PII: S0955-2219(96)00147-1

Gelcasting: From Laboratory Development Toward Industrial Production

Ogbemi O. Omatete, Mark A. Janney & Stephen D. Nunn

Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6087, USA

Abstract

Gelcasting, a ceramic forming process, was developed to overcome some of the limitations of other complex-shape forming techniques such as injection molding and slip casting. In gelcasting, a concentrated slurry of ceramic powder in a solution of organic monomers is poured into a mold and then polymerized in situ to form a green body in the shape of the mold cavity. Thus, it is a combination of polymer chemistry with slip processing and represents minimal departure from standard ceramic processing. The simplicity of the process has attracted industrial partners and by collaboration between them and the developers, the process is being advanced from the laboratory toward industrial production. © 1996 Elsevier Science Limited.

1 Introduction

The advantages of advanced ceramics over metals in harsh environments have led to extensive research in the last three decades to improve their reliability. That research has resulted in the development of toughened, more reliable ceramics. For example, silicon nitride[1] which is considered the most suitable ceramic for advanced heat engines, has been produced with an average tensile strength of 1 GPa and Weibull modulus of 13. Nevertheless, the production cost of silicon nitride parts compared to similar metal parts has remained prohibitive. Not only has the high purity ceramic powder used been expensive, but the shaping process to produce the desired parts has also been costly.[2,3] Consequently, about a decade ago, the Oak Ridge National Laboratory (ORNL), as part of its ceramic program, initiated a project to develop a new forming process.

The initial step was to evaluate the methods, current at the time, for making complex-shaped advanced ceramics. These include machining, injection molding, slip and pressure casting.[4–6]

Machining of green and fired parts can be used to produce any desired shape but is very expensive especially for fired parts. Where possible it should be avoided or minimized. Injection molding is the shape-forming process of choice for making complex-shaped ceramics. It has the following drawbacks: long binder removal times (up to seven days), thick section cracking, size limitations (< 3 cm diameter), and defects such as knit lines, short shots, flashing, sink marks, and thermal strains. For larger sizes, slip casting or pressure casting is used. Slip casting is a slow process with long forming times (hours), density variations, and is labor-intensive. Pressure casting is a modification of slip casting to improve the rate of casting.

Injection molding, slip casting and pressure casting all depend on the flow of a fluid slurry to fill the mold, followed by a process to harden the slurry. The problems with injection molding arise because the fluid flow required to fill the mold competes with heat transfer which is required to harden the slurry.[7] What is needed, therefore, is a process that separates these two steps and facilitates the removal of the vehicle that carries the ceramic powder.

Because injection molding is the leading forming process, several modifications or alternatives have been developed to overcome its limitations. Binderless injection molding,[8] which uses the freeze casting of water-based slurries and freeze-drying; methylcellulose gelation,[9] which utilizes the reversible inverse thermal gelation of methylcellulose (gels on heating); and agar gelation,[10] which depends on the gelation of aqueous agarose solution on cooling; all are modifications of injection molding. New forming processes which are alternatives to injection molding include: pressure casting,[11] which is a combination of slip casting and filter pressing and depends on proprietary polymeric filter materials; reversible deflocculation,[12] which is based on a degradable dispersant; direct coagulation casting,[13] which is based on enzyme catalyzed reactions; and gelcasting, which is reviewed here.

Whereas the modifications to injection molding discussed above represent improvements on the long binder burnout times, they still bear other inherent drawbacks of the process, such as size limitation. Pressure casting like slip casting has problems with density variation in large parts. Thus, about a decade ago, the need for a new process that reduced these limitations was still apparent. The objective at ORNL was, therefore, to develop a low-cost, high-reliability ceramic forming process that can produce near-net-shape parts with large sections.

2 New Process: Gelcasting

Gelcasting was developed at ORNL by combining traditional slip processing with polymer chemistry. In gelcasting, a concentrated slurry of ceramic powder in a solution of organic monomers is poured into a mold and then polymerized in situ to form a green body in the shape of the mold cavity. The monomer solution provides a low-viscosity vehicle to transport the fluid slurry into the mold and the polymer gel holds the ceramic powder in the desired shape. This process separates the mold filling step from the setting of the mix. Vinyl monomers are used in the process and, because they undergo a free-radical chain polymerization reaction, the setting is very rapid. The vehicle removal is in two steps: drying to remove the solvent (water) followed by pyrolysis to remove the polymer. The part is then fired to densify it.

The initial gelcasting process was developed by dissolving multifunctional acrylate monomers in organic solvents.[4,14] These monomers when polymerized by free-radical initiators formed highly crosslinked polymer–solvent gels. When ceramic powder was slurried in this organic solution and cast into a mold and polymerized, the gel held the powder in the shape of the cavity of the mold. The green body was air-dried, the binder was burned off, and the part was sintered to full density. The gelcasting concept was successfully demonstrated. In anticipation of environmental problems and the additional costs of the removal of the organic solvent, and because most ceramists prefer to work in water, an effort was begun to use water as the solvent.

