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GELCASTING

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- I. INTRODUCTION
- II. PROCESS OVERVIEW
 - Batching The Gelcast Slurry
 - Attaining High Solids Loading
- III. GEL CHEMISTRY
 - Monomer Selection
 - Initiation and Gelation
- IV. MOLDS AND THEIR USE
 - Mold materials
 - Slurry - Mold Interactions and Mold Release Agents
- V. BINDER BURNOUT OF GELCAST PARTS
- VI. MANUFACTURING ISSUES
 - Gelcasting Reproducibility Study
 - Overview Of Environmental, Health, And Safety Issues
- VII. APPLICATIONS OF GELCASTING IN CERAMIC PROCESSING
- VIII. SUMMARY AND CONCLUSIONS
- IX. ACKNOWLEDGEMENTS
- X. REFERENCES

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I. INTRODUCTION

Gelcasting is an attractive new ceramic forming process for making high-quality, complex-shaped ceramic parts.¹ A slurry made from ceramic powder and a water-based monomer solution is poured into a mold, polymerized *in-situ* to immobilize the particles in a gelled part, removed from the mold while still wet, then dried and fired. Gelcasting is a generic process. It is not limited to use with any particular ceramic powder because the processing additives are all organic and leave no cation impurities behind in the fired part. Ceramic parts from over a dozen different compositions (ranging from alumina-based refractories to high-performance silicon nitride) have been produced by gelcasting; it is a robust process; and, it can be quickly adapted for use with new materials and new applications.

Gelcasting is a highly versatile fabrication process. It has been used to make parts ranging in size from <1 g to >6 kg. Complex shapes with thin sections as small as 0.2 mm have been gelcast. Conversely, large rods up to 4 inches in diameter have been made. Gelcasting has been demonstrated in most of the major ceramic systems such as alumina, aluminum nitride, boron carbide, ferrites, silicon, silicon carbide, silicon nitride, zinc oxide, and zirconia as well as some of the more obscure ones such as cerium oxide, europium oxide, hydroxylapatite, and tin-doped indium oxide. Gelcasting is attractive for fabricating complex shapes such as turbine rotors and radomes, and for simple shapes such as large toroidal rings. Gelcast components can be made with highly

reproducible dimensions and typically exhibit a Weibull modulus for strength that is equivalent to or better than that for slip cast or dry pressed parts. Many gelcast articles are meant to be used in the as-cast and fired condition. Others are green machined before firing, either to introduce features that are difficult or expensive to mold in or to make specialty shapes for short production runs. Figure 1 shows several parts that have been gelcast including silicon nitride turbine rotors (1a, 1b), precisely green machined alumina mini-crucibles (1c), and an alumina radome (1d). A comparison of gelcasting with slip casting, injection molding, and pressure casting is given in Table 1. Gelcasting compares favorably with the other forming processes in all categories, and is the most desirable in many categories. Specifically, gelcasting provides a rapid forming cycle, good wet and dried strength, the option to use a range of mold materials, the ability to make large parts (>1m maximum dimension) having thick and thin sections, and few, if any, molding defects. Gelcasting is very close to traditional ceramic processing. It is a water-based process (although non-aqueous systems can also be used for systems such as aluminum nitride or other water sensitive powders). It uses the same dispersants and processing aids as are normally used for slip casting or spray drying. It uses standard mixing equipment such as ball mills for slurry preparation.

II. PROCESS OVERVIEW

The gelcasting process is based on a synthesis of ideas borrowed from traditional ceramics and from polymer chemistry. A process flow sheet is shown in Figure 2. The heart of the technology is the use of an organic monomer solution that can be polymerized to form a strong, crosslinked polymer-solvent gel. Water is the preferred solvent;²⁻⁵ however, organic solvent systems have been developed as well.^{6,7} The balance of this discussion will assume water as the solvent.

The aqueous monomer solution provides a low-viscosity vehicle that is combined with ceramic powder and appropriate dispersants to form a highly fluid slurry. Methacrylamide (MAM) is the preferred monomer and methylene bisacrylamide (MBAM) and poly(ethylene glycol dimethacrylate) (PEG-DMA) are the preferred crosslinkers. Ammonium persulfate (APS) is the free radical initiator used most often; tetramethylethylene diamine (TEMED) is frequently added to catalyze the breakdown of the APS and, therefore, to accelerate the polymerization and crosslinking reaction. The slurry can be easily poured into molds to form complex shapes. The monomer solution in the slurry is polymerized and crosslinked to form a polymer-water gel that permanently immobilizes the ceramic particles in the shape defined by the mold. Because the crosslinked polymer-solvent gel contains only about 15 to 20 wt % polymer, the solvent (which constitutes 80 to 85 wt % of the liquid vehicle) can readily be removed from the gelled part by a drying step. Once dried, the crosslinked polymer can be removed using standard thermal pyrolysis (binder burnout) procedures. There is only about 2-4 wt % polymer in the dried body (based on the weight of ceramic powder), which is similar to polymer contents found in dry pressed bodies. Furthermore, there are pore channels in the body (which are opened up during the drying stage) for the pyrolysis products to migrate through to the surface, thus preventing pressure buildup and consequent bloating or cracking of the body. Subsequent high firing to sinter and densify the part follows procedures typical of the ceramic composition that is being used.

Gelcasting depends on the formation of a crosslinked polymer-solvent gel as the setting mechanism that holds the particles in place.

Unlike systems that depend on a particular inorganic chemistry (e.g., ethyl silicate- or phosphate-bonded refractories, or sol-gel bonded ceramics), the gelcasting gel system is totally organic. Because of this, the process can be used to cast parts from any ceramic powder. Gel formation is shown schematically in Figure 3. Here the chain building monomer is depicted as "M" and the chain branching, or crosslinking, monomer is depicted as "X." Upon the addition of free radicals to the solution, the "M" monomers react to form long chains that are occasionally caused to branch by the incorporation of the "X" monomers. The result is a very high molecular weight polymer that fills space and traps the solvent molecules among its branches. The macroscopic result is a polymer-solvent gel.

Gelcasting possesses the desirable attributes of other ceramic slurry processes. High solids suspensions of well-dispersed particles are key to the process. The slurry can be processed in an entirely closed system; therefore, mixing, filtration (to remove agglomerates or particulate impurities), deairing (to eliminate bubbles), and mold filling can be accomplished without the danger of introducing contaminants or foreign material. Also, the high degree of homogeneity required to produce excellent parts can be retained. In addition, no significant change in the processing equipment commonly used in ceramic processing is required by the gelcasting process. No special molding machines or presses are needed. Neither are major changes in dispersants nor in other processing aids required when changing from a current process, say slip casting, to gelcasting. Hence, gelcasting represents a minimal departure from existing industrial practice.

Batching The Gelcast Slurry

Batching of gelcasting slurries follows procedures similar to those used for other ceramic processes. The inputs include the batch size, the relative proportions of the powders for the ceramic composition of interest, the densities of the ceramic powders, the gel premix composition, the amount and density of the dispersants, and the volume fraction solids required for the slurry. Table 2 gives a typical gelcasting batch sheet for a Si_3N_4 - 5 wt % Y_2O_3 - 5 wt % Al_2O_3 ceramic composition. For this slurry, we are using

2000g of ceramic and a 20 wt % 4:1 MAM-MBAM gel premix with a 20 wt % addition of glycerine plasticizer to help in green machining of the dried, gelcast parts.

The mixing and casting procedure proceeds as follows. Load all the liquid ingredients (gel premix, dispersants, plasticizer), the alumina and yttria, and half the silicon nitride (900g) into a 4-liter ball mill. Mill at high speed (50 to 100 RPM) for about two hours on a standard mill rack. Add another 1/4 of the silicon nitride powder (450g) and ball mill at high speed for two more hours. Add the remaining silicon nitride (450g); mill at slow speed (1 to 10 RPM) to incorporate the powder, if necessary. Then ball mill at high speed for two more hours. Note that the staged addition of the ceramic powder is required to achieve a high solids loading. The details regarding how fast a particular ceramic powder can be added to the mill and how long mixing must be continued between additions will vary from powder to powder. For example, with a powder such as Reynolds RCHPDBM alumina, the powder can be added essentially all at once.

After mixing is complete, transfer the slurry to an appropriate container. Deair under mechanical pump vacuum. Defoamers can be added at this point to aid in bubble removal.

Deairing is an essential step in gelcasting if high quality, defect free parts are to be obtained. There are three types of bubbles that can form during deairing. These include mechanically entrained air, dissolved air, and boiling solvent. In most gelcasting applications it is critical to remove both the entrained air, which was entrapped during mixing, and also the air dissolved in the solvent phase. Both of these can lead to the formation of strength limiting defects in the gelled part. Bubbles that form from solvent boiling will collapse when the vacuum is released. However, one needs to be careful not to use a vacuum level much higher than the vapor pressure of the solvent; an overly aggressive vacuum can lead to drying of the slurry resulting in the formation of flakes of dried material, which can act as flaws in the cast part. Often, the vacuum level is controlled by introducing water into the bottom of the bell jar during deairing. This assures that the vacuum level will not exceed the vapor pressure of water. Another way to guarantee

an appropriate vacuum level is to use a liquid ring vacuum pump.

After deairing is complete, add the TEMED catalyst with vigorous mixing. Then add the 10% APS solution, also with vigorous mixing. Additional deairing will be needed after the addition of the APS solution. Pour the gelcasting slurry into an appropriate mold. Gel at 50°C for 30-60 min. (Note that gelation can be accomplished at room temperature if a higher level of initiator and catalyst is used. However, the amount of time available for deairing and casting will be shortened relative to the high temperature gelling case.) Cool the mold before demolding to prevent too rapid drying of the part. Unmold the part and dry as you would any conventional wet ceramic. Controlled humidity drying may be required, especially for thick or large parts. This is standard ceramic practice for gelcasting as it is for drying extruded, slip cast, or pressure cast parts.

Attaining High Solids Loading

In gelcasting, just as in injection molding or extrusion, the slurry density is the same as the green density of the gelled part. Therefore, it is critical that the solids loading of the gelcasting slurry be controlled at a desired level. This typically means producing a flowable slurry (viscosity on the order of 200-300 cp) with as high a solids loading as possible. The high solids loading in the slurry produces a green body having the lowest possible shrinkage upon drying and firing to high density. In general, the lower the drying and firing shrinkage, the fewer problems one encounters with warping and cracking of the parts. (In some cases, such as in making gelcast foams, one requires controlled, lower density slurries. For such situations, one may add foaming agents or fugitive fillers to the gelcast slurry.)

