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RECENT DEVELOPMENTS IN HIGH PERFORMANCE CERAMICS

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ABSTRACT

Newly developed ceramic materials, fabrication processes, and advances in brittle materials design capability are having a significant impact on our ability to utilize ceramics as substitute materials. This paper will briefly review ceramic materials and their methods of fabrication. We will then consider the use of silicon nitride and silicon carbide ceramics in hot flow path components of gas turbines. Emphasis will be on the advantages of ceramics for this application, materials, and progress to date. Application of single and polycrystalline ceramics to optical systems such as high energy lasers will be reviewed. The detailed characterization and manipulation of grain boundaries in ceramics will be seen to be of great importance in both the high temperature structural and advanced optical areas of application.

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FOREWORD

A topical conference on "The Physics of Materials Technology" was one of the major features of the 1976 Annual Meeting of the American Physical Society. Five sessions of invited papers dealing with Materials Resources and Materials Science were held: namely, Materials Supply and Implications for Technology, Technology of Materials Supply, Technology of Materials Durability, Technology of Materials Substitutions, and Materials Conservation through Science-Intensive Technology. This paper was presented by the author on 4 February 1976 at the session on Technology of Materials Substitutions. As a large portion of this paper deals with technology developed in or associated with the ARPA "Brittle Materials Design/High Temperature Gas Turbine" program, the author would like to acknowledge ARPA, whose support of this program has been instrumental in taking these "high-performance" ceramics from the laboratory to the status of advanced state-of-the-art engineering materials.

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INTRODUCTION

Between now and the end of the century ceramics will be utilized in many applications where one would expect to encounter metals. In particular, we will begin to see ceramic materials being applied to load-bearing engineering applications. The substitution of "high performance" ceramic materials, such as silicon nitride, silicon carbide, various "glass-ceramics", and oxide ceramics for more conventional engineering materials will come about because they are abundant, low cost, high strength, and/or low thermal expansion, high temperature materials. The major impediment to their past utilization as tensile load-bearing components has been their inherent brittleness. Designers are learning to design around the brittleness problem and thus make ceramic materials available for a wider spectrum of engineering applications.^{1,2}

Ceramic materials have always been associated with high temperatures. Today the high temperature capabilities of the "new" engineering ceramics, such as silicon nitride and silicon carbide, are being focused on the critical areas of energy and materials shortages. Increased efficiency of heat engines requires higher working temperatures. The temperatures desired frequently exceed the temperature capabilities of current or projected metal alloy systems. Further, the availability of many elements required in high temperature alloys is at least as problematical as the availability of petroleum (Figure 1). Therefore, over the past five years there has been considerable interest in exploiting abundant ceramic materials in gas turbines as well as in other high temperature applications.

METAL	CURRENT SUPPLY (U.S. IMPORTS AS A PERCENT OF DOMESTIC USE 1970)	ULTIMATE SUPPLY (U.S. RESERVES AND RESOURCES)	CURRENT SOURCES
CHROMIUM	100	INSIGNIFICANT	USSR, SOUTH AFRICA, TURKEY
COLUMBIUM	100	DATA UNAVAILABLE	BRAZIL, NIGERIA, MALAGASY
NICKEL	91	LARGE, ASSUMING SIGNIFICANTLY INCREASED WORLD PRICE OR NEW EXTRACTION TECHNOLOGY	CANADA, NORWAY
COBALT	91	DATA UNAVAILABLE	ZAIRE, BENELUX COUNTRIES

Source of Data: Final Report of the National Commission on Materials Policy, June 1973,
U.S. Government Printing Office.

Figure 1. Present and potential availability of critical metals for high temperature turbine alloys.

1. *Brittle Materials Design, High Temperature Gas Turbine.* Ford Motor Company, Contract DAAG46-71-C-0112, ARPA Order 1849, Interim Reports.
 - a. McLEAN, A. F., FISHER, E. A., and HARRISON, D. E., AMMRC CTR 72-3, March 1972.
 - b. _____ and BRATTON, R. J., AMMRC CTR 72-19, September 1972.
 - c. _____, AMMRC CTR 73-9, March 1973.
 - d. _____, AMMRC CTR 73-32, September 1973.
 - e. _____, AMMRC CTR 74-26, April 1974.
 - f. _____, AMMRC CTR 74-59, September 1974.
 - g. _____ and MILLER, D. G., AMMRC CTR 75-8, April 1975.
 - h. _____, AMMRC CTR 75-28, October 1975.
2. *Ceramics for High Performance Applications.* J. J. Burke, A. E. Gorum, and R. N. Katz, ed., Brook Hill Publishing Company, Chestnut Hill, Massachusetts, 1974.

This paper will specifically focus upon the application of ceramics to the gas turbine engine, but it is important to appreciate that benefits similar to those to be described later in this paper can accrue to all heat engines.

Energy conversion is, perhaps, the largest single new area of opportunity for ceramic application. However, there are many other areas where ceramics are now being utilized or considered, and where they can yield significant savings of scarce resources. The following are typical examples.

- The use of fiber optic cables for data transmission will save copper and can reduce cable weight by a factor of 21.³
- The use of sodium vapor lamps, which require alumina (or other high temperature transparent ceramic) envelopes, to replace conventional filament lamps reduces tungsten wire usage (via 15 to 20 times longer lamp life) and delivers significantly more lumens per kilowatt.
- The use of silicon carbide igniters to replace continuous pilot lights on gas appliances can save as much as 25% of the gas consumed.

