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Forming of Silicon Nitride by Gelcasting\*

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**AUTHORS(S)**  
**(upper and lower case)**

**AFFILIATION(S)**  
**(upper and lower case)**

1. O. O. Omatete

1. Oak Ridge National Laboratory

P.O. Box 2008, Oak Ridge, TN 37831-6069

2. R. A. Strehlow

2. Oak Ridge National Laboratory

P.O. Box 2008, Oak Ridge, TN 37831-6088

3. B. L. Armstrong

3. Allied-Signal Aerospace Company

Garrett Ceramic Components Division  
19800 South Van Ness Avenue, Torrance,  
CA 90509

4. \_\_\_\_\_

4. \_\_\_\_\_

5. \_\_\_\_\_

5. \_\_\_\_\_

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## ABSTRACT

Gelcasting is a near-net-shape forming technique that is applicable to various types of powders. It is accomplished by casting a concentrated suspension of a commercial ceramic powder in a solution of a polymerizable monomer and then polymerizing. The monomer used in the process is acrylamide which undergoes a vinyl polymerization. A filled gel is formed, which is dried and processed further. Gelcasting of alumina, sialon and silicon nitride has been carried out as the principal part of the Oak Ridge National Laboratory (ORNL) program. Two rotors have been gelcast as part of a cooperative research agreement between Allied-Signal Aerospace Company and ORNL. Emphasis is placed on the unit-operations of the process. Because a requirement of the process is a castable suspension of more than 50 vol % solids loading, good dispersion is crucial. Drying, another key process, has been studied extensively. Data on the relationship of physical properties of products to some of the more significant processing variables is discussed. Environmental, safety and hygiene issues are summarized.

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## INTRODUCTION

The technique of gelcasting is based on a synthesis of ideas borrowed from traditional ceramics and from polymer chemistry(1). Unlike sol-gel forming in which the ceramic material is made during the processing, in gelcasting a suspension of commercially available ceramic powder in an aqueous solution of organic monomers is cast. After casting, the solution is polymerized to form a strong, crosslinked, polymer-water gel filled with the ceramic powder.

The monomer solution is a low viscosity vehicle. By undergoing polymerization, a mechanism is provided for permanently immobilizing the ceramic powder in the desired cast shape. Drying is readily accomplished and yields a dried part containing only about 3 wt % polymer compared to about 30 wt % in injection molding. This permits easy removal of the organic compound.

The technical objective of this work is to develop a practicable forming process that can be controlled to produce very high reliability engineering ceramics. Gelcasting was chosen for development because it:

1. was a generic process, potentially useful for silicon nitride,
2. could use commercially available powders,
3. was a near-net-shape process, and
4. used readily available equipment, thus requiring a minimum departure from conventional manufacturing practice.

In the course of this work an additional attractive feature of the process was found in that the dried parts can be readily and inexpensively machined, thereby increasing the range of potential applications.

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Several key considerations are required for ultimate commercial application of the process. They include attention to:

1. practicality;
2. environmental, safety, and hygiene aspects;
3. economic and market factors; and
4. development or application of in-process tests for quality control.

These varied emphases determine the range of work undertaken in the Advanced Ceramic Processing Program, including concentration on all of the unit operations of the process.

## PROGRAM PLAN

Uniaxial tensile strength was chosen as the principal dependent variable. The principal fabrication parameters serve as independent experimental variables. The key events in the development work were:

1. to design a tensile test specimen,
2. to analyze environmental, safety, and hygiene issues,
3. to develop the process and demonstrate the experimental technique for alumina, because many of the issues could be resolved with this easier to use ceramic,
4. to apply the method to silicon nitride, and
5. to begin a systematic application of the method to optimize the process steps for silicon nitride, including composition and sintering schedule variables in addition to other processing variables.

A cooperative research agreement to advance the work was made between ORNL and Allied-Signal Aerospace Company, Garrett Ceramic Components (GCC) Division, as follows:

1. GCC is to supply the material and instructions for casting their proprietary GN-10 formulation and a number of molds to cast the T-25 rotors.
2. ORNL is to supply the information on the gelcasting process for GCC's experimental use and also casts specimens for tensile testing along with a number of the rotors.
3. Both laboratories will evaluate the gelcast products independently.

## TENSILE TEST SPECIMEN DESIGN

Tensile test specimens were required that would be simple and economical to fabricate and provide a statistically adequate number of samples. A desired feature was to have a large volume under maximum stress. To meet these requirements a design was

selected that made use of glued end pieces on a square cross section bar with chamfered edges. The plate dimensions are shown in Fig. 1 and the cutting pattern for specimens in Fig. 2.