For most slurries, attaining a high solids loading requires identifying an appropriate dispersant system and an appropriate mixing method. Fortunately, most of the gel monomer systems are benign with respect to the dispersants used in ceramic processing. Therefore, standard dispersants such as those used in slip casting or spray drying may be used in gelcasting. There are, however, some differences that are encountered between formulating gelcasting slurries and slip casting

or spray drying slurries. These differences arise primarily because the solids loading required for gelcasting is higher than that required for either spray drying or slip casting. Spray drying slurries typically range between 25 and 45 vol % solids, depending on the powder being used and the spray drier conditions. Slip casting slurries range between 40 and 55 vol % solids, again depending on powder and casting conditions. It is preferred that gelcasting slurries be at least 50 vol % solids; higher solids loadings are desirable. A summary of some ceramics that have been gelcast and the dispersants used to attain high solids loadings is presented in Table 3. In most of the cases, solids loadings above 50 vol % can be achieved. In some cases, solids loadings above 60 vol % are attainable. However, sometimes these requirements cannot be met. Ube E10 silicon nitride, Starck B10 silicon carbide, TOSOH TZ zirconias, and Baikowski high purity aluminas are four examples of ceramic powders in which it is nearly impossible to achieve a solids loading above 45 vol % in a gelcast slurry. In all these cases, the powders are exceedingly difficult to disperse for any application, typically because they possess a high surface area.

For most ceramic powders, the choice of monomer premix system is not important with regard to dispersion. The gelcasting monomers are nonionic, do not specifically adsorb at the ceramic powder surface, and therefore, do not participate in the dispersion process. For example, RCHPDBM alumina can be gelcast utilizing Darvan 821A at 55 vol % solids in virtually any gelcasting premix composition. Similar behavior is exhibited by the Ube silicon nitrides. In one unique case, however, the monomer system is vital to the dispersion of the ceramic powder. Table 3 shows the example of TOSOH TZ8YS zirconia. The TZ8YS composition could not be dispersed in either 15 wt % 6:1 MAM-MBAM or 15 wt % 3:1 MAM-PEGDMA premixes using any standard dispersant at greater than 35 vol % solids. In contrast, the powder was easily dispersed at 45 vol % solids in a 20 wt % HMAM-MBAM premix using no dispersant at all. That is, the monomer solution acted as its own dispersant. Why the TZ8YS powder behaves this way is not understood.

Gelcasting slurries can be formulated using a wide range of mixing equipment

including ball mills, attritor mills, and vibratory mills. The choice of mixer is normally dictated by the experience of the processing engineer and the availability of equipment. Usually, an intermediate size of milling media is required. Balls or rods about 1 cm in diameter have been shown to be the most effective choice for lab scale ball mills (up to 10 liters). Media significantly smaller than this (say 1-3 mm diam) have too much surface area and are not effective in moving the slurry around in the ball mill. For production scale ball mills, larger media (up to 3 cm diam) may be effective because of the greater fall heights achieved in the larger diameter mills. For vibratory or attritor mills, the choice of media size is often dictated by the equipment rather than by the slurry. For slurry mixing, whether in a ball mill or attritor mill, a low media to powder ratio is used. Rather than the 10:1 or 20:1 media to powder ratio (by weight) that one would use for particle size reduction, a ratio on the order of 0.5:1 or 1:1 is most often used for mixing gelcasting slurries. This ratio provides more than enough shear to incorporate the powders with the liquid components of the slurry and to break up soft agglomerates. It does not significantly reduce the particle size of the powder or increase its surface area.

Achieving high solids often requires staging the addition of ceramic powder to the batch. In this approach, about 1/2 of the powder is added to the monomer premix and dispersant solution followed by intense mixing. Then, an additional amount of powder is added followed by additional mixing. This process is continued until all of the powder has been added. For difficult powders, the additions typically follow a pattern such as 1/2, 1/4, 1/4 or 1/2, 1/4, 1/8, 1/8 depending on how difficult it is to get the powders to wet out and disperse. For mixing using a ball mill, the last one or two additions of powder may require mixing at a very low speed, initially, followed by higher speed mixing as the powder additions are incorporated into the slurry. The low speed mixing is effective because many slurries become dilatant as additional powder is added. Mixing at slow speed allows the slurry to flow, even if slowly. Mixing a dilatant slurry at high speed simply centrifuges the slurry to the outer wall of the mill, and no mixing takes place. As the powder becomes fully incorporated into the slurry, the viscosity decreases and dilatancy

disappears. At that point, higher speed mixing can be used.

III. GEL CHEMISTRY

At the heart of the gelcasting process is a monomer solution that polymerizes upon the addition of free radicals to form a gel. The monomer solution consists of the solvent (typically water), a chain forming monomer, a chain branching (crosslinking) monomer, and a free radical initiator. The chain formers most commonly used are methacrylamide (MAM), hydroxymethylacrylamide (HMAM), N-vinyl pyrrolidone (NVP), and methoxy poly(ethylene glycol) monomethacrylate (MPEGMA). Sometimes these monomers are used in combination with one another; that is, one might choose to develop a gel system based on MAM and NVP or MPEGMA and HMAM. The crosslinkers most commonly used are methylene bisacrylamide (MBAM) and poly(ethylene glycol) dimethacrylate (PEGDMA). The free radical initiator system used most of the time is ammonium persulfate (APS) with tetramethylethylenediamine (TEMED) used as a catalyst to make the APS breakdown faster. Other initiators used include azobis (2-amidinopropane) HCl (AZAP), azobis [2-(2-imidazolin-2-yl) propane] HCl (AZIP), and azobis isobutyronitrile (AIBN), which is used in alcohol and other non-aqueous solvents. These reagents are summarized in Table 4.

Monomer Selection

The choice of monomer system and initiator system depends on several factors. Among these factors are gel strength, gel stiffness, gel toughness, wet strength, dry strength, green machinability, reactivity (including reaction temperature), and price. Two systems qualify as “standard” gelcasting monomer systems in that they have been used extensively in a wide range of ceramics. Those two systems are MAM-MBAM and MAM-PEG(1000)DMA. MAM-MBAM solutions are typically formulated at between 12 and 20 wt % total monomer (MAM plus MBAM) and at MAM to MBAM ratios between 2:1 and 6:1. MAM-PEG(1000)DMA solutions are also formulated at a total monomer concentration of 12 to 20 wt %; but, the MAM to PEG(1000)DMA ratios are typically between 1:1 and 3:1. The MAM to PEG(1000)DMA ratios are lower than the MAM to MBAM ratios

because the molecular weight of the PEG(1000)DMA is much higher than that of MBAM; therefore, for a given ratio of monomer to crosslinker, there are relatively fewer crosslinks (or branches) for the PEG(1000)DMA as compared with the MBAM. Therefore, a 3:1 ratio in MAM-PEG(1000)DMA is similar in crosslink density to a 6:1 ratio in MAM-MBAM.

A warning is in order regarding the cleanliness of monomers. Most monomers are supplied either as technical grade or reagent grade chemicals. As such, the purity of the monomers ranges from 95 to 99+% with the balance typically being other organic chemicals. However, the purity rating often does not reflect any “inert” content in the monomers because the suppliers do not routinely test for inert material. Very often, monomer solutions made from these technical or reagent grade monomers need to be filtered to remove contaminants. These include inorganic particulates such as dust and dirt and organic fibers such as paper. Using unfiltered monomer solutions can cause the formation of strength-limiting flaws in the fired ceramic parts.

In general, the strength of the gel and the gelcast ceramic increases with increasing total monomer concentration in solution and with increasing ratio of crosslinker to monomer. Thus a 15 wt % solution of 3:1 MAM-MBAM will be stronger and stiffer than a 15 wt % solution of 6:1 MAM-MBAM because of the higher MBAM concentration. A caveat exists, however, regarding the possible concentrations of monomers that can be used. For pure components, the solubility limit of MAM in water at ambient temperature (say 22°C) is about 22 wt % and the solubility limit of MBAM in water is about 2 wt %. Therefore, one could not make a 20 wt % 3:1 MAM-MBAM solution because that would require an MBAM concentration of 5 wt %. If such a high concentration is required, a second monomer needs to be added that will act as a cosolvent for the MBAM. One system that has been used is MAM-NVP-MBAM, which can easily be formulated at 20% total monomer with a monomer ratio of 1.5 to 1.5 to 1 MAM-NVP-MBAM.

Gelcasting systems formulated using PEG(1000)DMA are more easily machined in the green state than those formulated using

MBAM. Machinability can be further improved by adding a plasticizer to the formulation, which modifies the mechanical properties of the dry polymer. Typical plasticizers include glycerine and poly (ethylene glycol). Plasticizers are typically added at 10 to 20 wt % of the dry polymer, with a corresponding amount of the solvent (typically water) being replaced, as shown in the Example in Table 2.

Initiation and Gelation

The gelation reaction proceeds in two stages - initiation and propagation. The initiation interval is often called the “idle” stage because there is no macroscopic evidence that a reaction is occurring. That is, the viscosity of the solution or slurry does not increase and no heat is generated, as happens later during the propagation stage. An example of an initiation and propagation reaction for the acrylamide - methylenebisacrylamide gel system is shown in Figure 4. For acrylamide, a significant exotherm occurs during polymerization so the progress of the reaction can be followed by measuring the temperature of the solution as a function of time. Figure 4 shows that the rate of reaction increases rapidly with temperature and with APS concentration. Thus, there is a tradeoff that must be made between the speed of the reaction at a given temperature and the idle time (or pot life, in analogy to thermoset plastic compositions such as epoxies and urethanes). Very often, gelation is conducted at elevated temperature (between 40 and 80°C) where the faster reaction rate produces a gelled part in a short time. This allows one to retain a reasonable amount of time (30 to 120 min) at ambient temperature after the addition of the initiator to the slurry for deairing and mold filling. This prevents premature gelation, which destroys the usefulness of the slurry.