The first two of these examples introduces the importance of the optical as well as the mechanical properties of ceramics when considering their use as substitute materials. An exciting area of technology and materials science requiring the development of transparent ceramics where both optical and mechanical properties are crucial, namely, high energy laser windows, will be discussed. However, first it is desirable to briefly review ceramic materials and their fabrication, and then consider the current status of ceramics in gas turbine applications. Next, the concept of grain boundary engineering will be introduced. Both the development of improved silicon nitride for turbine application and potassium chloride laser windows will be reviewed from the viewpoint of grain boundary engineering.

WHAT ARE CERAMICS?

The classic definition of a ceramic as a product made by firing minerals at high temperatures (i.e., earthenware, porcelain, brick, glass, enamels) comes to us from the Greek word *Keramos* (burnt stuff). This definition is still largely accurate. However, today one usually considers ceramics as any inorganic, non-metallic material. Thus, the families of materials with their examples shown in Figure 2 include carbons and salts. One can even include ice and, in fact, much ice research has been performed by ceramists.⁴ The applications cited in Figure 2 tend to range from the most ancient to the most futuristic as one goes from top to bottom. Many of the more ancient applications represent a continuous record of technological growth and response to new demands. For example, the ancient use of ceramics as containers now includes the use of ceramic technology to contain nuclear waste materials, either by fusing them in a glass or hot pressing them in large blocks.⁵ This mention of glass forming and hot pressing, while somewhat removed from the definition of ceramics, brings us to our next area of consideration, ceramic fabrication.

3. *Optical Spectra*, January 1976, p. 28.

4. KINGERY, W. D. *Ice and Snow: Properties, Processes and Applications*. MIT Press, Cambridge, Massachusetts, 1963.

5. McCARTHY, G. J., and DAVIDSON, M. T. *Ceramic Nuclear Waste Forms: II. A Ceramic-Waste Composite Prepared by Hot Pressing*. *Ceramic Bulletin*, v. 55, no. 2, February 1976, p. 190-194.

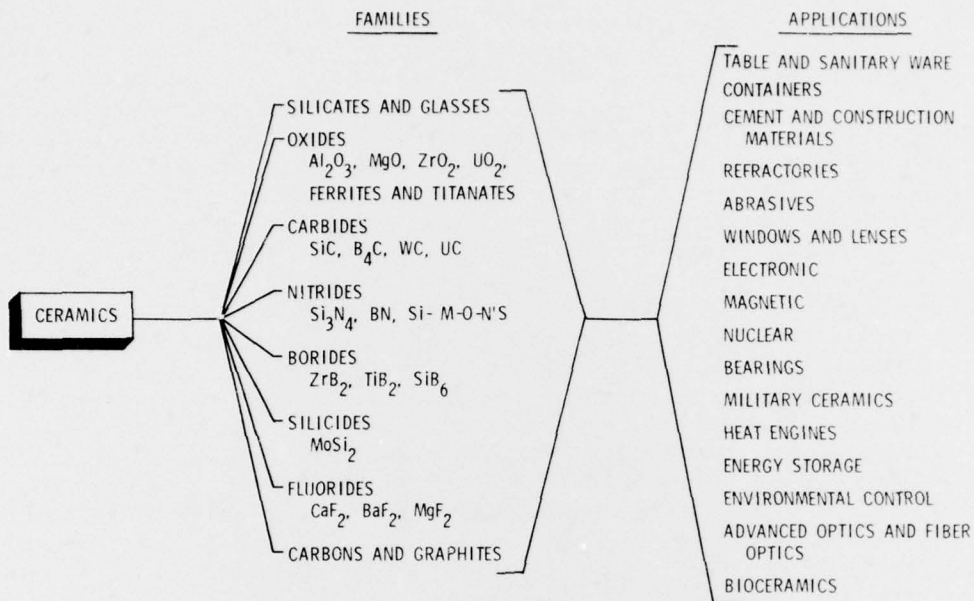


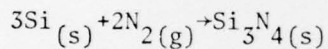
Figure 2. The families of ceramic materials with their applications.

CERAMIC FABRICATION

Ceramic materials may be processed by several major routes. Melt formation is the basis of the glass and glass-ceramic materials, as well as many single-crystal ceramics. Chemical vapor deposition has been used to produce both polycrystalline and single-crystal ceramics. Without considering glass, the bulk of engineering ceramics are formed by the consolidation of powders. The application of heat or the simultaneous application of heat and pressure will, in general, cause an aggregation of ceramic powders to become a well-bonded polycrystalline crystal body. This is known as sintering (or if pressure is involved, hot pressing). The driving force for sintering is the reduction of surface free energy of the powder aggregation. In general, sintering will occur when the surface free energy of a grain boundary γ_{GB} is less than twice the surface free energy of a powder surface in contact with its vapor environment γ_{SV} (i.e., air, N_2 , Ar, etc.). Thus when the individual powders consolidate into a densified and bonded ceramic there is a net reduction in the free energy of the system. If heat (and often pressure) are maintained, the system will continue to strive to lower its free energy by the process known as grain growth.⁶ Grain growth will continue until a metastable grain boundary array approximating a body-centered-cubic packed array of tetrakaidecahedra occurs. Sintering, densification, and grain growth often are accelerated by the use of additives which may or may not produce a separate grain boundary phase. Even in relatively pure, single-phase ceramics grain boundaries tend to be favored sites for segregation of impurities, porosity, and entrapped gases. Thus, it can be anticipated that grain boundary composition, structure, and processes occurring at grain boundaries can dictate the properties of the ceramic piece.

