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GELCASTING OF SILICON PREFORMS FOR THE PRODUCTION
OF SINTERED REACTION-BONDED SILICON NITRIDE

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Abstract

Gelcasting of silicon metal for the production of sintered reaction-bonded silicon nitride (SRBSN) was investigated in order to identify associated advantages over conventional forming techniques, i.e., die and isostatic pressing. Compacts were formed from identical powder mixtures by both gelcasting and pressing, and were nitrided and sintered to produce SRBSN ceramics using both conventional and microwave heating. Characterization of the samples included measurement of green density, green and nitrided pore structure, weight gain during nitridation, final density, microstructure, toughness, and flexural strength. It was found that a more uniform pore structure existed in the green gelcast samples. It is believed that this pore configuration aided in nitridation, and manifested itself in a more uniform final microstructure. In addition, improved mechanical properties were achieved in the gelcast samples. This improvement can be attributed to green microstructure homogeneity. An additional finding of this study was that microwave heating combined with gelcast forming resulted in SRBSN materials with improved mechanical properties.

Introduction

Silicon nitride-based materials are the leading candidates for use as high-temperature structural ceramics due to their excellent overall combination of mechanical and physical properties [1]. These materials are of interest in numerous applications for such diverse items as cutting tools, rotors for turbine engines, and valves and cam followers for gasoline and diesel engines. Significant progress has been made in recent years in producing silicon nitride materials with superior strength, fracture toughness, and creep resistance. However, these materials tend to be prohibitively expensive due to the high cost of the silicon nitride powders used to produce them. Reduction of cost has been recognized as a major need for the successful introduction of silicon nitride ceramics into the marketplace [2,3,4].

SRBSN is an attractive alternative to sintered silicon nitride for a number of reasons [5,6]. Silicon is economical compared to high purity silicon nitride powders and is more easily formed into shapes than silicon nitride powders. Also, silicon preforms undergo less sintering shrinkage than preforms made of silicon nitride powders. However presently, silicon preforms of complex shapes must be made by expensive cumbersome forming processes, such as injection molding. The door is open for inexpensive forming processes for making these silicon preforms.

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Gelcasting is a simple, inexpensive forming process which has been developed as a method for forming ceramic greenware. Gelcasting involves the preparation of a ceramic slip in a mixed monomer solution. After preparation of the slip, a combination of initiator and catalyst is added to polymerize and cross-link the monomers upon heating. Previous to this heating, the slip is poured into molds of potentially complex geometry, whose shape the final gel will assume. Numerous combinations of monomers, catalysts, and initiators have been developed for use with both aqueous and organic solvent systems as dictated by the ceramic powder being gelcast [7,8,9]. Also, it has been shown that gelcast preforms of alumina have up to five times the mechanical strength of die pressed green bodies of comparable volumes loading [10].

The present work was undertaken to develop a method for the fabrication of gelcast silicon preforms. It is felt that the excellent uniformity and dispersion that is achievable in liquid suspension can be frozen into the gelcast compact. It is also believed that this method will enable the formation of complex green bodies of high green strength. In addition, the present study was conducted to investigate the use of microwave heating for the nitridation and sintering of the gelcast silicon preforms. Previous studies have shown that microwave heating results in improved mechanical properties in the final SRBSN product [11,12].

Experimental

A Si metal based powder mixture designated TM-145 was used for this study. This composition consists of the following chemicals:

67 wt % Si-metal, Elkem metallurgical grade
13 wt % Y_2O_3 , Molycorp-5600
4 wt % Al_2O_3 , RCHP-DBM
14 wt % Si_3N_4 , Stark LCION
2 wt % SiO_2 , U.S. Silica-5 micron

The powder mixture was turbomilled for ~2 hours with 4 mm Si_3N_4 media in isopropanol (IPA) containing 0.5 wt % Darvan-C and 0.5 wt % PVP-K15 as dispersants, and using 4 mm Si_3N_4 media. After milling, the powder was dried and sieved through a 100 mesh screen.

100 g portions of the pre-milled TM-145 powder mixture were initially die pressed in stainless steel cylindrical dies using stearic acid in acetone as a mold release agent. After uniaxial pressing at 5 MPa, the samples were then bagged and isopressed at 117 MPa. The pressures for pressing samples were chosen such that the green densities were comparable to those obtained by gelcasting.