The amount of initiator required to start a reaction depends on the particular monomer, the crosslinker, the initiator, addition of a catalyst, and the reaction temperature. MAM-based solutions require a higher initiator concentration than do HMAM-based solutions; the MAM solutions are less reactive, perhaps because MAM polymerization is nearly athermal whereas HMAM polymerization is highly exothermic. Slurries gelled at ambient temperature require three to four times the initiator concentration of those gelled at 50°C.

Initiation using only APS proceeds slowly; but, adding TEMED drastically increases the rate of reaction. There are also effects of the ceramic powder on initiation.

The particular ceramic powder used can strongly influence the amount of initiator needed to gel the slurry. Many slurries, e.g., those based on alumina and silicon nitride, require more initiator than would be calculated based on the amount of neat solution present in the slurry. The surface of the ceramic somehow inhibits the breakdown of the initiator into free radicals, or perhaps scavenges those radicals. For both silicon nitride and alumina, the amount of initiator required increases with increasing surface area, although the relation is not linear. Thus, a slurry based on RC152 alumina ($S_g = 1.5 \text{ m}^2/\text{g}$) requires only about 1/2 the initiator required for a slurry based on RCHP ($S_g = 8 \text{ m}^2/\text{g}$). Other powders, such as silicon, actually promote initiation. MAM-MBAM based silicon slurries gel rapidly at ambient temperature even without a free radical initiator. Finally, the actual concentration of initiator needed to start a gelation reaction is quite small, typically 0.05 to 0.2 wt % of the liquid phase of the monomer solution.

One caution needs to be made regarding the addition of initiators to the gelcasting slurry. All the initiators used in gelcasting water-based slurries are highly ionic and acidic (typically about pH 2). The combination of high ionic strength and acidity can cause coagulation problems in some slurries. Most of the time, a gelcasting slurry is highly loaded with ceramic powder and is at the edge of colloidal stability. This means that it only takes a little push to change the slurry from a dispersed state to a coagulated state. Local changes in pH or ionic strength that accompany the introduction of the initiator into the slurry can cause local coagulation of the slurry and the formation of clumps. To prevent or at least reduce coagulation, several steps are recommended. First, the initiator should be added using vigorous mixing of the slurry. In this way the highly concentrated initiator solution is quickly diluted by the slurry, which reduces the tendency for coagulation. This will introduce some air into the slurry, but the air can be removed by deairing. Second, if necessary, the pH of the initiator solution can be adjusted to match the pH of the slurry. We

have shown that this does not affect the initiation reaction. Third, the initiator concentration can be reduced from 10 wt % to between 2 and 5 wt %. The lower ionic strength of the diluted solution will reduce the tendency of the slurry to coagulate. This will slightly lower the final solids loading of the slurry because more initiator solution has to be added to the slurry, but sometimes this step is necessary to prevent coagulation. Finally, after the initiator is added, the slurry should be screened before deairing. This assures that any clumps that might have formed in the slurry due to coagulation are removed.

IV. MOLDS AND THEIR USE

Mold selection, mold fabrication, and mold use are critical aspects of successful gelcasting. Our experience has shown that proper selection of mold material, fabrication method, filling method, and mold release can make the difference between producing excellent parts and producing “also rans.”

Mold materials

A variety of mold materials have been studied for use in constructing gelcasting molds. A summary of those materials is given in Table 5. The most commonly used mold materials are aluminum, glass, polyvinylchloride (PVC), polystyrene (PS), and polyethylene (PE). Aluminum, and especially aluminum that has been hard anodized, is the mold material of choice for permanent molds. Aluminum is easily machined to exacting tolerances. It is relatively inexpensive. Hard anodized aluminum provides an excellent wear surface that holds up well to heavy use. More important, the anodized layer provides a surface that releases better from gelled parts than does a bare aluminum surface. In several gelcasting applications, a plain aluminum mold was inadequate for use because the gelcast parts stuck severely in the mold. Anodizing the mold provided much better release and made the mold serviceable.

Glass is widely used in plate and tube form for initial casting trial in the lab. Gelled parts tend to release well from glass, with less dependence on the choice of mold release than with many other substrates. This is probably the result of the extremely smooth surface provided by glass. Unfortunately, glass is

difficult to machine and, therefore, it is not very useful for production molds.

PVC is used extensively for gelcasting rods, tubes, and rings. PVC pipe is widely available in many sizes up to several feet in diameter. PVC tends to produce a thin, ungelled layer (0.1 mm) at the surface of the gelcast part, irrespective of the mold release used. This ungelled layer is used to advantage for removing parts from the molds; the ungelled layer acts as a lubricant and makes extracting gelled parts from long tube molds quite easy. For making large rings, we typically use two concentric pieces of PVC pipe separated by a neoprene rubber gasket, Figure 5. The neoprene serves to align the two pipe sections and provides an excellent surface against which to gel. No ungelled layer has been observed for gelcasting slurries in contact with neoprene.

PE and PS are used in the lab for making test samples. In the early stages of a gelcasting investigation, typically when still working on initiator addition levels and gel times and temperatures, making small samples of arbitrary shape is required. PE and PS serve this need well. Labware such as beakers, test tubes, Petri dishes, etc. make good molds for initial gelcasting tests. One problem with PE and PS is they tend to produce a thin ungelled layer at the face in contact with the polymer, similar to that produced by PVC.

Many other materials are used for special mold applications in gelcasting. These include meltable core materials, high purity graphite, plaster, and various polymeric casting compounds.

One of the more interesting mold applications is in the area of meltable cores for making hollow gelcast parts. Materials suitable for meltable cores include various low melting point waxes (especially investment casting pattern waxes), Wood’s metal, and several indium-based alloys. The melting point of the core material should be between about 40°C and 80°C. Also, the core material should undergo only a small change in volume on melting to prevent setting up large strains in the gelled part during core removal.

As an example, consider the part and mold shown in Figure 6. This part requires a mold and a core (or mandrel) to form its complex shaped wall. However, after the part is gelled, the core cannot be removed mechanically

without destroying the part. Enter the meltable core. By using a core material that melts at a temperature below the boiling point of the gelcasting solvent, one can remove the core from the gelled (but still wet) gelcast part. The core material can be reused at this point by recasting in the core-forming mold. We have used this technique for gelcasting hollow parts in both alumina and silicon nitride.

The following procedure is typically used for meltable cores. The slurry is loaded into a mold. A temperature at least 10°C below the melting point of the alloy or wax is used to gel the slurry. The part is then removed from the mold and placed into hot water. The water serves two purposes: first, it prevents the gelled part from drying prematurely; second, it heats the wax or alloy to a temperature above its melting point, at which point the core flows out of the part. To make sure that all of the core material is removed, the part is rinsed several times. The part is then cooled to an appropriate temperature for drying. Alternatively, the part can be heated in an oven at 100% relative humidity. The saturated water vapor prevents the gelled part from drying during the core removal process. In either case, the gelled part is not adversely affected by the heating operation.

High purity graphite is sometimes used as a mold material if the articles being gelcast are required to retain ultra high purity. Graphites can be obtained that are suitable for semiconductor applications with total impurities on the order of 1 ppm. Graphite is easily machined, and so makes a reasonable mold material. Selection of the mold release is also a concern when high purity must be maintained. Many mold releases contain silicone oils and organophosphate esters, which would be detrimental to many ceramic systems. A 100% organic mold release is required if ultra high purity is to be maintained in the fired part.

Plaster molds are ubiquitous in ceramic processing. Unfortunately, the porosity inherent in the plaster creates a problem for gelcasting; it dries out the slurry. Two approaches have been used to correct this problem: coatings and fillers. One can sometimes paint or seal a plaster mold to prevent it drawing water out of the gelcast slurry. Unfortunately, many paints and lacquers produce ungelled layers on the surface of the gelcast parts. Appropriate sealants have

to be determined by trial and error. Filling the pores is another approach. The simplest filler is water; simply saturate the mold before using it for gelcasting. This works best if the water used for saturating the mold contains 1-2 wt % ammonium persulfate. Otherwise, the oxygen dissolved in the water tends to inhibit gelation at the mold surface. By saturating the mold with water, good quality gelcast parts have been produced in plaster molds.

Polymeric casting compounds should be attractive for making gelcasting molds. Unfortunately, the two most popular casting compounds, silicone rubber and urethane compounds, both produce thick (1-2 mm) ungelled layers at the surface of the gelled parts. In the silicone rubber case, we have demonstrated that the main issue is oxygen dissolved in the rubber, which inhibits the gelation reaction. If silicone rubber molds are first degassed (say in a vacuum oven at 50°C followed by backfilling with nitrogen) and if gelation is conducted in a nitrogen atmosphere, good quality parts can be gelcast. However, such procedures are not appropriate for production and we do not recommend the use of silicone rubber. The cause of the ungelled layer produced by urethane compounds is not known.

A sample of molds used in gelcasting is shown in Figure 5. These include an anodized aluminum plate mold, a glass and neoprene plate mold, a PVC/neoprene gasket ring mold, a PVC tube mold, an anodized aluminum piston mold, a wax turbine mold, and a steel turbine mold.

Slurry - Mold Interactions and Mold Release Agents

The gelcasting slurry can interact with the mold in several different ways. There can be simple wetting of the mold surface by the slurry, which upon gelation produces a minimum amount of interaction. Or, there can be aqueous corrosion of the mold by the solution, which upon gelation causes severe sticking of the gelled part to the mold surface. The interaction of the slurry with the mold surface can be adjusted through the use of coatings. These coatings are called mold release agents. The desired result of using a mold release agent is to reduce or eliminate the interaction of the gelled part with the mold surface so that the part can be easily removed

from the mold. Mold release agents come in a variety of compositions including waxes, oils, greases, polymer dispersions, polymer resin solutions, oils, fatty acids and fatty acid derivatives, inorganic powders, and combinations of the above. Many of the commercial mold releases used in the polymer processing industry (i.e., those used for injection and compression molding) are effective for gelcasting. Other materials that are sometimes effective as mold release agents include cooking sprays, petroleum jelly, and various spray lubricants. Somewhat surprisingly, aerosol PTFE (polytetrafluoroethylene) sprays have performed universally poorly in gelcasting applications. The release agents used most often in our lab include Polyester Parfilm (useful for many different slurries, but contains TiO_2 as a contaminant), Axel F-57 (best release for silicon nitride, contains organophosphate esters), Axel AZN (contains organophosphate esters), WD-40 (totally organic, ultrahigh purity applications, good for alumina), and petroleum jelly, Table 6.