6. KINGERY, W. D. *Introduction to Ceramics*. John Wiley and Sons, New York, Chapter 12, 1960.

A general flow chart for ceramic processing via the particulate consolidation route is shown in Figure 3. Because of the general hardness associated with structural ceramics such materials can be very difficult to machine. Thus fabrication methods which can reduce or eliminate machining are essential to significantly increase utilization of ceramics as substitute materials. During the past ten years much progress has been made in the areas of reaction sintering, reaction bonding, and injection molding of ceramic preforms to very close tolerances. In particular, perhaps, the most promising advance in ceramic processing technology in the last decade has been the "marriage" of polymer and ceramic processing to produce "green" preforms for the above processes. Injection molding of ceramic-filled polymer preforms has become highly developed in the past few years. We will briefly consider the injection molding process as it applies to reaction-bonded silicon nitride (RBSN), reaction sintered silicon carbide, and conventionally sintered alumina. In the case of injection-molded RBSN, a polymer is filled with silicon metal powder (to as much as 70%),⁷ which is injected at modest temperatures (ca 100 to 200 C) into a die which produces a preform of precise dimensions. This preform is heated slowly (about 300 C), to remove the polymer, then the Si powder preform is carefully placed in a furnace and nitrided in an atmosphere of pure N₂ (ca 1300 to 1450 C) for 24 to 48 hours. The nitridation process of such a Si preform is a remarkable if still somewhat imperfectly understood event. For



there is a 23% expansion in the solid volume compared to Si; yet, when this reaction is carried out on a preform there is essentially no change in dimensions (~0.1%)! The reason for this appears to be that the first Si₃N₄ to form, does

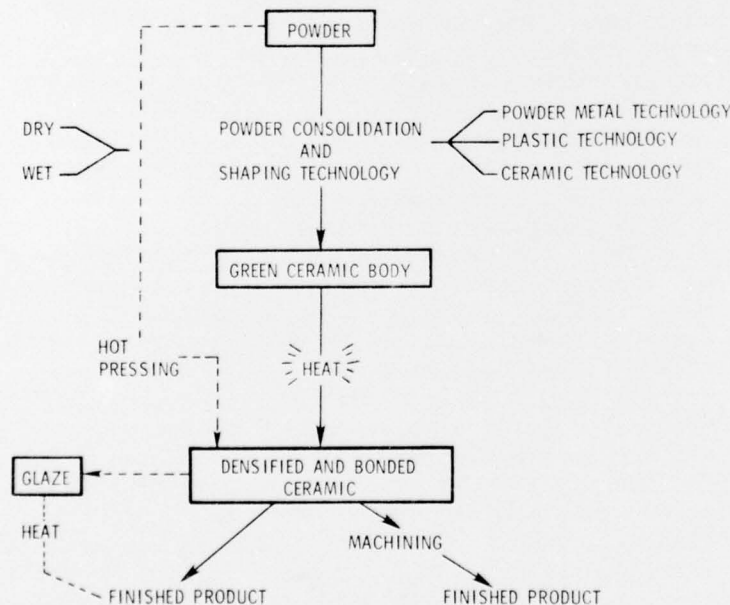


Figure 3. A general flow chart for ceramic processing via the particulate consolidation route.

7. McLEAN, A. F., and DAVIS, D. *The Ceramic Gas Turbine - A Candidate Power Plant for the Middle and Long-Term Future.* SAE Paper 76 02 39, February 1976.

so by a complex solid-liquid-vapor whisker growth into the void space of the Si preform.⁸ The net result is that what appears to be a rather complex series of processing steps, and what is a complex series of chemical reactions, yields a product of great technological import--an engineering ceramic which can be mass produced to tight dimensional tolerances with little or no machining and at low cost.

Reaction-sintered silicon carbide can be formed by a similar process.⁹ Here SiC powder, a polymer, and carbon powder are mixed and molded into a desired shape. The part is then heated to carburize the polymer, and Si metal is "wicked" through the pores reacting with the free carbon to form additional SiC which bonds the material together. The end product is SiC plus a small percentage of free silicon. Such parts show very little shrinkage. Preforms for conventionally sintered ceramics can also be produced by injection molding. Both sintered SiC and Al_2O_3 have been fabricated via this route. Here typical ceramic loading of the polymer is approximately 50 to 60% which leads to about an 18% change in linear dimensions upon firing to nearly full density. These dimensional changes can be accounted for in designing the preform so that the fired part will have the desired dimensions. Figure 4 shows an injection-molded nozzle from the ARPA/Ford small vehicular gas turbine.^{1h} Such stators have been made of both reaction-bonded silicon nitride and reaction-sintered silicon carbide, and each material has demonstrated over 150 hours durability in test rigs operating at 1950 F.

The main point to be made is that not only are high performance structural ceramics well along in development and applications, but the processing technology to make complex engineering shapes via mass production routes which minimize machining is also proceeding apace. This development of a processing technology is essential to create a viable technology base from which ceramics can be exploited as substitute materials in sophisticated engineering applications such as gas turbines.