The chemical constituents of the gelcasting system have been described in a previous publication [13]. A 500 g portion of the pre-milled TM-145 powder mixture was added to a (IPA) solution containing the gelcast chemicals and milled with 4 mm Si_3N_4 media in a small attritor mill for 30 min. A mixture of catalyst and initiator was then added to induce polymerization and cross-linking. Glass plates separated by 1 cm thick rubber gaskets were used to cast flat plates from 100 g portions of the ceramic slurry. The slips were gelled in a oven at 65°C for approximately one hour. After gelling and cooling to room temperature, the gelcast pieces were dried overnight in a closed dessicator box. Some of the gelcast pieces were then isopressed at 103 MPa.

All samples underwent binder removal in an air furnace to a final condition of 525°C for 1 h. The samples were then nitrided in either a graphite element or a custom-built 2.45 GHz multimode microwave furnace. Sample crucibles and conditions for the nitridation and sintering have been discussed in previous publications [11,12].

The weight gain values for nitridation of the samples processed by microwave heating were measured after the single-step nitridation and sintering treatment. Weight gains for nitridation of the samples processed by heating in a graphite furnace were made after the nitridation step. Densities of sintered pieces were determined using the Archimedes method. The pore structure of

the green and nitrided samples was measured using a Micromeritics AutoPore II 9220 mercury porosimeter. The final microstructure of both fracture surfaces and polished plasma etched surfaces of selected sintered samples were viewed with a Hitachi S-800 SEM. 3 mm by 4 mm by 45 mm size specimens were machined from sintered samples for mechanical properties measurements. Flexural strength testing was done by four point bending with inner and outer spans of 20 mm and 40 mm, respectively. Fracture toughness values were measured using Chantikul's method of four point bending of specimens indented with a Vickers indenter at a 10 kg load [14].

Results and Discussion

Table 1 lists the sample abbreviations, including a description of the forming method and furnace type used for processing, which are used in the graphs and tables.

Table 1. Sample Description

| Forming Process | Furnace Type | Designation |
|------------------------|------------------|-------------|
| Die and Isopressed | Microwave | DI-MW |
| Die and Isopressed | Graphite element | DI-GE |
| Gelcast | Graphite element | G-GE |
| Gelcast and Isopressed | Microwave | GI-MW |
| Gelcast and Isopressed | Graphite element | GI-GE |

Measured values of green density, weight gain during nitridation, and sintered density are given in Table 2. The weight gain data indicates that the level of nitridation appears to be independent of the forming process. The lower values weight gains observed in the microwave processed samples are due to weight losses during sintering. The theoretical maximum weight gain is 66 wt %, however values approaching 60 wt % are taken to signify near complete nitridation, since weight losses occur during the sintering step [15]. Similarly, there appears to be no relationship between the final sintered densities and the green densities of the materials. A density of 3.3 g/cm³ was calculated to be the theoretical density.

Table 2. General Properties

| Sample Type | Green Density % T.D. | Weight Gain During Nitridation | Sintered Density % T.D. |
|-------------|----------------------|--------------------------------|-------------------------|
| DI-MW | 57.0 | 57.0 | 97.4 |
| DI-GE | 57.0 | 60.0 | 98.4 |
| G-GE | 56.3 | 59.5 | 98.5 |
| GI-MW | 60.5 | 58.8 | 98.0 |
| GI-GE | 60.4 | 60.7 | 99.1 |

Three green body samples, one formed by die pressing and isopressing, one by gelcasting and isopressing, and one by gelcasting alone, were analyzed by mercury porosimetry. Figures 1 and 2 demonstrate the incremental and cumulative pore areas as a function of pore diameter. These plots show two significant populations of pores in the green samples. The populations of the smallest diameter pores are thought to be a result of sample compression at very large mercury pressures, hence will be ignored. The pore populations at higher pore diameters demonstrate that the gelcast sample had the largest pores and the narrowest pore size distribution, furthermore; the die and isopressed sample had the smallest pores and the widest size distribution. Uniform packing of the fine particles in the gelcast suspension would be expected to produce a green compact with pores of a narrow distribution. Conversely, the presence of agglomerates in the dried and sieved powder mixture would account for a broader pore size distribution.

No distinct differences were seen in the mercury porosimetry data from the analyses performed on samples following nitridation (data not shown). The filling of pores which occurs during the nitridation process appears to mask the differences that are present in the green compacts.