The effectiveness of a particular mold release agent is dictated by complex interactions among the gelcasting slurry, the mold surface, and the mold release agent. Predicting which mold release agent will be effective for a particular combination of gelcasting slurry and mold material is difficult. The best approach is Edisonian. As an example, consider the results of a series of tests described in Table 6. In this study, a single alumina gelcasting slurry was tested in five different plate molds (aluminum, anodized aluminum, polymethylmethacrylate (PMMA), Lexan® polycarbonate, and window glass) with seven different commercial mold releases. As an example of how different the results can be for slightly different conditions, consider the behavior of the slurry with aluminum and anodized aluminum using the release AZN. For the aluminum case, the gelled part bonded strongly to the mold face and the plate tore during removal from the mold. In contrast, for the anodized aluminum case, the gelled part exhibited good release and the part did not tear upon removal.

Selecting a mold release depends not only on the slurry and the mold surface; it also depends on the geometry of the part. In some situations, one may want absolutely no interaction in one part of a mold but a little bit

of interaction in another region of the mold. Consider gelcasting a crucible. The mold for such a part is shown schematically in Figure 7. Removing the gelled crucible from the mold and core can be a challenge. To take the mold apart, the core is extracted from the mold. (Initial extraction is often accomplished using jack screws built into the core piece.) One would prefer that the gelled crucible release completely from the core and adhere at least a little to the mold. This is especially true if the crucible is thin walled; it may need to remain in the mold for a time to partially dry so it is strong enough to support its own weight and to be handled. If the part adheres to the core instead, it will create problems during drying since the part will shrink onto the core and crack. Gelcasting parts like crucibles may require using two different mold release agents, one for the mold and another for the core.

V. BINDER BURNOUT OF GELCAST PARTS

Before a ceramic part can be sintered, the organic processing aids that are incorporated in the body during fabrication must be removed. One advantage of gelcasting is the small amount of polymer that remains in the green body after drying. The dried gelcast body contains only about 2 to 6 wt % polymer, which depends on the solids loading of the slurry, the concentration of monomers in the premix, and the density of the powder. A 45 vol% solids silicon nitride body (Si_3N_4 , 5 wt % Al_2O_3 , 5 wt % Y_2O_3) made using a 15 wt % 4:1 MAM-MBAM premix contains about 5.5 wt % polymer in the dried gelcast part. In contrast, an injection molded silicon nitride part having the same solids loading would contain about 27 wt % polymer, nearly five times as much. A 55 vol% solids alumina body made using the same premix contains only 2.4 wt % polymer in the dried part.

The details of how the gelcast polymers pyrolyze were determined by thermal analysis. Simultaneous differential thermal analysis and thermogravimetric analysis (DTA/TGA) was conducted in air on the neat dried gels of both MAM-MBAM (6:1 monomer to crosslinker ratio) and MAM-PEGDMA (3:1 ratio). Pyrolysis of dried silicon nitride-based gelcast parts was also conducted; the gelcast ceramic parts were tested in both air and nitrogen. A standard thermal analyzer was used for the

analysis. The silicon nitride gelcast parts were based on E10 silicon nitride with 5 wt % additions each of alumina and yttria. The slurry solids loading was 45 vol%; 0.5 wt % Dolapix PC33 was used as dispersant. A premix consisting of 15 wt % MAM-MBAM at a 6:1 monomer to crosslinker ratio was fused to make the slurries.

The results of the pyrolysis studies of the neat gels are given in Figure 8a. The two neat gels showed similar pyrolysis behavior in air. Pyrolysis occurred mainly between 250°C and 620°C. There were four identifiable thermal events at about 300°C, 350°C, 440°C, and 550°C. The details of weight loss and heat generation are only slightly different for the two gels. Essentially all of the polymer was combusted; no visible ash remained after testing.

Pyrolysis of the gelcast silicon nitride parts in air proceeded somewhat differently from that of the neat gels. Comparing the pyrolysis of the MAM-MBAM neat gel with the silicon nitride MAM-MBAM gelcast part shows that the silicon nitride powder accelerates the pyrolysis of the gel, Figures 8a and 8b. Pyrolysis of the silicon nitride part is completed by about 550°C. The neat gel is not fully pyrolyzed until it reaches about 620°C. The silicon nitride particles also tend to alter the shape of the DTA trace for pyrolysis; the four thermal events that are quite distinct in the pyrolysis of the neat gel become blurred in the gelcast silicon nitride case.

Pyrolysis of the silicon nitride part in nitrogen shows even more deviation from the neat MAM-MBAM results in air. First, the pyrolysis exhibits essentially no thermal events; it proceeds by a thermal scission process only. This is not too surprising since there is no oxygen available for combustion of the polymer. Second, there is a sizable carbonaceous residue that remains in the part after pyrolysis. The residue amounts to about 15% of the original polymer weight in the gelcast part. Residues of this magnitude are typical for pyrolysis in neutral atmospheres for many polymers used in ceramic processing such as methylcellulose, poly (vinyl alcohol), and poly (vinyl butyral). For most ceramics, this residue would not be desirable. However, for ceramics such as silicon carbide and boron carbide, one might choose to conduct the binder burnout in a neutral or reducing

environment to take advantage of the carbon produced.

Binder burnout of gelcast parts follows procedures that are similar to those used for die pressed or isopressed parts made from spray dried powders. The amount of polymer contained in the two types of ceramic bodies is similar. Similar times at temperature are required to pyrolyze the polymers and to allow gases to escape from the body. Heating rates on the order of 0.5 to 1°C/min to temperatures as high as 650°C have been used successfully for both silicon nitride and alumina gelcast parts. Slower heating rates are sometimes dictated if the gelcast parts are especially large or if the thermal conductivity of the parts is especially low. These accommodations in the thermal cycle are similar to those required for die pressed or isopressed parts of similar size or composition. A supply of combustion air is typically required in the binder burnout furnace. Oxygen depletion can easily occur if combustion products are not swept out of the furnace and replaced by fresh air. In addition, an off-gas afterburner that converts pyrolysis products to carbon dioxide and water may be required for production binder burnout to meet local or national air quality standards. Again, these requirements are typical for binder burnout of spray dried ceramic powders and represent no deviation from standard ceramic practice.

VI. MANUFACTURING ISSUES

Gelcasting Reproducibility Study

To assess the reproducibility of the gelcasting process for producing ceramic components, a series of silicon nitride batches was prepared under identical conditions and gelcast. The batches consisted of 45 vol.% UBE E-10 silicon nitride with 5 wt.% Y_2O_3 and 5 wt.% Al_2O_3 in a MAM/MBAM monomer solution. The one-kilogram-size batches (ceramic powder weight) were turbomilled in a 4-inch diameter vessel at 500 RPM for 1.5 hr. PVP K-15 and Darvan 821A were added as dispersing aids. The initiator, AZIP, was added to the suspension in the turbomill at the completion of the milling time. Eleven batches were prepared for the repeatability study. Each batch was prepared on a different day over a period of 18 days. Every effort was made to be consistent in the preparation method. The

pH of the slurries was measured after milling and was consistently 8.7.

The milled slurry was cast into rod molds (0.5 inch diam x 1.5 inch long), plate molds (4 x 4 x 0.5 inch), and a button-head tensile rod mold (see Figure 9). The molds were then placed in an oven at 60°C for one hour to gel the slurry. After cooling, the gelled samples were removed from the molds and placed in a controlled humidity and temperature chamber for the initial drying phase. The chamber was maintained at 25°C and 92% relative humidity. The samples were left in the chamber for 16 hr before being removed to complete the drying process under ambient conditions. Samples were then placed in a desiccator for storage.

The dimensions of the dried tensile rod specimens cast from the eleven batches were measured at the points shown in the drawing in Figure 9. These locations were chosen because they could be precisely measured using calipers. The results of the measurements are given in Table 7. The uniformity of the castings is shown clearly by the standard deviation values which indicate a variation of only 0.1% to 0.3% about the average value for the dimensions measured.

The samples cast in the rod molds were fired at 1850°C for two hours under 50 psi nitrogen pressure. The diameter of the green and fired samples and the density after firing are shown in Table 8. The average value and standard deviation for the 54 samples are also shown in the table. As these results show, the gelcasting process is very reproducible. The rod diameters in the green state showed a standard deviation of only 0.02 mm or about 0.1%. In the fired state, the standard deviation of the diameters was about 0.3%. This difference is probably due to the slightly higher variability of the fired density which showed a standard deviation of 0.6%. It is interesting to note, however, that the batch-to-batch variation was no greater than the typical scatter within a given batch of material as shown in Table 8. This suggests that while there is room for improvement in the uniformity within a batch, the reproducibility of the process is very good.

Samples for 4-point bend strength measurement were prepared from plates cast from the eleven batches. The plates were fired at 1850°C for 2 hr. under 50 psi nitrogen pressure. The strength tests were run at room temperature. The results of these tests are

summarized in Table 9. The overall strength for the batches was 583±84 MPa, with a Weibull modulus of about 8.0. This indicates relatively low uniformity among the batches. This is probably due to the scatter in the measured densities for the plates cast from these batches, which is also shown in Table 9. This may have resulted from non-uniform heating of the samples during firing due to the arrangement of the plates in the crucibles.

Overview Of Environmental, Health, And Safety Issues

As is common with polymer systems, some of the gelcasting components are reactive (e.g., oxidizers, corrosive, flammable) chemicals. Some monomers and prepolymers exhibit a capacity to sensitize exposed workers and all are potentially irritating. After polymerization and curing, a stable compound results. Several chemicals used in the gelcasting process are closely related to those used in dentistry, food processing and cosmetics.

Normally, the main environmental, health, and safety (EH&S) focus is on the chemicals in their most hazardous phase, that is, before polymerization. During this phase of the process, it is recommended that a combination of engineering controls and personal protective equipment be used to reduce worker exposures. Similarly, attention should be given to reducing environmental releases of unreacted components.