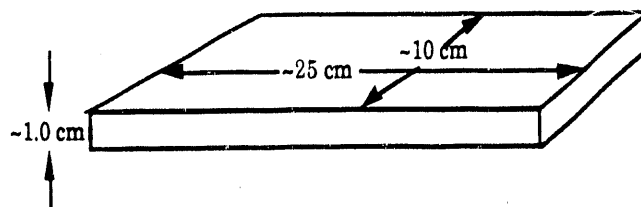


Fig. 1. Plate dimensions for tensile test specimens.

	A	B
Top	8	8
	7	7
	6	6
	5	5
	4	4
	3	3
	2	2
Bottom	1	1

16 specimens per plate  
0.6 cm square cross section  
approx 8 cm long.

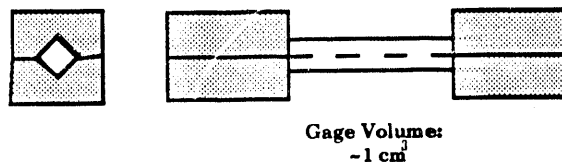


Fig. 2. Typical cutting pattern and sketch of tensile specimens for gelcasting studies.

## PROCESS FLOW CHART

Figure 3 displays the unit operations of the gelcasting process. Several are common to many processing methods and are treated here briefly. The significant unit operations for successful application of gelcasting to the processing of sub-micron ceramic powders are *dispersion*, *casting*, and *drying*. Steps unique to gelcasting include initiator addition, catalysis, and heating to polymerize the monomer. These steps, however, do not present unusual difficulty in processing advanced powders, and they are not considered in detail.

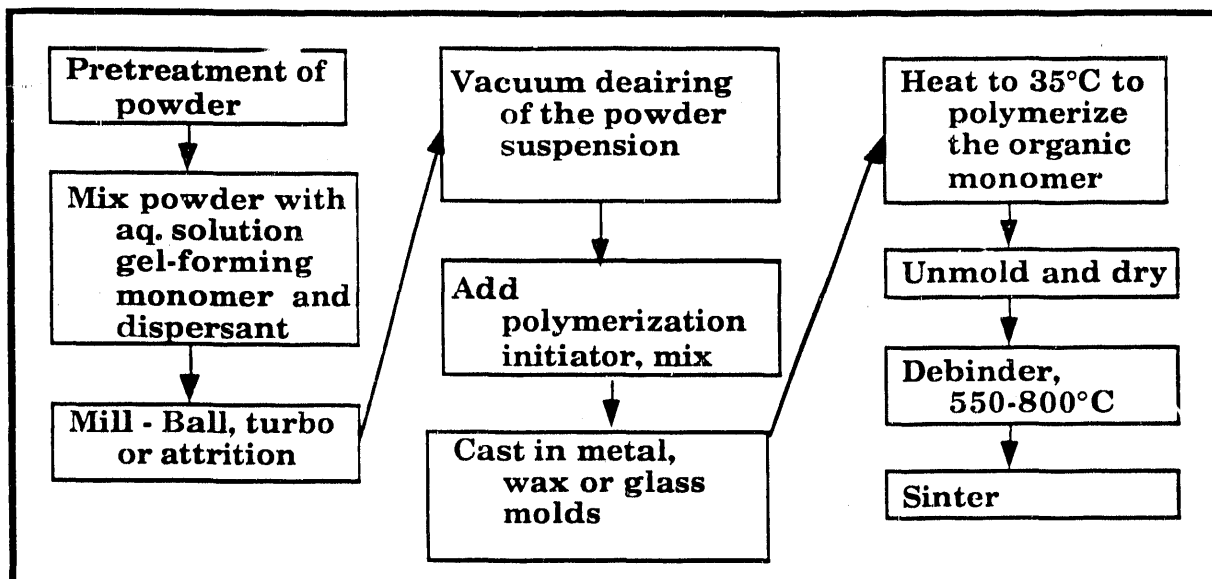


Fig. 3. The flow chart for the gelcasting process.

**PRETREATMENT** – Powders may be pretreated by calcination or chemical reaction.

**DISPERSION** – The requirement of high solids loading for gelcasting was especially troublesome for silicon nitride because of the difficulty of dispersing it adequately. The key requirements that were addressed in the work reported here are for a castable suspension with at least 50 vol % solids and characterized drying conditions that will avoid significant deformation of cast products.