Figures 3 and 4 give the values of strength and toughness, respectively, for SRBSN samples formed and processed as indicated in Table 1. These results show that the flexure strengths of all die pressed samples were lower than the two types of gelcast samples, irrespective of heating method. Also, these results show that the gelcast-isopressed sample processed by microwave heating had a higher strength than gelcast-isopressed material processed by conventional heating. However, the die pressed-isopressed sample processed by microwave heating showed the reverse result. The lower strength of the die pressed, microwave processed material may be due to a general observation made in several experiments that microwave radiation can preferentially heat flawed areas within samples, with resulting negative effects. Microwave heating of both die pressed-isopressed and gelcast-isopressed samples gave slight improvements in the toughness values, as compared to conventional heating of both of these sample types.

SEM photomicrographs of polished and plasma etched surfaces of selected sintered SRBSN materials are shown in Fig. 5. The grain structure of both die pressed-isopressed and gelcast-isopressed materials which were processed in the microwave furnace contain numerous large acicular grains. The gelcast-isopressed and the die pressed-isopressed materials which were processed in the graphite furnace appear to have fewer acicular grains, and these grains have a smaller aspect ratio than microwave processed materials. The slightly larger toughness values of the microwave processed materials (Fig. 4) are probably due to these microstructure differences.

Conclusions

A method has been developed for gelcasting silicon metal and sintering aids into green preforms for the production of SRBSN. This gelcasting method was shown to be superior to a traditional die press forming process. The dispersion and uniformity that is regularly achievable in liquid suspensions of ceramic powders can be preserved in a solid compact through the gelcasting route. This preservation leads to uniform pore structure, which is especially important in the reaction bonding of Si metal, where infiltration of nitrogen gas is crucial. The uniformity of the green and nitrided pieces is then found in the sintered SRBSN ceramics.

In addition, this study reinforces similar studies which have shown that microwave heating can be used to fabricate SRBSN materials with superior strength and toughness, compared to those produced using conventional heating techniques. This superior strength and toughness of the SRBSN materials is due to the increased numbers of acicular silicon nitride grains.

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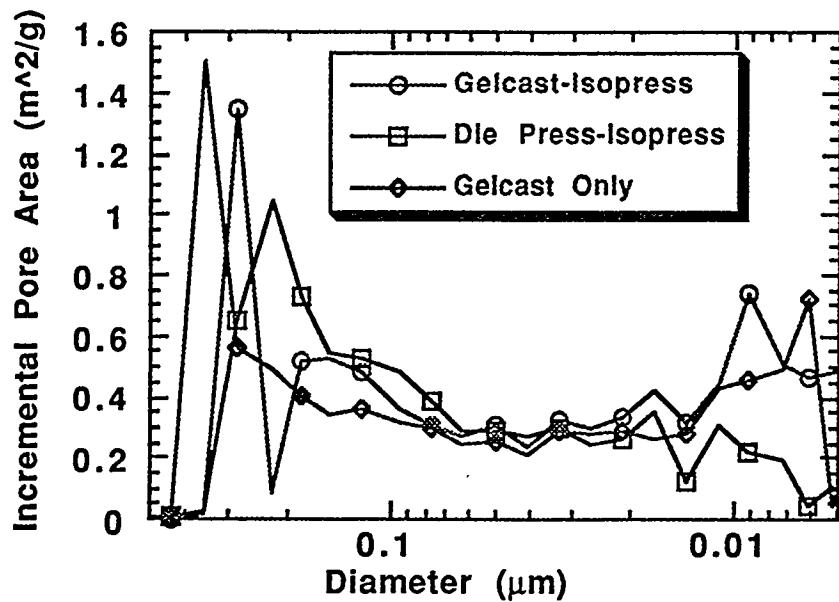


Figure 1. Incremental pore area as a function of pore diameter for green body compacts formed by die press-isopress, gelcast only, and gelcast-isopress methods.