Table 10 presents health and safety information using a common rating scheme⁸ to summarize the health, fire, and reactivity characteristics of each material. Chemicals having a rating of 0-1 should be considered relatively nonhazardous, those with ratings of 2-3 are believed to pose a moderate risk and a rating of 4 indicates severe hazard potential. The criteria used in Table 10 are those used by the Oak Ridge National Laboratory (ORNL). The ORNL ranking scheme is similar to, but more conservative than, the NFPA (National Fire Protection Association) code⁸ and offers a high degree of worker protection.

Table 10 also includes a “yes” or “no” notation to suggest the potential of the various chemicals as carcinogens or reproductive hazards. If a chemical meets the broad criteria established by the Occupational Safety and Health Administration (OSHA) Laboratory

Standard, 29 CFR (Code of Federal Regulations) 1910.1450, as a potential or suspect carcinogen or reproductive toxin, it is listed with a "Y" in the appropriate column. Since this information may be based on weak evidence, it is intended primarily for use in communicating *potential* hazards.

Only two of the gelcasting chemicals are assigned occupational exposure limits by OSHA. Where oral-lethal dose testing information is available, it has been presented in the last column. The lethal dose resulting in the death of 50 percent of the tested animals, in this case rats, is given as an LD₅₀ in milligrams of chemical per kilogram of animal weight (mg/kg). This information can be used to compare relative health risks. For reference, a chemical with an LD₅₀ of greater than 50 mg/kg is considered to be of low to moderate oral toxicity. All the gelcasting reagents fall in this category.

Chemical safety reviews indicate that the primary or acute health consideration for the chemicals relate to their action as irritants. For reference, the ranking system used in preparing Table 10 ranks isopropyl alcohol as a level 1 irritant. Handling practices used for the mild irritants, rated as a 1 or 2, should be similar to those used for industrial alcohols. Since risk also relates to potential for contact with chemicals, the actual hazard associated with a chemical can be lowered by reducing the likelihood of contact or exposure through appropriate engineering control and personal protection equipment, e.g., use of gloves.

In summary, the gelcasting components considered here are uniquely low-hazard materials. If standard hygiene and safety practices are followed, these chemicals can be used safely in both the research and development laboratory and in industrial settings. No unique controls are required beyond those used for other standard ceramic industry chemicals.

VII. APPLICATIONS OF GELCASTING IN CERAMIC PROCESSING

Gelcasting represents a small departure from traditional slurry processing operations such as slip casting and spray drying. It is a water-based process. The behavior of a gelcast slurry will be similar to the behavior of other slurries made with that particular ceramic

powder. The same dispersants and processing aids can be used. We have proved that the gelcasting monomers do not interact adversely with standard ceramic processing additives such as dispersants, lubricants, and defoamers. In addition, no significant change in the processing equipment that is conventionally used in ceramic processing is required by the gelcasting process. Therefore, gelcasting represents a small modification to existing industrial practice. The biggest difference between gelcasting and the more traditional slurry processes is the solids loading. Gelcasting requires a higher solids loading (50 to 60 vol%) as compared with that typically used in slip casting and spray drying (25 to 55 vol%). The solids loading must be high in gelcasting because the solids loading in the slurry becomes the green density of the cast part. Frequently, only small modifications to standard ball mill practice are required to process gelcasting slurries.

Gelcasting retains many desirable attributes of other ceramic slurry processes. The slurry can be processed in an entirely closed system; mixing, filtration (to remove agglomerates or particulate impurities), deairing (to eliminate bubbles), and mold filling can be accomplished without the danger of introducing contaminants or foreign material. Also, the high degree of homogeneity required to produce excellent parts can be retained.

Gelcasting provides a method for manufacturing large, complex-shaped components such as turbine rotors that require highly uniform properties. As an example, consider the rotor shown in Figures 1b. After drying, the green density of several sections of the rotor were determined by the Archimedes immersion method, Figure 10. The variation in green density was extremely low. All the sections except one were within 0.2% of the average green density of 53.77%_{th}. That one section was within 0.4% of the average. Thus, the total variation in green density from highest to lowest section was only 0.6%_{th}. This is an especially significant accomplishment given the large variation in cross sectional thickness in the rotor. The hub of the rotor is about 50 mm in diameter and the blade tips are only 1.5 mm thick. A similar set of density determinations for a slipcast rotor of the same ceramic composition produced a range of green

density variation $>2.5\%$ th, which caused cracking of the parts during firing.

Gelcasting can also be useful in the manufacture of large components having simple shapes. As an example, consider a 60 cm (24 inch) diameter ring having a 2.5 cm (1 inch) square cross section. Such a ring could be made by die pressing a spray dried powder. However, one quickly encounters an equipment issue. The ring has a projected area of 590 cm² (92 in²). If it is compacted even at the modest pressure of 69 MPa (10,000 psi), the total load required is 420,000 kg (920,000 lbs). This would require a large press (approx. 500 tons). Presses of this size are not common in ceramic processing shops. One could also consider isopressing such a ring around a mandrel. However, that would require an isopress having an inside diameter of at least 70 cm (28 in). Industrial scale isopresses this large are rare. In contrast, such a ring can be made very easily by gelcasting. A mold for the part can be machined from metal or plastic at very little expense. The forming operation consists of pouring the appropriate gelcasting slurry into the mold and then initiating the gelling reaction. This can be accomplished at elevated temperature (50-60 °C) using standard additions of APS/TEMED as initiators. Alternately, gelation can be achieved at room temperature by increasing the APS/TEMED concentration by a factor of 2 to 10 (depending on the ceramic and monomers used) over that used for elevated temperature gelation. Figure 1c shows a 1/2 scale (30 cm diam) ring of nickel zinc ferrite made using this gelcasting method.

During the development of the gelcasting process, it was observed that the dried parts were exceptionally strong, even though they contained only 3-5 wt % organic binder.⁹ Strengths in the range of 3 to 4 MPa (500 to 600 psi) are common. This is believed to be due in large part to the highly uniform distribution of the binder throughout the casting, which is on the same scale as the powder particles. An additional factor is the inherent strength of the crosslinked polymer, which is quite large. The high strength of the green body is of great advantage for handling of the parts before firing and for being able to produce large castings.

The dried parts can be easily machined.¹⁰ Although gelcasting was developed as a near-net-shape forming process, green machining of gelcast materials can be particularly useful for producing prototypes, for custom manufacturing, or for adding features to a cast part that would be too difficult or too costly to include in the mold. Figure 11 shows a typical part that was green machined from a rectangular block of gelcast silicon nitride using a computer controlled 3-axis milling machine. Cutting speed tests showed that for machining a flat-bottomed groove 3.2 mm wide and 9.5 mm deep (0.125 x 0.375 in.) using three passes, rates of 0.85 - 6.35 cm/sec (0.33 - 2.50 in./sec) could be used without damaging the sample.¹⁰ An interesting observation of the machining characteristics of gelcast ceramics is that the tools removed the material from the billet as turnings or shavings. Monitoring by health physics personnel showed that there was a minimal amount of airborne dust generated; no protective breathing apparatus was required for workers. Recent studies have shown that adding a plasticizer such as glycerine or poly (ethylene glycol) to the gelcasting formulation markedly improves the machinability of green gelcast parts. As an example, webs as thin as 2 mils (0.002 inch) have been routinely machined.

Finally, it should be mentioned that gelcasting works as well for metal powder forming as for ceramic powders. We have demonstrated the ability to gelcast and sinter near net shape parts in tool steel,¹¹ a nickel-based superalloy,¹² aluminum alloys, and stainless steel. Furthermore, we have green machined parts from many of these metal powder compositions, further demonstrating gelcasting's versatility.

VIII. SUMMARY AND CONCLUSIONS

Gelcasting has been demonstrated to be a viable forming technique for a variety of ceramics ranging from submicron technical ceramics to mm sized refractories. It is useful for forming large parts (up to 1 m in diam), complicated parts (turbines), small parts (down to <0.1 mm dimension), hollow parts (such as crucibles and cones), and thin-walled parts. Gelcast parts are reasonably strong in the gelled state and extremely strong in the dried condition. The high green strength allows

gelcast parts to be green machined to form features that are difficult or expensive to mold into the gelled part.

There are five keys to using gelcasting effectively. The first is making a slurry having the desired green density; the slurry density and the green density are the same for gelcast part. Development of excellent dispersant systems is critical. The second is choosing an appropriate monomer/crosslinker combination; the monomer/crosslinker chemistry, concentration, and ratio will determine the mechanical properties of the gelled and dried part. The third is selecting an appropriate initiator chemistry and initiator concentration to produce a strong gelled part and to provide an appropriate working time for the slurry. The fourth is selecting (discovering) an appropriate combination of mold material(s) and mold release agents to ensure that the part can be removed from the mold; mold release agent selection is often the most difficult aspect of developing an effective gelcasting system. The fifth is drying the gelled part in a manner appropriate to produce a stress free, unwarped part.

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Table 1. Comparison of gelcasting process parameters with those for slip casting, injection molding, and pressure casting.

| Property | Gelcasting | Slip casting | Injection Molding | Pressure Casting |
|--------------------------------------|--|--|--|--|
| Molding time | 5-60 min | 1-10 hrs | 10-60 sec | 10 min - 5 hr |
| Strength (As-formed) | Moderate to high depending on gel system | Low | High | Low |
| Strength (Dried) | Very High | Low | N/A | Low |
| Mold Materials | Metal, glass, polymer, wax | Plaster | Metal | Porous plastic |
| Binder Burnout | 2-3 hours | 2-3 hours | Up to 7 days | 2-3 hours |
| Molding defects | Minimal | Minimal | Significant | Minimal |
| Maximum Part Dimension | > 1 meter | > 1 meter | ~30 cm, 1 dimension <u>must</u> be 1 cm | ~1 meter |
| Warping during drying/binder removal | Minimal | Minimal | Can be severe | Minimal |
| Thick/thin sections | No problem | Thick section increases time of cast | Problems with binder removal in thick sections | Thick section increases time of cast |
| Particle size | Viscosity goes up as size goes down | Casting time goes up as size goes down | Viscosity goes up as size goes down | Casting time goes up as size goes down |

Table 2. Batch sheet for a silicon nitride, 5 wt % alumina, 5 wt % yttria gelcasting batch.