An absolute requirement of the gelcasting process is a high concentration of powder in a castable suspension. This requirement is necessary to minimize the shrinkage during the drying step. Somewhat arbitrarily, we specified that a minimum loading of 50 vol % is needed for successful gelcasting. Alumina dispersions are typically made using protracted mechanical shaking and then final ball-milling to form suspensions of 56 to 63 vol %. However, when applied to silicon nitride the method was not successful. Silicon nitride forms mixtures with high dilatancy, making it difficult to cast the suspension.

After testing a variety of powders(2) and dispersants, using several basic techniques, it was found possible to produce powder loadings in the desired range. The most successful approach was to use high shear at a low solids content (25 vol %) and to slowly add more powder while applying continuing high shear.

Using ORNL formulations based on Denka 9S powder, 16 plates for tensile testing were cast and are in various stages of processing. The formulation

initially had a large amount of the sintering aids, yttrium oxide and alumina.

Some earlier gelcast silicon nitride specimens have been tensile tested. The strengths were inadequate because of insufficient milling of the sintering aids. Later preparations are believed to be much improved, but have not yet been tested. In addition, approximately 12 sialon plates have been cast and are either in process or have been processed through to a sintered body. In the course of this work, a set of preparations was made following the work of Hoffman, et al.(3) In these preparations, a suspension containing 48 vol % was successfully prepared, mixed, and cast using Starck LC-12SX powder that had been oxidized in accordance with the reported work.

The silicon nitride powder Grade UBESN-E10 presented a unique difficulty in dispersion studies. Initially, UBESN-E10 silicon nitride suspensions were prepared at volumetric concentrations of about 40% and then concentrated using vacuum. Although this led to parts with generally satisfactory appearance, we believe they contained agglomerates that formed during the concentration step. Continuing work(4) has shown that this material is readily amenable to the general processing procedure described above.

**MILLING AND AGGLOMERATE REMOVAL** – Complete dispersion or elimination of hard agglomerates is required for advanced ceramic materials. Ultrasonication causes premature polymerization and, therefore, has not been employed in the dispersion procedures. Milling of the suspensions or filtering are needed for the process.

**VACUUM DEAIRING** – A variety of techniques have been applied for deairing. A rotary evaporator and stirring a beaker in a vacuum desiccator using a magnetic stirrer are commonly employed.

**INITIATOR AND CATALYST ADDITION** – The chemistry of the gelcasting process is based now on a water solution of the compound, acrylamide, along with a crosslinking compound N,N'-methylene-bisacrylamide(5). These are sufficiently water soluble that a range of ratios of crosslinker to acrylamide may be used. This permits control of the gel hardness. An ammonium persulfate solution is used as an initiator, along with a catalyst, tetramethylethylenediamine.

When this mixture is heated to about 35°C, polymerization occurs in less than an hour. After adding the initiator and catalyst, the working time for the mixture is limited. The amounts of initiator and catalyst to be used are experimentally determined for each powder formulation.

**CASTING** – Several simple and complex parts have been cast including gears, threaded units, rods, plates and other forms. As part of the cooperative research agreement, two rotors were cast, along with three plates for tensile test specimens. Although the suspension had been well-deaired, small bubbles were evident on the part's surface. We believe these problems are correctable and are due to the pouring technique or possibly inadequate deairing or wetting of the mold.

**ACTIVATION OF THE POLYMERIZATION** – The heat of polymerization is 19.8 kcal/mole (82.9 kJ/mole) and can produce an excursion of 20 to 25 °C. Heating of castings to accelerate the polymerization, therefore, is restricted to a temperature of less than 50° C in order to prevent boiling with consequent degradation of properties. There is also a trade-off between temperature and catalyst content, which affects working time and is a function of the formulation.

**UNMOLDING** – Unmolding may be accomplished mechanically or, in the case of wax molds, by melting or dissolving.

**DRYING** – Work with alumina showed that to avoid severe warping(6), drying of the parts was best carried out using a slow drying step at room temperature at high relative humidity. Practical considerations, however, favor short processing times. Accordingly, a set of studies with alumina, silicon nitride, and sialon was begun to optimize the drying rate procedure.

Ceramic plates gelcast in molds (228.6 x 90.2 x 8.89 mm) were dried at room temperature in a chamber where the humidity was controlled. Variation of the mass and shrinkage of the plates with time were

measured. The data show that drying of gelcast ceramic parts is different from the drying of either pure gels or typical ceramics. Fig. 4 shows the drying rates as a function of moisture content for sialon plates. Fig. 5 shows the similarity for alumina, silicon nitride, and sialon at one level of relative humidity.