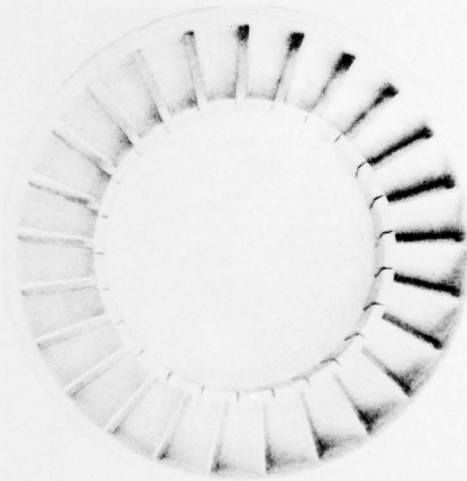


Figure 4. State-of-the-art: injection-molded silicon nitride and silicon carbide stators.

- 8a. PARR, N. L., and MAY, E. R. W. *The Technology and Engineering Applications of Reaction-Bonded Si_3N_4* . Proc. Brit. Ceram. Soc., v. 7, February 1967, p. 81-98.
- 8b. MESSIER, D. R., and WONG, P. *Kinetics of Nitridation of Si Powder Compacts*. Am. Ceram. Soc., v. 56, 1973, p. 480-485.
9. BROWN, W. G., and OLSON, D. L. *Effect of Initial Carbon Content on the Strength of Reaction-Bonded Silicon Carbide*. Ceramic Bulletin, v. 55, no. 3, March 1976, p. 311-312.

CERAMICS IN THE GAS TURBINE

As stated in the Introduction, the primary means of increasing the efficiency of the gas turbine is to increase the turbine inlet temperature (TIT). If it can be increased to about 2500 F using uncooled ceramic hot flow path components, the following advantages accrue:

- Vehicular Turbines (regenerative, all hot flow path components, ceramic): fuel savings of 30% over today's Otto cycle gasoline engine; reduced emissions; multi-fuel capability; and low cost (no superalloys).⁷
- Stationary Engines (uncooled vanes only): operating in combined gas turbine/steam turbine modes one can approach efficiencies of 50% or higher; residual or coal-derivative fuels can be used; dollar per kilowatt savings of 12% (at 2400 F) are predicted.¹⁰

In light of our current energy problems, these are goals certainly worth striving for.

Turbine designers have been intrigued by the possibility of applying ceramics for over 30 years. However, it was not until about seven years ago that we had:

- thermal-shock-resistant ceramics such as Si_3N_4 , SiC, and LAS (glass-ceramics) developed to the point that they could be considered true engineering materials, and
- sufficiently developed analytic capability to handle the complex job of detailing the stress state to the degree required in brittle materials design.

The thermal-shock-resistant ceramics mentioned above are actually families of ceramic materials in much the same sense that steels or brasses are alloy families. An example is shown in Figure 5 where properties of the various members of the silicon nitride materials family are outlined.

The properties of the silicon nitride family of materials, as well as the silicon carbides, satisfy most of the requirements for ceramic turbine components shown in Figure 6. This figure lists two levels of requirements. Those listed in level 1 must be attained if a ceramic can function at all in a turbine, hence they represent the minimum technical requirements. To go from a technical possibility to an engineering possibility the requirements listed in level 2 must be attained. To even begin to assess the potential for achieving the level 2 requirements, as well as to get a better definition of where we stand with respect to level 1 requirements vis-à-vis a real engine, mandates that one take a systems approach and initiate the development of a gas turbine engine based on ceramic technology.¹¹

Based on the favorable projections in the state-of-the-art for both materials and design capabilities, and the need for a systems approach, the Department of Defense's Advanced Research Projects Agency (ARPA) initiated a program in 1971 to

10. ROBSON, F. L., and GIRAMONTI, A. J. *Ceramics for High Performance Applications*. Brook Hill Publishing Company, Chestnut Hill, Massachusetts, Chapter 6, 1974, p. 147.

11. *Structural Ceramics*. National Academy of Sciences, Washington, D. C., NMAB Report 320, 1975.

HOT PRESSED $\text{Si}_3\text{N}_4 + \text{MgO}$ - 110 TO 140 KSI, MOR; $T_{\text{MAX}} < 2400$ F; RELATIVELY HIGH COST
 $\text{Si}_3\text{N}_4 + \text{Y}_2\text{O}_3$ - 130 TO 180 KSI, MOR; $T_{\text{MAX}} > 2500$ F; RELATIVELY HIGH COST

RBSN - ALL PROPERTIES \uparrow (ρ), AS $\rho \uparrow$: MOR \uparrow ; O_2 RESISTANCE \uparrow ; FABRICABILITY \downarrow ;
 COMPLEX SHAPES EASILY PRODUCED WITH LITTLE OR NO MACHINING; LOW COST;
 STRENGTH RANGE: -15 KSI (2.2 G/CC) \rightarrow 40 KSI (2.6 G/CC)

SINTERED - $\text{Si}_3\text{N}_4 + \text{MgO}$; RELATIVELY NEW MATERIAL PROPERTIES WILL PROBABLY BE MIDWAY
 BETWEEN HPSN AND RBSN

ALL FORMS OF Si_3N_4 ARE PROFOUNDLY INFLUENCED BY THE EXISTENCE OF GB PHASES, SOME
 PROPERTIES, i.e., CREEP, ARE DOMINATED BY SUCH PHASES

Figure 5. Silicon nitride: an alloy/processing family of materials.