| Component | Role | Additive Concentration or level | Relative Weight (%) | Weight (g) | Density (g/cm³) | Volume (ml) |
|------------------------|-------------------------------|--|----------------------------|-------------------|-----------------------------------|--------------------|
| Ceramic batch size | | | | 2000.00 | | |
| Amount of media | silicon nitride, 1 cm diam | | | 1000.00 | 3.200 | 312.50 |
| Silicon nitride | ceramic powder | | 90.00 | 1800.00 | 3.23 | 557.28 |
| Alumina | ceramic powder | | 5.00 | 100.00 | 3.96 | 25.25 |
| Yttria | ceramic powder | | 5.00 | 100.00 | 5.01 | 19.96 |
| Total ceramic | | | 100.00 | 2000.00 | 3.32 | 602.49 |
| Dolapix PC33 | dispersant | 100 % active | | 20.00 | 1.040 | 19.23 |
| 4:1 MAM/MBAM in water | monomer solution | 20 % solution in water | | 560.73 | 1.000 | 560.73 |
| Glycerine | plasticizer | 20 wt % of monomer | | 24.78 | 1.260 | 19.66 |
| 100% TEMED | catalyst | 0.1 x acceleration | | | | 0.26 |
| 10% APS sol'n | initiator | 1.0 x acceleration | | | | 2.60 |
| Total liquid | | | | 580.73 | 0.964 | 602.49 |
| Total slurry | | | | 2580.73 | 2.177 | 1185.31 |
| Solids loading (vol %) | | | | | | 50.00 |

Table 3. Dispersants commonly used for gelcasting ceramics.

| Ceramic | Dispersant | Dispersant Composition | Gel System* (aqueous unless specified) | Solids Loading (vol %) |
|---|---|--|---|---|
| Al ₂ O ₃ | Darvan 821A ^a | Poly (acrylic acid) - NH ₄ ⁺ salt, 5000 MW | MAM-MBAM MAM-PEGDMA | RC152, 63% ^f RCHP, 55% ^f CR6, 45% ^g |
| Si ₃ N ₄ | Dolapix PC33 ^b | Poly (acrylic acid) with aminomethyl propanol | MAM-MBAM, MAM-PEGDMA MAM-NVP-MBAM | E05, 53% ^h E10, 45% ^h |
| SiC | Adjust sol'n to >pH 11 | Tetramethyl ammonium hydroxide (TMAH) | MAM-MBAM MAM-PEGDMA | 45/55 blend of 3 μm & 44 μm particles, 65% ⁱ B10, 45 % ^j |
| ZrO ₂ | none | none | HMAM-MBAM monomer only; limited to <35% with MAM-MBAM or MAM-PEGDMA | TZ8YS, 45% ^k |
| Sn-doped In ₂ O ₃ (ITO) | Darvan 821A ^a | Poly (acrylic acid) - NH ₄ ⁺ salt, 5000 MW | MAM-MBAM | Indium Corp, milled ITO, 50% ^l |
| AlN | PVP K15 ^c | Poly (vinyl pyrrolidone) | MAM-MBAM in isopropanol | AR100, 50% ^m |
| AlN | Emphos CS 1361 ^d w/ Foamaster DS ^e | Proprietary dispersant and defoamer combination | MAM-MBAM | AR100WR, 50% ^m (water resistant AlN) |

*Gel compositions typically 15 to 20 wt% total monomer in aqueous solution;
MAM-MBAM ratio between 3:1 and 6:1; MAM-PEGDMA ratio between 2:1 and 4:1.
APS/TEMED initiator used in most cases. AZIP used for zirconia.

- a R.T. Vanderbilt & Co., Norwalk, CT.
- b Zschimmer and Schwarz, Berlin, FRG.
- c GAF Inc., NY, NY.
- d Witco Chemical, Houston.
- e Henkel Chemical, NY.
- f Reynolds Metals Inc., Richmond.
- g Baikowski International, Raleigh, NC.

- h Ube Industries, America, NY.
- i Norton-Saint Gobain, Worcester, MA.
- j H.C. Starck, Berlin.
- k TOSOH America, NY.
- l Indium Corp., Utica, NY.
- m ART, Inc., Buffalo, NY.

Table 4. Monomers, initiators, and defoamers for gelcasting

| Component | Chemical Name | Vendor | Price (lab) | Price (bulk) |
|---------------------|--|--|--------------------|---------------------|
| MONOMER | | | | |
| MAM | methacrylamide | Aldrich Chemical Co. Milwaukee | \$15/500g | \$7/lb |
| NVP | vinyl-2-pyrrolidone | Aldrich | \$31/kg | \$4.20/lb |
| HMAM | hydroxymethylacrylamide | Aldrich | \$19/500g | \$8/lb |
| MPEGMA | Methoxy poly(ethylene glycol) monomethacrylate | Polysciences, Inc. Warrington, PA | \$50/100g | |
| MBAM | methylenebisacrylamide | Aldrich | \$10/100g | \$7/lb |
| PEG(1000)DMA | poly(ethylene glycol) 1000 dimethacrylate | Polysciences, Inc. | \$55/100g | \$16/lb |
| INITIATOR | | | | |
| APS | ammonium persulfate | Aldrich | \$15/100g | |
| TEMED | tetramethyl-ethylene diamine | Aldrich | \$13/100g | |
| AZAP | azobis (2-amidinopropane) HCl | Wako Chemical Co. Richmond, VA | | |
| AZIP | azobis [2-(2-imidazolin-2-yl) propane] HCl | Wako Chemical | | |
| DEFOAMER | | | | |
| Foammaster DS | Proprietary | Witco Organics Div. Houston | | |
| Surfynol 104E | Acetylenic diol | Air Products & Chemicals Allentown, PA | | |
| Dapro 1139 | Proprietary | Daniel Products, Co. Jersey City, NJ | | |
| DowCorning AntiFoam | Silicone oil emulsion | Dow Corning, Inc Midland, MI | | |

Table 5. Mold Materials For Gelcasting

| Material | Advantages | Disadvantages | Applicability |
|---------------------|---|--|--|
| Aluminum | Machinable, inexpensive | Poor release in some cases. | Widely used |
| Anodized aluminum | Machinable, inexpensive, better mold release than plain aluminum for most gelcasting systems. | | Best performing mold material |
| Brass | Machinable | Corrodes, mold release a serious problem | Not recommended |
| Glass | Inexpensive, readily available, good release. | Limited shapes | Lab tests for plates, rods, and tubes |
| Graphite | Machinable, ultra-high purity can be maintained | Porous | Specialty situations where maintaining purity is critical |
| Indium alloys | Castable, low melting point available (<80°C for use as core material), reusable | | Melttable cores |
| Neoprene rubber | Inexpensive, good mold release | Limited shapes | Often used as gasket material in large diameter PVC or metal ring molds and in glass plate molds |
| Plaster | Inexpensive, molds often already on hand in ceramic manufacturing operations | Porous, must be sealed or filled | Initial trials |
| <u>Polyethylene</u> | Inexpensive, machinable | Ungelled layer at surface of some grades | Test runs in lab, initial trials |

| Material | Advantages | Disadvantages | Applicability |
|--------------------|---|--|--------------------------------------|
| PVC (rigid) | Inexpensive, wide range of sizes available | Thin ungelled surface region typically forms. Can be used to advantage for removing tubes from molds. | Rings, tubes, rods |
| Silicone rubber | Moldable | Thick ungelled layers form at mold surfaces unless mold is outgassed and molding is conducted in nitrogen. | Generally not used. |
| Stainless steel | Machinable, no corrosion | Expensive | Limited |
| Steel (mild) | Machinable, inexpensive | Rusts | Limited |
| Teflon® | Machinable, inert | Ungelled layers form at mold surfaces | Not recommended |
| Urethane compounds | Moldable | Thick ungelled layers form at mold surfaces. | Generally not used. |
| Wax | Machinable, moldable, inexpensive, low melting point available (<80°C for use as core material) | Reaction layer encountered with some wax compositions which leads to spalling of fired ceramic surface. | Short run prototypes, meltable cores |
| Wood's metal | Castable, low melting point available (<80°C for use as core material) | Lead content | Meltable cores |
| | | | |

Table 6. Mold - mold release interactions for an alumina gelcast slurry.¹

| Substrate Surface | Mold Release | Interaction |
|--------------------------|---------------------|---|
| Aluminum | F-57 ² | Stuck hard to mold face; large chunks of gelled slurry stuck to mold face. |
| | PP ³ | Excellent release. |
| | 606 ² | Excellent release; very thin wet film (solution, not slurry) at interface. |
| | 1212 ² | Excellent release; very thin wet film at interface. |
| | AZN ² | Gelled part bonded strongly to the mold face. Partial tearing of gelled plate was observed. |
| | FF-19R ² | Excellent release at interface, but a thin adherent (powder) coating on the mold face. |
| | WD40 ⁴ | Excellent mold release; noncontaminating, contains no cation impurities. |
| Anodized Aluminum | F-57 | Considerable sticking of gelled plate to mold face in several spots. |
| | PP | Excellent release; slightly wet (liquid) at mold face. |
| | 606 | Excellent release; very thin wet (liquid) film at interface. |
| | 1212 | Excellent release; very thin wet (liquid) film at interface. |
| | AZN | Good release; no sticking or tearing. |
| | FF-19R | Excellent release, no adherent coating on mold face. |
| | WD40 ⁴ | Excellent mold release; noncontaminating, contains no cation impurities. |
| PMMA ⁵ | F-57 | A lot of sticking of gelled plate to mold face, ungelled layer present. |
| | PP | A wet, ungelled layer at interface between part and mold. No sticking. |
| | 606 | Poor gelation; required an extra 30 min in the oven (60 min total). |
| | 1212 | Poor gelation; required an extra 30 min in the oven (60 min total). |
| | AZN | Easy removal of green plate from mold, though a thin ungelled layer existed at the interface. |
| | FF-19R | Very good release of gelled plate from mold; a thin ungelled layer existed at the interface. |

| Substrate Surface | Mold Release | Interaction |
|-------------------|--------------|---|
| Lexan® | F-57 | A wet, thin ungelled layer at the large mold face of the plate |
| | PP | A wet, thin ungelled layer at the large mold face of the plate. |
| | 606 | Ungelled layer on both large mold faces. |
| | 1212 | Ungelled layer on both large mold faces. |
| | AZN | A wet, thin ungelled layer at the mold face of the plate. |
| | FF-19R | A wet, thin ungelled layer at the mold face of the plate. FF-19R released easier than AZN. |
| Glass | F-57 | Uniform wetting of ungelled layer which spread over the large mold face of the green plate. |
| | PP | The PP coating caused ungelled layer to "breakup" on the large mold face. |
| | 606 | Good release. |
| | 1212 | Excellent release. |
| | AZN | Excellent release and no ungelled layer on mold face of sample. |
| | FF-19R | Excellent release and no ungelled layer on mold face of sample. |

¹ 55 vol % RCHP-DBM, 15 wt% 4:1 MAM-MBAM solution, 0.5 wt% Darvan 821A; APS/TEMED acceleration at 1.0 µl/0.1µl per g slurry; 4 x 4 x 0.5 inch plate molds, gelled in 60°C convection oven for 30 min.

