (1978), pp 579-588.**

Discusses "mineralization" mechanism effective in sintering of "sialon" compositions. Mineralizers are impurities added intentionally or accidentally. Glassy second phases degrade mechanical properties. Also considers processing techniques.

57. **Gauckler, L. J., Boskovic, S. Petzow, G., and Tien, T. Y., "Liquid Phase Sintering of β-Si_3N_4 Solid Solution Containing Alumina", Ceramics for High Performance Applications — II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 559-571.**

Densification of β-Si_3N_4 solid solution containing 60 equivalent percent Al in the system Si/Al/N/O was investigated. The sintering mechanism <1600 C was related to chemical reactions. At higher temperatures a liquid forms which aids densification.

58. **Gauckler, L. J., Boskovic, S., Petzow, G., and Tien, T. Y., "Status Report on Densification of β-Si_3N_4 Solid Solutions Containing AlN: Al_2O_3 During Chemical Reaction", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 405-414.**

Reports on investigation of densification of β-Si_3N_4 solid solutions in the system Si-Al-N-O. Different chemical mixtures yielding the same final composition were used as starting materials. A nitride-containing liquid that became a glass at lower temperatures formed during sintering.

59. Gauckler, L. J., and Petzow, G., "Representation of Multicomponent Silicon Nitride Based Systems", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 41-62.

Discusses representation of phase relationships in Si_3N_4-oxide systems and gives diagrams and experimental results on systems involving Si, Al, Be, Li, Mg, Ga, O, and N in various combinations.

60. Gauckler, L. J. Prietzel, S. Bodemer, G., and Petzow, G., "Some Properties of β-$Si_{6-x}Al_xO_xN_{8-x}$", Nitrogen Ceramics, edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 529-538.

Properties determined include lattice parameter, density, E, hardness, bend strength, toughness, thermal expansion, thermal conductivity, and thermal shock behavior. Strength was comparable to HPSN, but thermal shock resistance was inferior.

61. Gazza, G. E., "Sintered Silicon Nitride", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachussetts (1978), pp 1001-1010.

Studies on the sintering of Si_3N_4 are reviewed. Methods of enhancing sinterability of current Si_3N_4 material and processing technology are discussed. Experimental parameters used for sintering and preliminary data on physical and mechanical properties of resultant products are cited.

62. Gebhardt, J. J., Tanzilli, R. A., and Harris, T. A., "Chemical Vapor Deposition of Silicon Nitride", Proceedings of the Conference on Chemical Vapor Deposition, Fifth International Conference, 1975, edited by J. M. Blocher, Jr., H. E. Hintermann, and L. H. Hall, The Electrochemical Society, Princeton, New Jersey (1975), pp 786-800.

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 α-Si_3N_4 at 1500 C. Deposits showed preferred orientation and residual stresses. Material had outstanding resistance to oxidation and creep.

63. Geiss, R. H., and Clarke, D. R., "Combined Analytical and High Resolution Microscopy – A Case Study", Proceedings of the 35th Annual Meeting of the Electron Microscopy Society of America, Boston, Mass, 1977, edited by G. W. Bailey, Claitor's Publishing Division, Baton Rouge (1977), pp 146-147.

Phases, composition, structure, and form of HPSN fluxed with Y_2O_3 were studied by various electron microscopy techniques. A third phase was found between Si_3N_4 and $Si_3Y_2O_3N_4$ grains by use of lattice field imaging.

64. George, W., and Vaughan, G. N., "Calculation of Thermal Stresses in Tubular Ceramic Components", Science of Ceramics, Volume 7, Societé Francaise de Ceramique, Paris (1973), pp 87-104.

Stresses in reaction-sintered Si_3N_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%.

65. Gielisse, P. J., Kim, T. J., and Choudry, A., "An Experimental Investigation of the Dynamic and Thermal Characteristics of the Ceramic Stock Removal Process", Surfaces and Interfaces of Glass and Ceramics, Vol. 7, Materials Science Research, edited by V. D. Frechette, W. C. La Course, and V. L. Burdick, Plenum Press, New York and London (1974), pp 137-148.

Al_2O_3 and Si_3N_4 ceramics were ground using diamond grinding wheels. The effect of environment is more pronounced at low wheel speeds and for lower strength materials. Wheel speed was inversely expotentially related to the cutting force, which is directly related to the fracture modulus of the material.

66. Glaeser, W. D., "Alpha Phase Silicon Nitride Production – Some Aspects of Nitriding Kinetics and Powder Morphology", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Mass., (1978), pp 549-557.

Si_3N_4 powder was prepared by placing a Si powder charge in a nitriding furnace and heating at $>1150°$ in a flow of NH_3 or mixture of N and H. The kinetics of nitridation were determined to establish the parameters required for optimum α-phase formation in a continuous process.

67. Glandus, J. C., and Boch, P., "Elastic and Anelastic Properties of Nitrogen Ceramics", Nitrogen Ceramics edited by F. L. Riley, Noordhoff International Publishing, Leyden, The Netherlands (1977), pp 515-519.

Discusses title properties and gives results of measurements of G and E for Si_2N_2O and Si-Al-O-N compounds. Briefly considers thermal shock.

68. Glandus, J. C., and Boch, P., "Mechanical Properties of Silicon Oxynitride", Science of Ceramics, Vol. 9, British Ceramic Society, Stoke-on-Trent, England (1977), pp 455-462. (In French)

Mechanical properties were determined for hot pressed Si_2N_2O containing 5% MgO or Y_2O_3 and sintered at 1560 to 1750°. The material containing $Y_2O_3$was more creep-resistant and remained rigid at $<1600°$.

69. Godfrey, D. J., "The Performance of Ceramics in the Diesel Engine", Ceramics for High Performance Applications – II, edited by J. J. Burke, E. M. Lenoe, and R. N. Katz, Brook Hill Publishing Company, Chestnut Hill, Massachusetts (1978), pp 877-892.

Potential benefits from ceramic applications to the diesel engine are briefly reviewed. Experiments with RBSN pistons, combustion chambers, and turbocharger rotor are described.

70. Godfrey, D. J., and May, E.R.W., "The Resistance of Silicon Nitride Ceramics to Thermal Shock and Other Hostile Environments", Ceramics in Severe Environments, Volume 5 of Materials Science Research, proceedings of the 6th University Conference on Ceramic Science, North Carolina State University at Raleigh, December 7-9, 1970, edited by W. Wurth Kriegel and Hayne Palmour III, Plenum Press, New York (1971), pp 149-162.

The properties of Si_3N_4 ceramics relevant to thermal shock are described, and results of testing and hardware trials are discussed. The technology of Si_3N_4 materials, and their potential for other hostile environments, is reviewed.