The rate falls linearly from the value at high moisture. The data indicate that the drying is diffusion-controlled from the beginning. This diffusion occurs from a shrinking core of wet gel and leads to shrinkage of the drying body immediately after casting.

Even more significant, from the combined standpoints of processing time and of deformation, is the observation that shrinkage is rapid early in the drying period. This is shown in Fig. 6. The total shrinkage during drying is directly related to the volumetric solids content of the casting mixture. This means that for part-to-part size uniformity, the most important control quantity is the solids content or density of the casting mixture.

Figure 6 shows the early period shrinkage for three levels of relative humidity, normalized to a total drying shrinkage of 3.0%. The most rapid change for lower levels of humidity is in the first 3 to 4 hours: 85% of the shrinkage occurred in this time. The fact that the shrinkage rate can be controlled is best illustrated by the data for 96% relative humidity. The value of linear shrinkage during drying is typically about 3.0%. The further shrinkage during sintering is about 11.5%. This implies that particle packing in the dried body is about 69%. Substantially the same values have been obtained for all powders studied so far.

The model for drying that we are using leads us to believe that castings do not show increases in warpage after the initial shrinkage period. If this proves to be the case, optimization of the drying operation would involve drying at high humidity until a specifiable shrinkage had occurred, followed by accelerated drying, possibly by humidity decrease alone. We have not yet determined the most efficient drying protocol for gelcast tensile specimen plates.

**ORGANIC REMOVAL** – The organic compound is removed by heating in air to a temperature that will not oxidize the part or by heating in a nitrogen environment. The temperature program for organic removal is based on the thermogravimetrically measured decomposition of polyacrylamide.

**SINTERING** – The principal formulation used was chosen to give readily sinterable materials, due to the absence of hot isostatic pressing capability. Sintering will be a variable in future work.

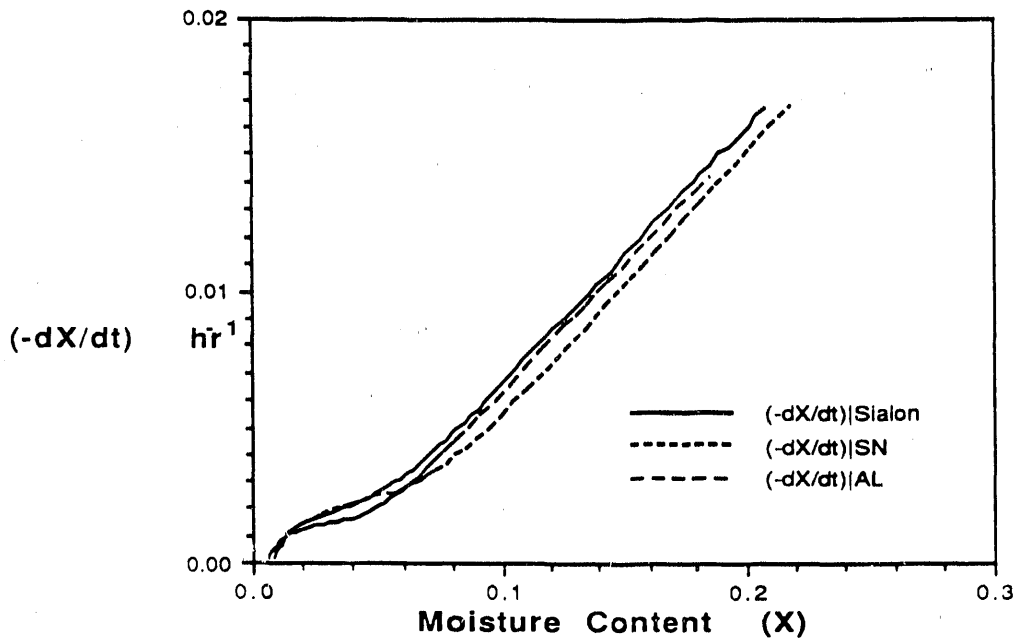


Fig. 5. Drying rate data at 75% relative humidity for three powders of comparable particle size. Note that no constant rate drying period is observed.