² Axel Plastics Research Laboratories, Inc., Woodside, NY

³ Polyester Parfilm, Price-Driscoll Corp., Waterford, CT

⁴ WD-40 company, San Diego, CA.

⁵ Poly (methylmethacrylate)

Table 7. Dimensions (mm) of dried gelcast silicon nitride tensile rod specimens.

| | Position | | |
|----------------|----------|-------|------|
| | 1 | 2 | 3 |
| Mold Dimension | 18.87 | 14.15 | 7.54 |
| Sample: | | | |
| R1 | 18.36 | 13.77 | |
| R2 | 18.44 | 13.79 | 7.26 |
| R3 | 18.44 | 13.77 | 7.32 |
| R4 | 18.36 | 13.79 | 7.26 |
| R5 | 18.36 | 13.79 | 7.29 |
| R6 | 18.36 | 13.79 | 7.29 |
| R7 | 18.42 | 13.79 | 7.32 |
| R8 | 18.36 | 13.77 | 7.29 |
| R9 | 18.47 | 13.79 | 7.29 |
| R10 | 18.42 | 13.79 | 7.29 |
| R11 | 18.34 | 13.77 | 7.24 |
| Mean: | 18.39 | 13.79 | 7.29 |
| Std. Dev.: | 0.04 | 0.01 | 0.02 |
| Variation (%): | 0.23 | 0.09 | 0.31 |
| Shrinkage (%): | 2.49 | 2.51 | 3.20 |

Table 8. Dimensions (mm) and densities (g/cm³) for silicon nitride rod samples.

| Batch Number | Green | Diameter | Fired | Diameter | Fired | Density |
|--------------|-------|----------|-------|----------|-------|---------|
| | Avg | St. Dev. | Avg | St. Dev. | Avg | St.Dev. |
| R1 | 17.12 | 0.016 | 13.74 | 0.026 | 3.13 | 0.005 |
| R2 | 17.12 | 0.006 | 13.72 | 0.019 | 3.12 | 0.010 |
| R3 | 17.08 | 0.017 | 13.70 | 0.020 | 3.12 | 0.010 |
| R4 | 17.10 | 0.021 | 13.72 | 0.041 | 3.13 | 0.013 |
| R5 | 17.11 | 0.015 | 13.73 | 0.004 | 3.13 | 0.005 |
| R6 | 17.11 | 0.013 | 13.71 | 0.024 | 3.13 | 0.006 |
| R7 | 17.10 | 0.015 | 13.73 | 0.033 | 3.14 | 0.018 |
| R8 | 17.10 | 0.015 | 13.70 | 0.015 | 3.10 | 0.006 |
| R9 | 17.08 | 0.021 | 13.76 | 0.081 | 3.09 | 0.024 |
| R10 | 17.09 | 0.021 | 13.71 | 0.023 | 3.11 | 0.009 |
| R11 | 17.10 | 0.010 | 13.69 | 0.005 | 3.14 | 0.005 |
| Overall | 17.10 | 0.021 | 13.72 | 0.037 | 3.12 | 0.019 |

Table 9. Density, strength, and Weibull modulus of samples cut from gelcast silicon nitride plates

| Batch Number | Density (%) | Number of Samples | Average Strength, (MPa) | Standard Deviation (MPa) | Weibull Modulus |
|--------------|-------------|-------------------|-------------------------|--------------------------|-----------------|
| R1 | 96.6 | 10 | 615 | 112 | 6.2 |
| R2 | 95.8 | 15 | 612 | 53 | 13.4 |
| R4 | 95.0 | 12 | 542 | 31 | 20.9 |
| R5 | 95.0 | 11 | 567 | 43 | 15.3 |
| R6 | 94.7 | 10 | 544 | 66 | 9.4 |
| R7 | 96.1 | 12 | 621 | 79 | 9.0 |
| R8 | 96.1 | 10 | 623 | 58 | 12.5 |
| R9 | 94.6 | 10 | 551 | 69 | 9.2 |
| R10 | 96.1 | 10 | 500 | 65 | 8.8 |
| R11 | 96.8 | 6 | 692 | 94 | 8.4 |
| Overall | 95.7 | 106 | 583 | 84 | 8. |

Table 10. Health and safety summary for low-toxicity gelcasting reagents.

| REAGENT | H* | F* | R* | CAR* | REP* | HEALTH CONCERN ² | EXPOSURE LIMITS ^{3**} | LD ₅₀ (oral) rats, mg/kg |
|---------------------------|----|----|----------------|------|------|-----------------------------|-----------------------------------|-------------------------------------|
| Gelcasting | | | | | | | | |
| MAM | 2 | 1 | 1 | N | N | Irritant | TLV=1 mg/m ³ | 459 |
| NVP | 1 | 1 | 1 | N | N | Irritant | NE | 1470 |
| MPEGMA | 1 | 0 | 1 | N | N | Irritant | NE | NE |
| HMAM | 2 | 0 | 0 | N | N | Irritant | NE | NE |
| MBAM | 2 | 0 | 0 | N | Y | Irritant | NE | 390 |
| PEG (1000)DMA | 1 | 1 | 1 | N | N | Irritant | NE | 8500 |
| APS | 2 | 0 | 0 ¹ | N | N | Irritant, Sensitizer | TLV=2 mg/m ³ | 820 |
| TEMED | 1 | 3 | 0 | N | N | Irritant | NE | 1580 |
| | | | | | | | | |
| Ceramic Processing | | | | | | | | |
| Alumina | 1 | 0 | 0 | N | N | Irritant | 10 mg/m ³ | |
| Silicon nitride | 1 | 0 | 0 | N | N | Irritant | 10 mg/m ³ | |
| Darvan 821A ^a | 1 | 0 | 0 | N | N | Irritant | NE | |
| Dolapix PC33 ^b | 1 | 1 | 0 | N | N | Irritant | NE | |
| PVPK15 ^c | 1 | 1 | 1 | N | N | Irritant | 10 mg/m ³ | |
| | | | | | | | | |
| Lab Chemicals | | | | | | | | |
| Acetone | 2 | 3 | 0 | N | Y | Irritant | 750 ppm (1780 mg/m ³) | 5800 |
| Acetic Acid | 3 | 2 | 1 | N | Y | Irritant, Corrosive | 10 ppm | 3310 |
| Isopropanol | 1 | 3 | 0 | N | Y | Irritant | 400 ppm | 5840 |

*H=health, F=fire, R=reactivity, CAR=carcinogen, REP=reproductive toxin; rating numbers are per Oak Ridge National Laboratory which are more conservative than those used by NFPA.

**TLV (threshold limit value) = 8 Hour Time Weighted Average Limits in Milligrams of Contaminant Per Cubic Meter of Air (or in parts per million, ppm), recommended by the American Conference of Governmental Industrial Hygienists (ACGIH); NE= None Established; TLV for all "nuisance dusts" perceived to be low toxicity is set at 10 mg/m³.

¹ Reactive-Oxidizer Per J. T. Baker Inc.

² Acute health concern is listed; systemic effects should be considered if long-term exposures are anticipated.

³ MAM limit from Russian literature.

MAM - methacrylamide

NVP - n-vinyl pyrrolidone

MPEGMA - methoxy poly (ethylene glycol) monomethacrylate

HMAM - hydroxymethylacrylamide (also known as n-methoylacrylamide)

MBAM - N,N - methylene bisacrylamide

PEG(1000)DMA -poly (ethylene glycol) dimethacrylate

APS - ammonium persulfate

TEMED - tetramethylethylenediamine

^a R.T. Vanderbilt, Norwalk, CT.

^b Mobay Chemical, Inc., Pittsburgh.

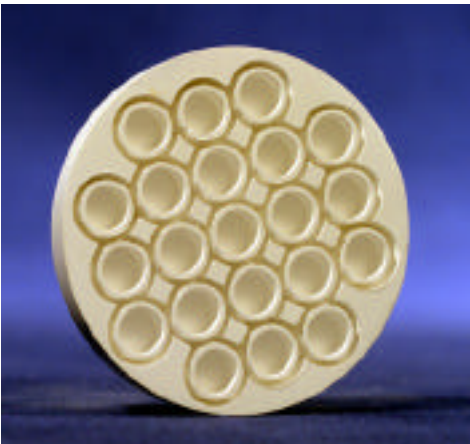
^c GAF Corp., NY.



(A)



(B)



(C)



(D)

Figure 1 Parts that have been gelcast include silicon nitride turbine rotors (1A - 15 cm diam tangential turbine, 1B - 18 cm diam radial turbine, courtesy J. Pollinger, AlliedSignal Ceramic Components, Torrance, California), green machined alumina mini crucibles (block is 6 cm in diameter, 1C), and an alumina radome (20 cm base diameter, 60 cm tall, 1D).