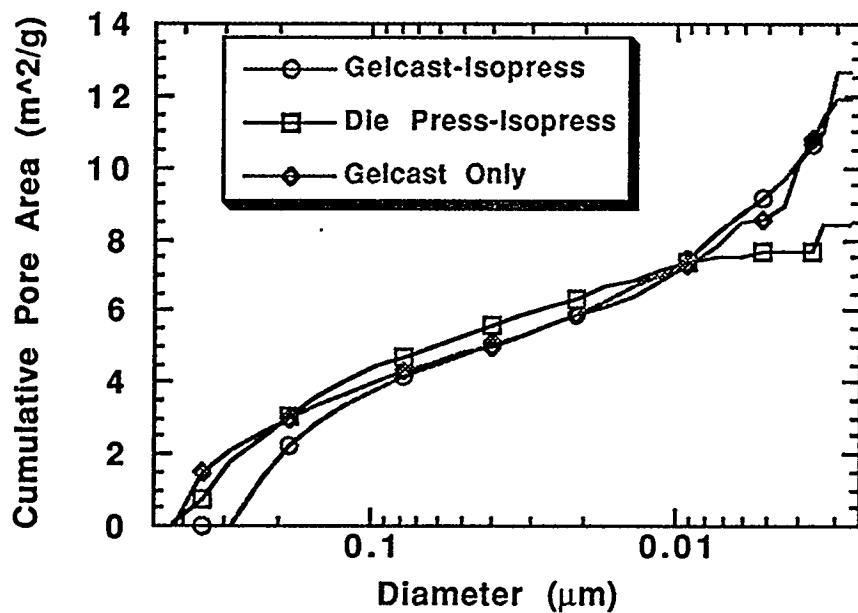


Figure 2. Cumulative pore area as a function of pore diameter for green body compacts formed by die press-isopress, gelcast only, and gelcast-isopress methods.

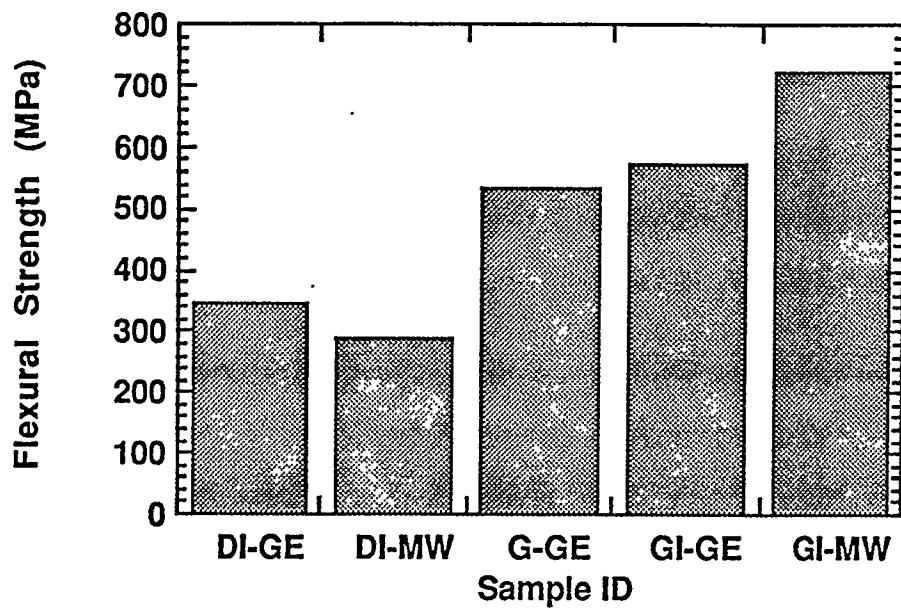


Figure 3. Strength values for sintered SRBSN materials processed in graphite element and microwave furnaces for samples defined in Table 1.