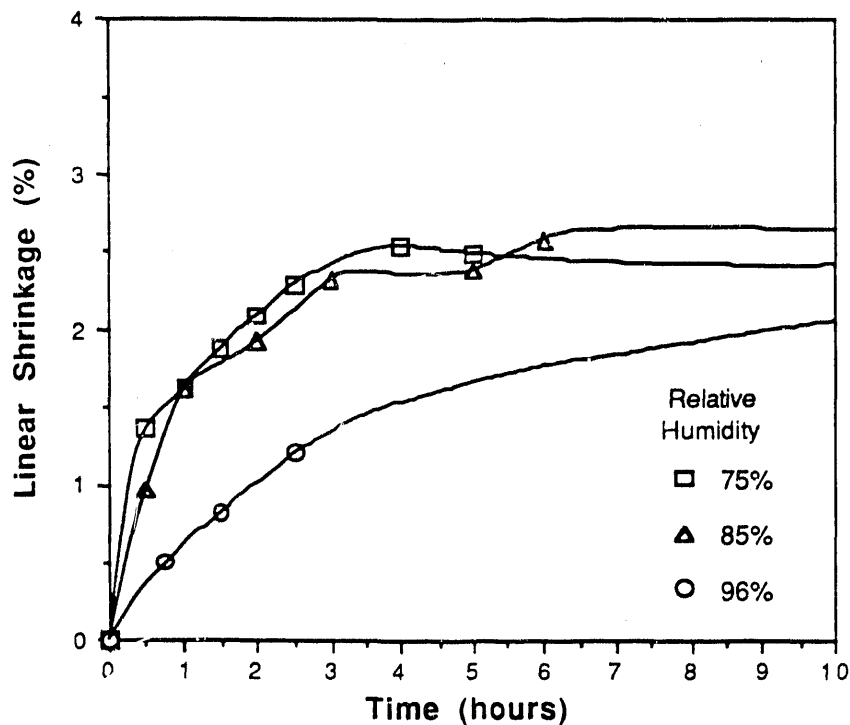


Fig. 6. Early shrinkage of sialon gelcastings.

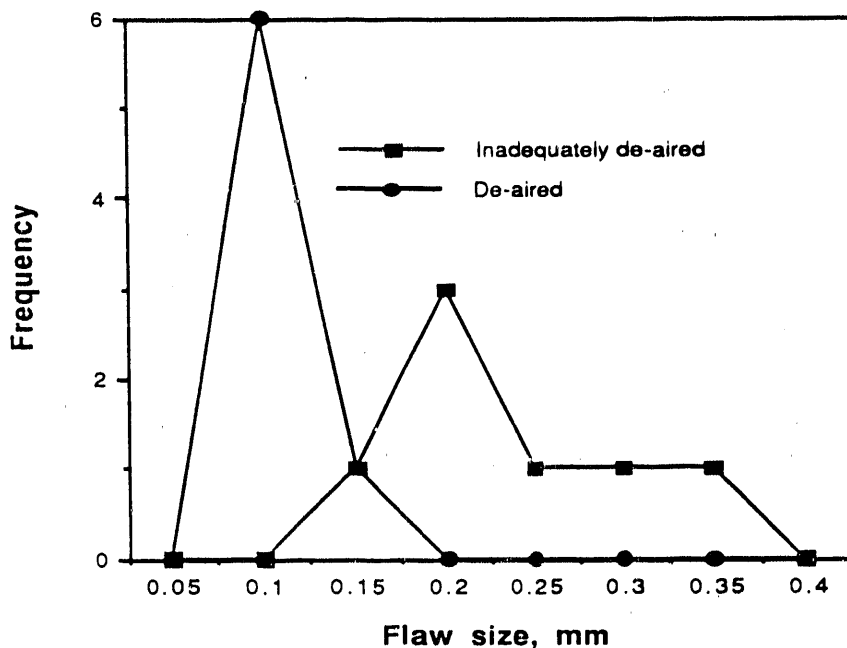


Fig. 7. Distribution of flaw sizes calculated for gelcast alumina specimens.

## ENVIRONMENTAL, SAFETY, AND HEALTH CONSIDERATIONS

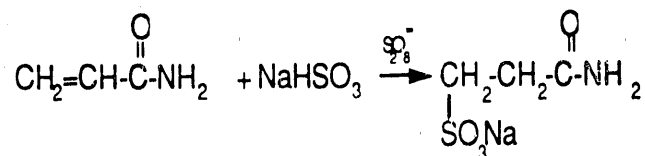
As with other procedures for treating materials, this process generates waste. In addition to the more usual materials of ceramic processing, gelcasting uses the substance, acrylamide, which is a known neurotoxin(7-9). The following issues have been addressed:

1. General laboratory practice
2. The handling of acrylamide powder and concentrated solutions
3. Decontamination procedures for spills
4. Waste handling for all steps of the process
5. Exhaust to the environment
6. Acrylamide monomer content of the products and air-borne dusts formed during machining.