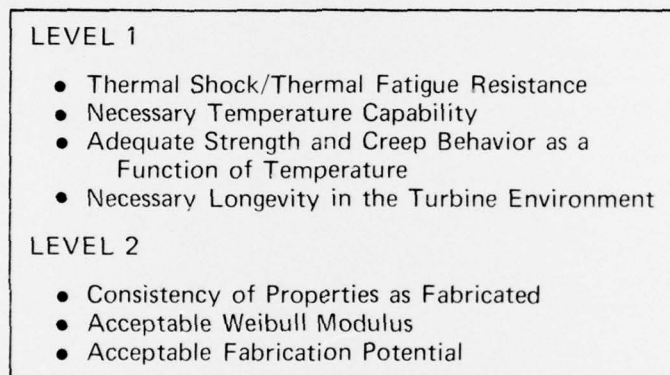


Figure 6. General properties required of ceramics in a gas turbine.

accelerate ongoing work in this area and awarded a contract to the Ford Motor Company with Westinghouse Electric Company as subcontractor to develop a design capability with brittle materials. This design capability was to be demonstrated via the successful application of ceramic hardware in hot flow path components to operate at 2500 F uncooled for 200 hours in a vehicular engine and 100 peaking cycles in an electrical power generating size turbine test rig.

As of today the principal results of the ARPA program include the following:

Vehicular Engine

- All stationary hot flow path components (inlet nose cone with integral transition duct, stators, and shrouds, all of RBSN) have demonstrated at least 100 hours durability in engine testing to 1930 F (using metal turbine wheels). Figure 7 illustrates these components with their demonstrated engine durability times.

MAXIMUM DEMONSTRATED COMPONENT LIFE IN A 1930 F INLET TURBINE ENGINE

March 1975 - Maximum Engine Hours

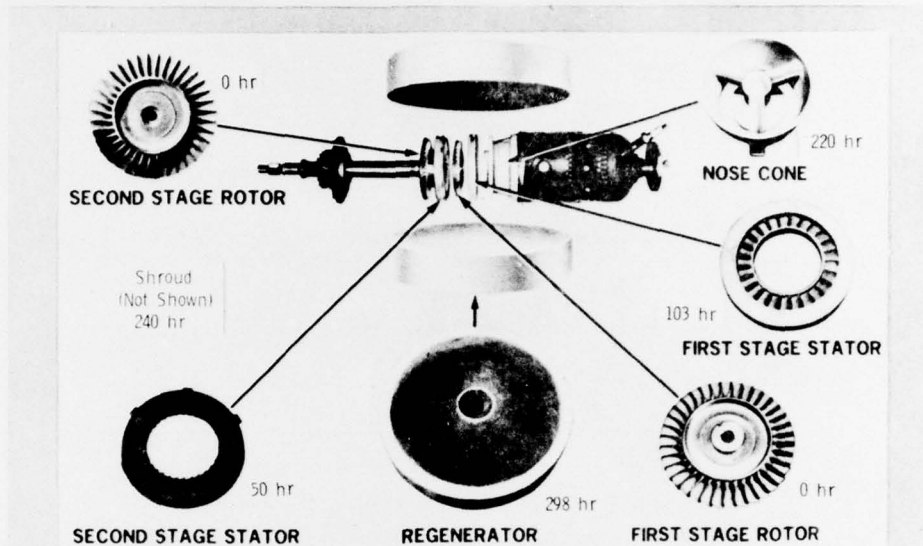


Figure 7. Ceramic hot flow path components.

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- A reaction-sintered silicon carbide combustor has been rig tested for 200 hours over a representative duty cycle including 25 hours at 2500 F.
- Aerodynamically functional ceramic turbine wheels have been fabricated and cold spun with encouraging results.*

Stationary Engine

- Hot-pressed-and-machined silicon nitride vane assemblies have been tested for 106 peaking cycles at 2240 F, including two emergency shutdown simulations. Tests showed hot-pressed Si_3N_4 vanes can survive emergency shutdowns from 2240 F.
- Limited tests at 2500 F have shown mixed results, but clearly indicate that commercially available hot-pressed silicon nitride can survive upwards of 50 peaking cycles at 2500 F.

Together with this impressive progress in design and hardware demonstration we have witnessed major improvements in ceramic materials processing and properties essential to the further utilization of these materials. Much research, development, and demonstration work is still required, however. Some of the general R&D needs include:

*Note added in proof: In March 1977 Ford successfully hot spin tested a 28-bladed duo-density rotor in an engine test rig at 2200 F and 45,000 rpm for 10 hours. The rotor survived and is available for further test.

- Improved high temperature strength materials to allow for rotors and higher reliability stationary components operating at TIT's of 2500 F or higher. Improvements in Si_3N_4 , SiC, and development of new materials are important here.
- Better definition of the long-term response of turbine ceramics to the environment encountered in turbines.
- Improved fabrication and processing techniques leading to assured reproducible high quality materials via low cost techniques.
- Development of adequate quality assurance via nondestructive evaluation and/or proof testing procedures.
- Further improvements in design capability.

While the attainment of the above improvements will require more intensive R&D in all areas of ceramic materials science and engineering, two areas may be singled out for particular attention. These are improved processing capability and ceramic "alloy" design, with particular emphasis on control of grain boundary structure and reactions in the case of the nitrides and carbides of silicon. Some of the recent advances in ceramic processing have already been discussed above, but more work is required in this area to assure that properties obtainable in laboratory specimens can be scaled up in the sizes and quantities required for actual systems application. This requirement for an improved "science of ceramic processing" is becoming increasingly recognized. The second area, that of ceramic alloy design, involves what can be referred to as "grain boundary engineering". Grain boundary engineering can be defined as the deliberate selection and control of composition, structure, and processes occurring in the grain boundary. It is in this area that the author believes there are many potential areas of interaction between the physics and ceramics communities, especially in the characterization of the grain boundary. Characterization of the structure of and reactions occurring in the grain boundary of the nitrides and carbides of silicon represents a particular vexing problem due to the small extent of these boundaries (typically less than 200 Å wide) and the fact that they may be amorphous rather than crystalline. In spite of these problems which are currently limiting grain boundary science, much can be done by grain boundary engineering.