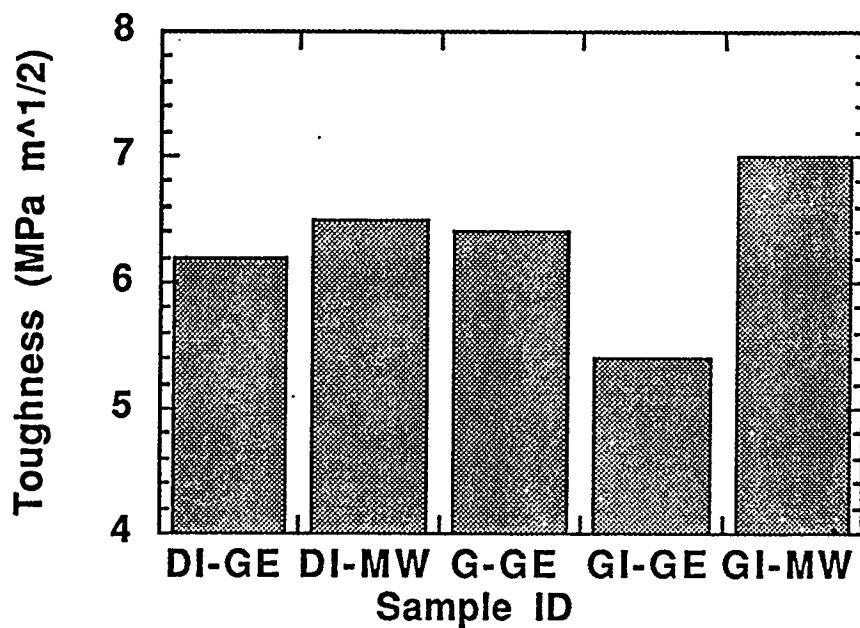


Figure 4. Toughness values for sintered SRBSN materials processed in graphite and microwave furnaces for samples defined in Table 1.