Acrylamide's acute toxicity does not pose great problems. The principal problem is the neuro-toxicity of the substance after long term exposure (months or years) at levels of about 5 mg/kg of body weight. This led to a NIOSH recommended maximum concentration of 0.3 mg/m<sup>3</sup> in air (10 h exposure) at the workplace. OSHA's PEL and TLV have been set at 0.03 mg/m<sup>3</sup>. The vapor pressure of acrylamide at room temperature is about 0.007 torr (0.9 Pa). This corresponds to approximately 33 mg/m<sup>3</sup>. The fundamental control of acrylamide is therefore exercised by avoiding spills and storage practices that could routinely permit buildup to

this concentration and by prompt neutralization of solutions that may contain unreacted acrylamide.

The neutralization of acrylamide is part of the procedure for waste handling and is by the addition of bisulfite ion (HSO<sub>3</sub><sup>-</sup>) in the presence of a peroxide:



Analyses were also conducted for acrylamide monomer present in alumina gelcastings. The highest value obtained was 20 ng acrylamide/g casting. Dust control when machining dried parts is needed, in any event, because of the fine ceramic dusts that may be generated.

Although the level of care required for this process is not unusual in the chemical process industries, potential ceramic users have been hesitant. Consequently, we are developing alternatives in the process materials.

## RESULTS OF TENSILE TESTING OF ALUMINA

The first processing variable examined was the extent of de-airing. Air is introduced during mixing of

the suspension. If air is not removed adequately, small bubbles can be entrained that impair strength. Two levels of de-airing were examined for these specimens.

The tensile strengths of the specimens were found to be 156 MPa and 253 MPa respectively for the specimens without and with adequate de-airing. Using an estimate for  $K_{Ic}$  of  $4 \text{ MP} \cdot \text{m}^{1/2}$  the critical flaw sizes were estimated and are plotted in Fig. 7. For these two sets the average estimated flaw size decreased from 0.2 mm to 0.08 mm. These values correspond to the observed void size in the inadequately de-aired specimens and to the measured agglomerate size in the well-deaired series. The Weibull moduli were estimated at 7 and 14 for the two specimen sets. For continuing studies with alumina, milled slips are being investigated.

## CONCLUSIONS

This paper describes gelcasting of some sub-micron ceramic powders including silicon nitride. The gelcasting of silicon nitride will be continued at ORNL and under a cooperative agreement between ORNL and GCC. Sintering aid variation, processing variables, and sintering schedule are planned to be evaluated using the uniaxial tensile strength of produced test specimens.

## ACKNOWLEDGEMENT

The assistance of Ms. C. A. Walls (ORNL) in performing much of the experimental work reported here is gratefully acknowledged.

## REFERENCES

1. M. A. Janney, "Method for Forming Ceramic Powders into Complex Shapes," U.S. Patent 4,894,194, January 16, 1990.
2. ALUMINA: Reynolds RC-HP; Malakoff Industries, Malakoff, TX. SIALON: AA; Vesuvius Research, Pittsburgh, PA, SILICON NITRIDE: UBE; SN E10, E03, and ESP; Ube Industries, New York, NY; STARCK S, S1, LC10, and LC12SX; Herman Starck, New York, NY; DENKA 9S and 9FW; Denka, New York, NY, U.S.A.
3. M. J. Hoffman, A. Nagel, P. Greil, and G. Petzow, *J. Am. Ceram. Soc.* **72**(5), 765-769 (1989).
4. Dale Wittmer, consultant, private communication.
5. Patent Pending.
6. G. W. Scherer, "Theory of Drying," *J. Am. Ceram. Soc.* **73**(1), 3-14 (1990).
7. "Criteria for a Recommended Standard - Occupational Exposure to Acrylamide," NIOSH (National Institute of Occupational Safety and Health) Report, DHEW(NIOSH)-77-112, EPA-560/11-80-016, July, 1980.
8. "Acrylamide," Environmental Health Criteria 49, World Health Organization, Geneva, 1985.
9. W. H. Montgomery, "Polyacrylamide," in Water Soluble Resins, ed. Robert L. Davidson and M. Sittig, Reinhold Book Corporation, 2nd ed. 1962.

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