GRAIN BOUNDARY ENGINEERING IN HOT-PRESSED Si_3N_4

State-of-the-art high-strength, hot-pressed silicon nitride (HPSN) has resulted from a series of developments involving: empirical selection of densification aids, control of high temperature strength-limiting reaction products in the grain boundary via a variety of strategies, and selection of new families of densification aids specifically chosen to yield grain boundary phases with improved properties. Thus, the development of hot-pressed silicon nitride provides a textbook case study of grain boundary engineering. The history of this development will now be reviewed.

As the result of an empirical study to obtain a densification aid which would lead to the production of near full density, high-strength HPSN, Deeley

et al.¹² demonstrated that MgO gave superior results over other additives considered. Further optimization of the MgO-Si₃N₄ system was carried out by Lumby and Coe¹³ who showed the significance of using high α -Si₃N₄ powder and the importance of time at temperature during hot pressing on development of strength in the HPSN body. The work of many other investigators in the U.S. and U.K. (especially Prof. K.H. Jack at the University of Newcastle upon Tyne)¹⁴ further characterized the grain boundary phase and its role in the α - β transformation.¹⁵ This latter transformation appears to be required to obtain the highest strength HPSN. A summary of this line of development is presented in Figure 8. While HPSN produced this way had properties which were encouraging for gas turbine application, in-depth studies of creep and high temperature modulus of rupture (MOR) at ~2100 F and beyond indicated that in contrast to RBSN, HPSN had a significant fall-off in properties (as illustrated in Figure 9). Much inferential evidence from auger spectroscopy, TEM, creep behavior, etc., pointed to the MgSiO₃ "glassy" grain boundary phase being responsible for this behavior.

The central problem faced by ceramists was how to find a way to create a more refractory grain boundary. In spite of the experimental difficulties in direct characterization of this grain boundary glass phase (namely, that the small volume percent of this "amorphous" phase in a crystalline matrix is not amenable to X-ray diffraction methods and its small extent rules out microprobe and similar direct techniques) and having to rely on inferential results, significant improvements in HPSN have been made by applying the grain boundary engineering strategies listed in Figure 10.

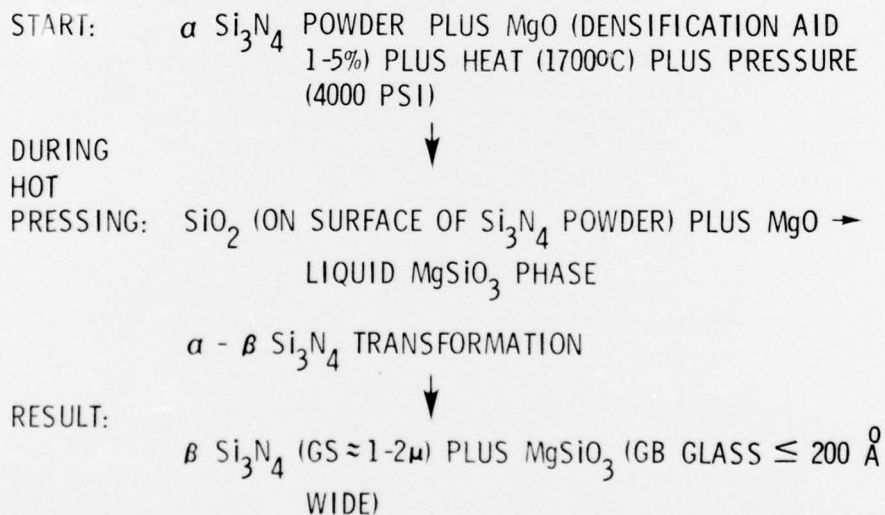
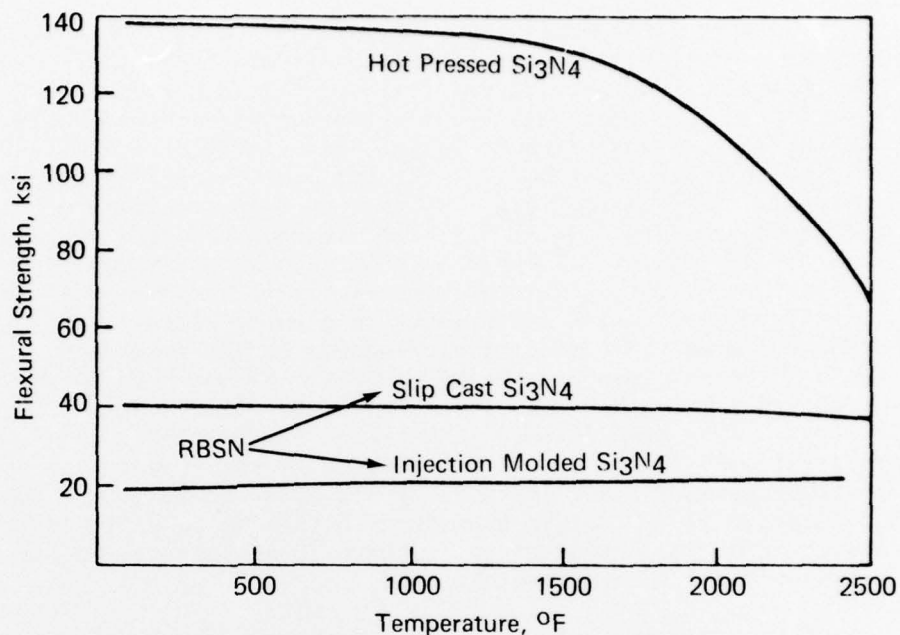


Figure 8. Hot pressing of silicon nitride.