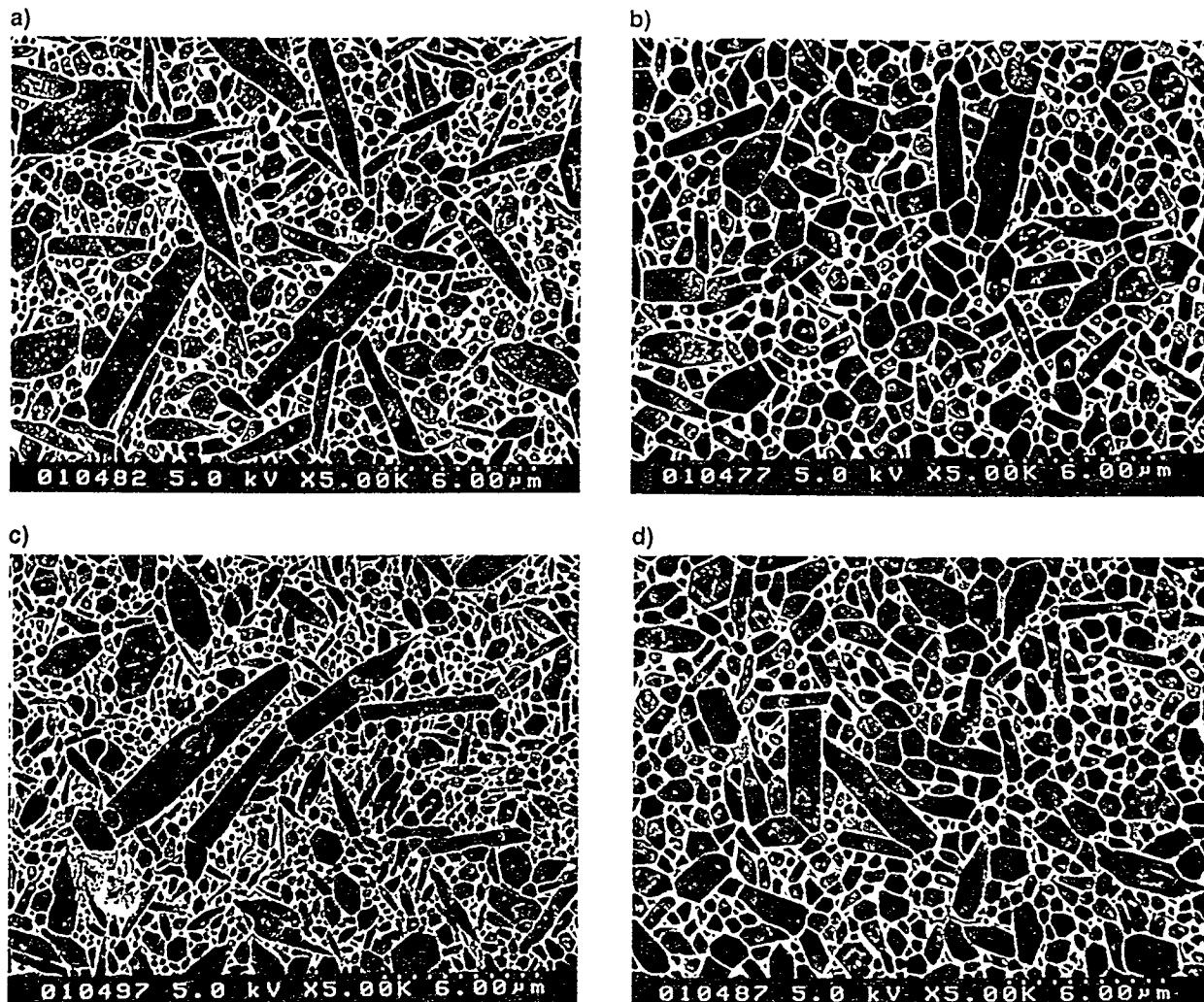


Figure 5. SEM photomicrographs showing the microstructure of SRBSN materials produced from preforms which were a) die pressed-isopressed and processed in a microwave furnace, b) die pressed-isopressed and processed in a graphite furnace, c) gelcast-isopressed and processed in a microwave furnace, and d) gelcast-isopressed and processed in a graphite furnace.

References

1. R. N. Katz, Nitrogen Ceramics 1976-1981, pp. 3-20 in *Progress in Nitrogen Ceramics*, ed. F. L. Riley, Martinus Nijhoff Pub., The Hague, Netherlands (1983).
2. L. M. Sheppard, "Cost-Effective Manufacturing of Advanced Ceramics," *Am. Ceram. Soc. Bull.*, 70[4]692-707(1991).
3. T. Quadir, R. W. Rice, J. C. Chakraverty, J. A. Breindel, and C. C. Wu, "Development of Lower Cost Si_3N_4 ," *Ceram. Eng. Sci. Proc.*, 12[9-10], 1952-1957 (1991).
4. J. M. Schoenung, "Analysis of the Economics of Silicon Nitride Powder Production," *Am. Ceram. Soc. Bull.*, 70 [1] 112-116 (1991).
5. A. J. Moulson, "Reaction-Bonded Silicon Nitride: Its Formation and Properties," *J. Mater. Sci.*, Vol. 14, pp. 1017-1051 (1979).
6. F. L. Riley, "Nitridation and Reaction Bonding," pp. 265-288 in *Nitrogen Ceramics*, F. L. Riley (ed.), Noordhoff, Netherlands (1977).
7. O. O. Omatete, M. A. Janney, and R. A. Strehlow, "Gelcasting-A New Ceramic Forming Process," *Ceramic Bulletin*, 70 [10], Oct. 1991.
8. M. A. Janney and O. O. Omatete, "Method for Forming Ceramic Powders into Complex Shapes," U. S. Patent No.4,894,194, Jan. 16, 1990.
9. M. A. Janney and O. O. Omatete, "Method for Molding Ceramic Powders using Water-Based Gelcasting," U. S. Patent No. 5,028,362, July 2, 1991.
10. S. D. Nunn, O. O. Omatete, C. A. Walls, and D. L. Barker, "Tensile Strength of Dried Gelcast Green Bodies," *Ceram. Sci. & Engr. Proceed.*, 15, [4]. 493-8, 1994.
11. J. O. Kiggans, C. R. Hubbard, R. R. Steele, H. D. Kimrey, C. E. Holcombe, and T. N. Tiegs, "Characterization of Silicon Nitride Synthesized By Microwave Heating," in *Ceramic Transactions, Microwaves, Theory, and Applications in Materials Processing*, Am. Cer. Soc., Westerville, Ohio, 267-272 (1991).
12. J. O. Kiggans and T. N. Tiegs, "Characterization of Sintered Reaction Bonded Silicon Nitride Processed By Microwave Heating," pp. 285-290 in *Microwave Processing of Materials-III*, Vol. 269, Materials Research Soc., Pittsburgh, PA 1992.
13. O. O. Omatete, J. P. Pollinger, and K. O'Young, "Optimization of the Gelcasting of Silicon Nitride Formulation," to be published in the Proc. of the 19th Annual Cocoa Beach Conf., Jan. 12, 1995.
14. P. Chantikul, G. R. Anstis, B. R. Lawn, and D. B. Marshall, "A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: II, Strength Method," in *Jour. Amer. Ceram. Soc.*, 58 539-544 (1981).
15. B. F. Jones and M. W. Lindley, "Strength, Density, Nitrogen Weight Gain Relationships for Reaction Sintered Silicon Nitride, *J. Mater. Sci.*, Vol. 10, pp. 967-972, 1975.