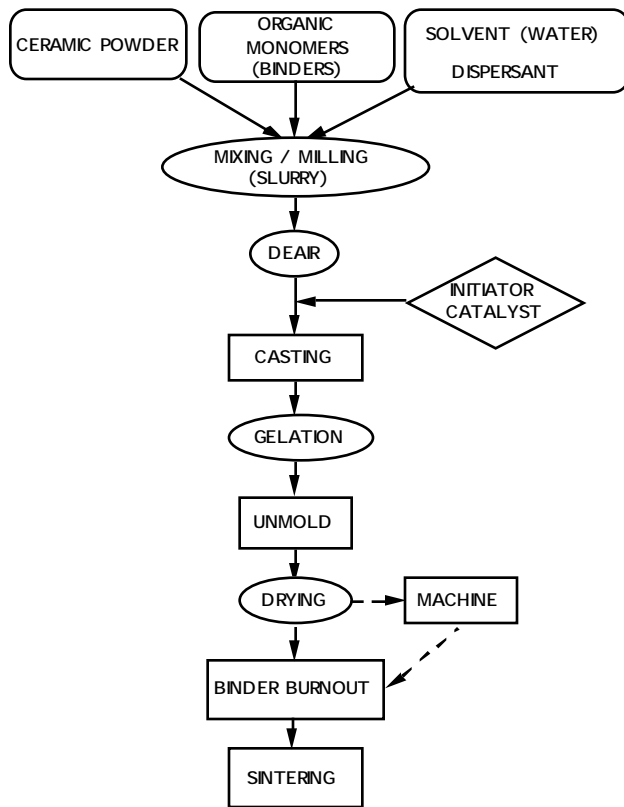


Figure 2. Gelcasting follows a flow chart similar to that for other ceramic processes such as slip casting and spray drying.

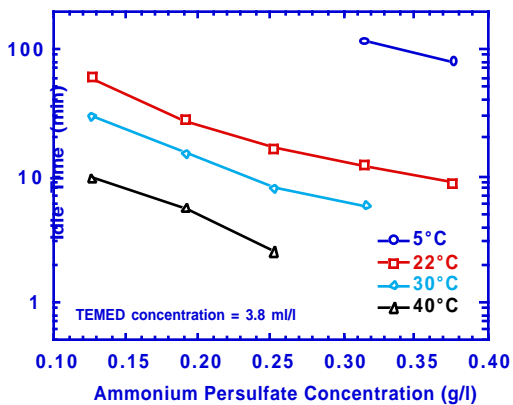
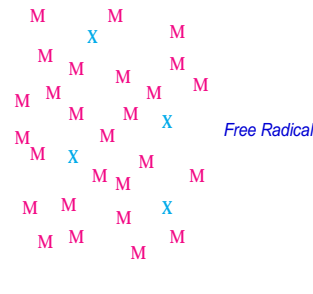


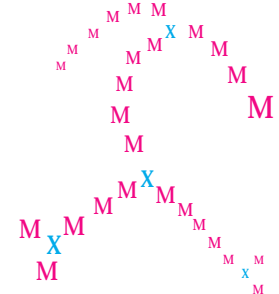
Figure 4. The idle time prior to polymerization for a 14.6 wt% acrylamide - methylenebisacrylamide aqueous solution (M/X ratio = 23:1) was a function of temperature and initiator concentration.

Monomers in Solution



Liquid solution

Polymer-Solvent Gel



Solid Gel

Figure 3. The key to gelcasting is a monomer solution that polymerizes to form a polymer-solvent gel.

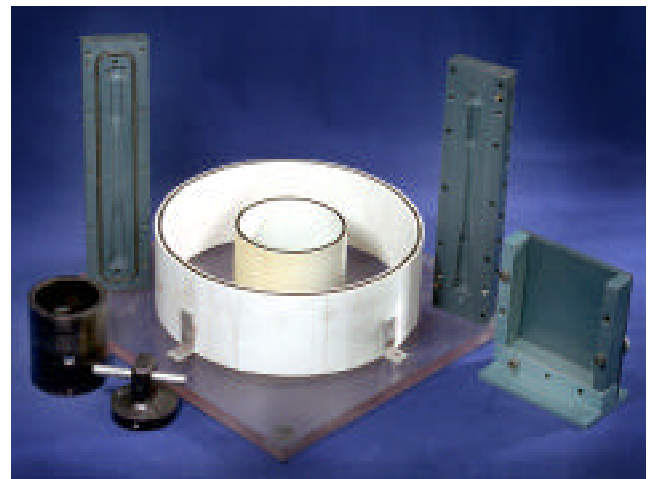


Figure 5. A sample of molds used for gelcasting: anodized aluminum, piston (three piece - open top); anodized aluminum, dogbone tensile specimen (two piece); PVC, ring (three piece with O-ring seal against top plate - not shown); and, anodized aluminum, plate.

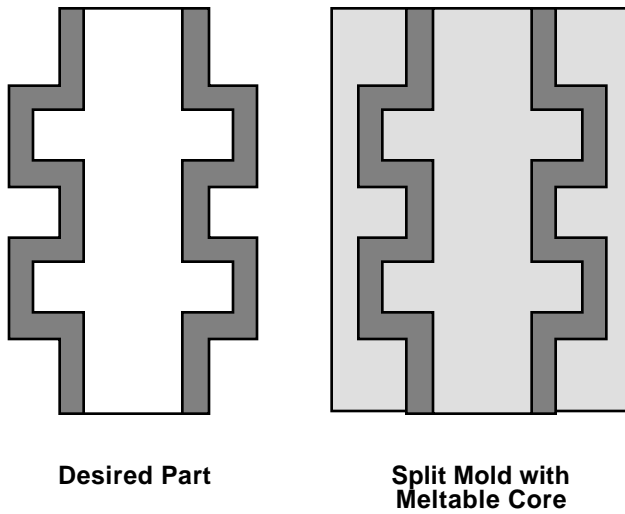


Figure 6. A split mold with meltable core must be used to fabricate gelcast parts having re-entrant angle or occluded regions.

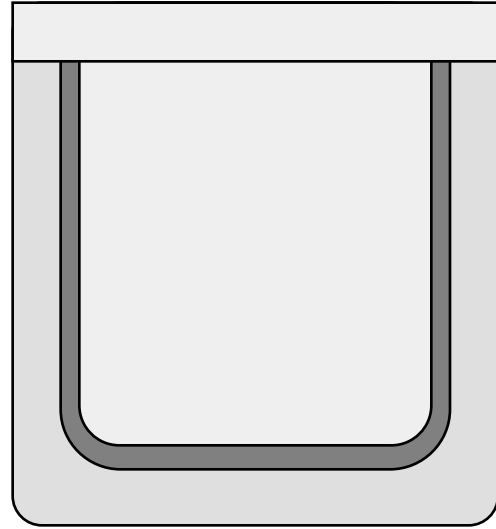
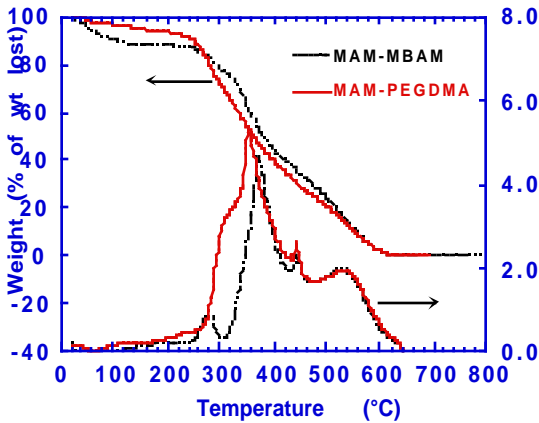
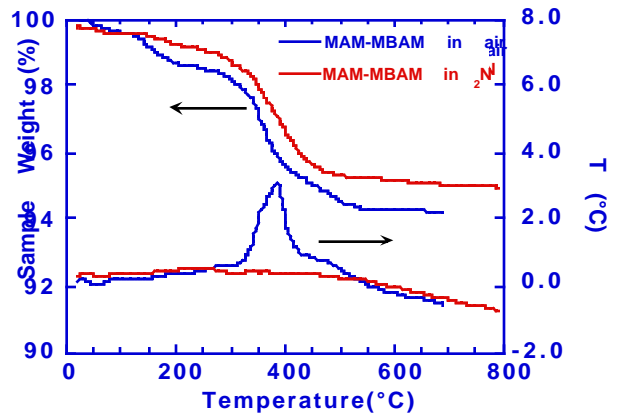


Figure 7. Schematic of a thin-walled crucible gelcasting mold.



(8a)



(8b)

Figure 8. The pyrolysis of neat MAM-MBAM (6:1 ratio) and MAM-PEGDMA (3:1 ratio) dried gels (a) in air was similar. Essentially no residue of the binder was left after firing. The pyrolysis of gelled MAM-MBAM silicon nitride samples in air was quite different from that in nitrogen (b). Pyrolysis in nitrogen resulted in about 0.5 wt % carbon residue.

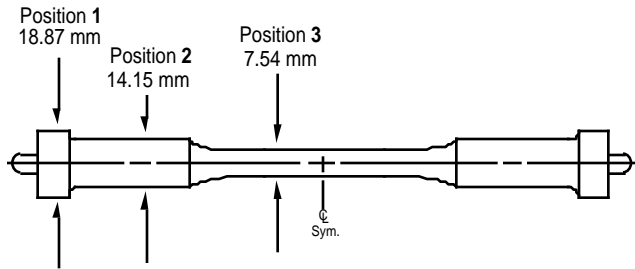


Figure 9. Schematic of a button head tensile rod specimen showing the positions that were used to determine the dimensional uniformity of gelcast silicon nitride samples.

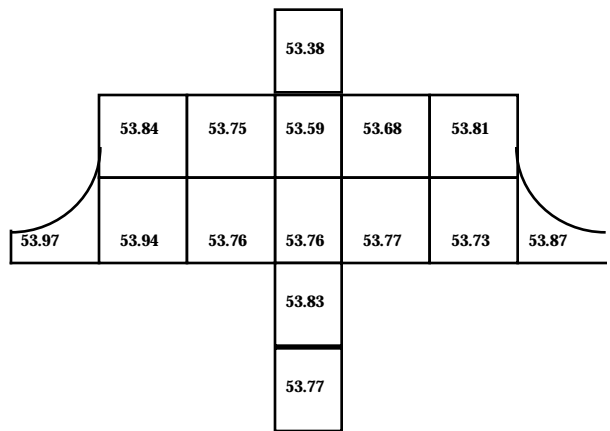


Figure 10. The green density in a dried, gelcast, seven-inch-diameter silicon nitride rotor was very uniform. The average density was 53.77%_{th}. One measurement (53.38%) was 0.4% below the average. All the other values were within $\pm 0.2\%$ of the average density. Data courtesy of J. Pollinger, AlliedSignal Ceramic Components, Torrance, California.



Figure 11. Gelcast silicon nitride can be easily machined in the green state and then fired to full density. Machining was accomplished on a computer controlled three-axis milling machine. (Techno/Isel Series Three CAM Production Center, New Hyde Park, NY)