12. DEELEY, G. G., HERBERT, J. M., and MOORE, N. C. *Dense Silicon Nitride*. Powder Metallurgy, no. 8, 1961, p. 145-151.
13. LUMBY, R. J., and COE, R. F. *The Influence of Some Process Variables on the Mechanical Properties of Hot-Pressed Nitride*. Proc. Brit. Ceram. Soc., v. 15, 1970, p. 91-101.
14. JACK, K. H. *Ceramics for High Performance Applications*. Brook Hill Publishing Company, Chestnut Hill, Massachusetts, Chapter 14, 1974, p. 265.
15. DREW, P., and LEWIS, M. H. *The Microstructures of Silicon Nitride Ceramics During Hot-Pressing Transformations*. J. Mater. Sci., v. 9, 1974, p. 261-269.

Figure 9. Flexural strength of HPSN compared to RBSN.



STRATEGIES TO INCREASE THE HIGH-TEMPERATURE BEHAVIOR OF HOT-PRESSED Si₃N₄

1. Reduce Ca, Na, etc., impurities to make the grain boundary MgSiO₃ glass more refractory.
2. Develop a densification aid to yield a more refractory glass than MgSiO₃.
3. Develop a nonglass grain boundary.
4. Eliminate the grain boundary phase by promoting sintering via volume diffusion.

Figure 10.

The reduction of impurities which cause the grain boundary glass to soften at lower temperatures than would otherwise be the case was investigated by Lange¹⁶ and Kossowsky¹⁷ at Westinghouse and Richerson¹⁸ at the Norton Company. This approach was successful in improving the situation but two problems remained. First, the levels of Ca, Na, and other alkali and alkaline earth elements (which were shown to be the main problem) would have to be controlled very tightly in production, hence, increasing costs. Secondly, even pure MgSiO₃ is strength-limiting at about 2400 F.

16. LANGE, F. F., and ISKOE, J. L. *Ceramics for High Performance Applications*. Brook Hill Publishing Company, Chestnut Hill, Massachusetts, Chapter 11, 1974, p. 223.
17. KOSSOWSKY, R. *The Microstructure of Hot-Pressed Silicon-Nitride*. *J. Mater. Sci.*, v. 8, 1973, p. 1603-1615.
18. RICHERSON, D. W. *Effect of Impurities on the High Temperature Properties of Hot-Pressed Silicon Nitride*. *Bull. Am. Ceram. Soc.*, v. 52, no. 7, July 1973, p. 560-562.

The next development was undertaken by Gazza¹⁹ at AMMRC, who reasoned that $Y_2O_3 \cdot SiO_2$ glasses and compounds would be more refractory than $MgO \cdot SiO_2$ glasses or compounds. Further, it was reasoned that due to a larger ionic radius of the Y cation as opposed to Mg, the Y would be prone to remain in the grain boundary and not diffuse away from it as has been observed with Mg. This would contribute to high temperature stability. It was also thought that it might be possible to devitrify the $Y_2O_3 \cdot SiO_2$ glass phases and form crystalline yttrium silicates in the grain boundary. As it has been subsequently shown by Prof. Jack and his students,²⁰ yttrium silicates in the grain boundary may form yttrium silicon oxynitrides which can accommodate relatively large amounts of Ca and other impurity cations which are present in commercial purity Si_3N_4 powder. Thus, Y_2O_3 appeared to be an attractive alternative to MgO as a densification aid to improve the high temperature properties of HPSN. As shown in Figure 11, the predicted improvement using Y_2O_3 has been borne out. Similar improvements in creep behavior at 1400 C have been noted.^{1h} Much work remains to be done on the Y_2O_3 additive material and if care is not taken to be in the proper area of the $Y_2O_3-SiO_2-Si_3N_4$ phase diagram, a phase instability can occur at 1000 C.²¹ Nevertheless, the development of $Y_2O_3-Si_3N_4$ represents both a successful materials development and a successful case study of grain boundary engineering and as such can serve as a paradigm for future developments.

An alternative solution to the problem would be to eliminate the grain boundary phase altogether. However, to do so requires the promotion of true sinterability, via volume diffusion, in Si_3N_4 powders. While various teams are pursuing research to this end, no one has yet achieved the goal. However, they

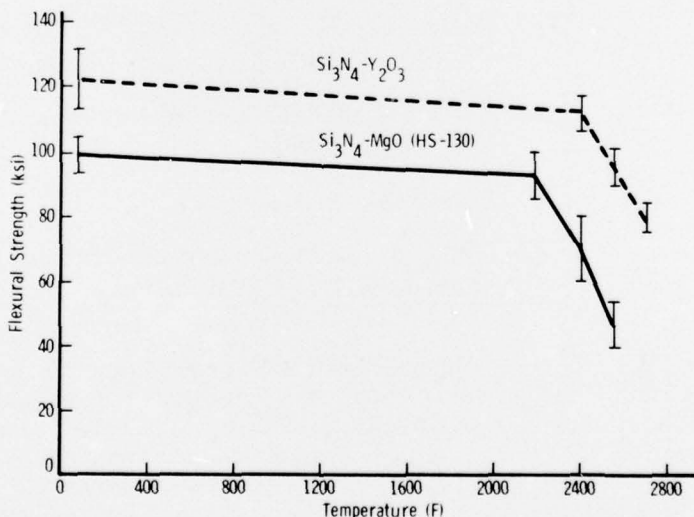


Figure 11. Strength versus temperature for $Si_3N_4 + Y_2O_3$ versus $Si_3N_4 + MgO$.

19. GAZZA, G. E. *Hot-Pressed Si_3N_4* . J. Am. Ceram. Soc., v. 56, no. 12, 1973, p. 662.

20. RAE, A. W. J. M., THOMPSON, D. P., PIPKIN, M. J., and JACK, K. H. *Special Ceramics 6*. The British Ceramic Research Association, 1975, p. 347-360.

21. LANGE, F. F., personal communication.

have been greatly encouraged by the recent achievements of Prochazka²² in promoting the sintering of SiC via additions which enhance volume diffusion. What is possible in SiC may very likely also be possible in Si₃N₄.

GRAIN BOUNDARY ENGINEERING IN HIGH ENERGY LASER WINDOW MATERIALS

High-power lasers may profoundly influence future materials selection and materials substitution considerations in the energy conversion area if laser-induced fusion becomes a reality. Assuming chemical lasers are used, then the availability of suitable laser windows can be one of the major system-limiting factors. Much attention has recently been focused on high energy laser windows.²³ The problem is that the best materials from an optical standpoint (i.e., those having a low value of absorption coefficient β) are generally single crystals of materials having rather poor mechanical properties. On the other hand, materials which are superior mechanically (generally polycrystalline ceramic materials) have rather poor optical properties. The degradation of optical properties associated with the presence of grain boundaries is not necessarily an intrinsic characteristic of the grain boundary (at least not for optically isotropic, crystal systems). This degradation is usually thought to result from extrinsic factors, such as porosity or impurity segregation at the grain boundary. As described earlier in this paper, conventional powder processing technology methods frequently result in such porosity or impurities being introduced into the system and subsequently segregated at the grain boundary. Several groups have been attempting to produce "clean" or intrinsic grain boundaries in such optically isotropic materials as the alkali and alkaline earth halides.

One exciting avenue of development has been to start with a single crystal, deform it, thereby introducing strain centers (i.e., tangles of dislocations), and then annealing until the dislocations form networks and eventually become grain boundaries. This process, called press forging, is shown schematically in Figure 12. Recent Air Force-sponsored work²⁴ has demonstrated that press forging

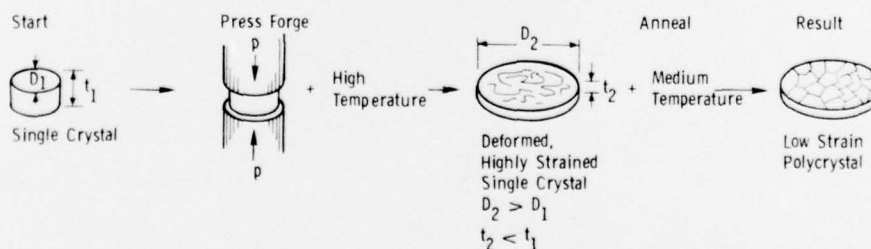


Figure 12. Press forging of single crystals.

22. PROCHAZKA, S. *Ceramics for High Performance Applications*. Brook Hill Publishing Company, Chestnut Hill, Massachusetts, Chapter 12, 1974, p. 239.
23. *High-Power Infrared-Laser Windows*. National Academy of Sciences-National Academy of Engineering, Washington, D. C., NMAB Report 292, 1972.
24. HARRISON, W. B. *Halide Material Processing for High-Power, Infrared Laser Windows*. Air Force Materials Laboratory, AFML-TR-75-109, July 1975, p. 210.

a single crystal of a KCl-KBr alloy significantly increased strength with very little effect on the absorption coefficient. The strength in one case for a press-forged polycrystal was ~5800 psi compared to ~1400 psi for the single crystal, whereas the absorption coefficient was only $3.4 \times 10^{-3} \text{ cm}^{-1}$ for the polycrystalline material compared to $3.14 \times 10^{-3} \text{ cm}^{-1}$ for the single crystal (at $10.6 \text{ } \mu\text{m}$).

Thus, we have a case where benign, essentially intrinsic grain boundaries can be produced for optical purposes, while at the same time fulfilling the traditional role of grain boundaries by exerting a strong influence on mechanical strength.

CONCLUSIONS

The abundance, low cost, and unique mechanical and physical properties of ceramics place them at the forefront of candidate materials for resource substitution and conservation.

While the role of ceramics will undoubtedly grow in importance and more sophisticated use for many of the applications cited in Figure 2, the author believes that the main application of ceramics as substitute materials will be dictated by their high temperature structural and unique optical properties. The paper has stressed the importance of ceramic fabrication in both providing the economic basis necessary to exploit ceramics as substitute materials, and in determining the microstructure and hence the behavior and performance of the materials. In the latter areas, as an example, we have focused upon "grain boundary engineering" in gas turbine and laser window ceramics.

Through advances in both design with and of ceramic materials as discussed above, ceramics will continue to serve society by both conservation of scarce resources and, more importantly, by offering the potential for increased systems performance in many areas.

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