The search for water-soluble monomers led to the acrylamide gel system which is used in biotechnology for gel electrophoresis. The acrylamide system produced excellent results, and became the standard gelcasting system.[15,16] Aqueous gelcasting, where the solvent is water, and nonaqueous gelcasting, where the solvent is organic had, thus, been successfully developed. The initial detailed
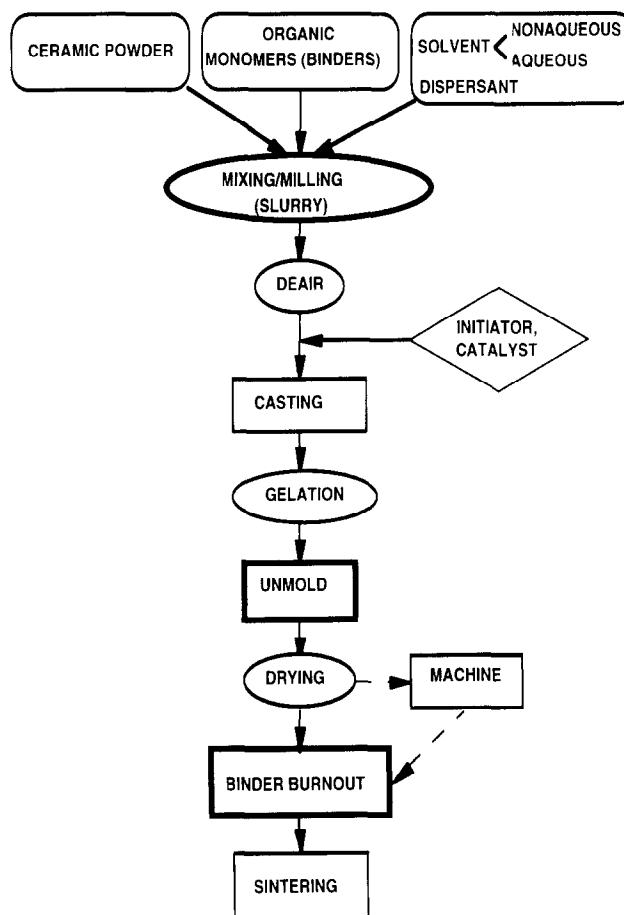

Fig. 1. Detailed flowchart of the gelcasting process.

studies of aqueous gelcasting were carried out using alumina.[5] The acrylamide system established aqueous gelcasting as a major advanced ceramic forming process[4] and demonstrated some of its advantages. Figure 1 shows the detailed flowchart of the gelcasting process which is quite similar to a standard slip process. Instead of the usual polymer binder system, the binders here are monomers and initiator/catalyst is added later to effect the in situ polymerization.

It is important to distinguish gelcasting from the sol–gel process. In gelcasting, a high solids loading of a commercial powder in a solution of organic monomers is poured into a mold and then polymerized into an organic gel which holds the powder together. In sol–gel, the solid is usually produced as part of the process in the form of an inorganic gel with low solids loading.

3 Key Aspects of Gelcasting

3.1 Premix solution

The premix solution is the solution of organic monomers in which the ceramic powder is suspended. It usually consists of a solvent which determines if the process is aqueous or nonaqueous

gelcasting, and two types of organic monomer. The main monomer has a single double bond and, if polymerized alone, forms a linear polymer. The second monomer is the crosslinking monomer which has at least two double bonds. When they are polymerized together, a crosslinked, polymer–solvent gel results. In the acrylamide system the monomer is acrylamide (AM) and the crosslinker is N,N'-methylenebisacrylamide (MBAM); the standard premix solution contains 15 wt% total monomers in water with the mass ratio of AM to MBAM set at 24:1. In a typical 50 vol% suspension of Al_2O_3, after drying, the polymer is less than 4 wt% of the green body.

3.2 Low-toxicity monomers

Although acrylamide gels have been used for decades in biology for gel electrophoresis in DNA and other analyses, and the polymer itself is safe, the acrylamide monomer is neurotoxic. A concerted research effort was undertaken to find less toxic monomers to replace acrylamide. With the assistance of an industrial hygienist, several monomers were examined based on their environmental, safety and health implications. The most important factor was the health hazard rating (4 = Extreme, 3 = High, 2 = Moderate, and 1 = Low). Acrylamide, which has the highest health hazard rating of 4, has been replaced by methacrylamide with a moderate rating of 2. The crosslinking monomer is either the MBAM (rating = 2) or poly(ethylene glycol) dimethacrylate (rating = 1).

3.3 Rheology of gelcasting slurries

In gelcasting, the solids loading of the slurry becomes the green density of the cast part. Consequently, it is important to have as high a solids loading as possible in the slurry. For advanced ceramics, to have uniform grain growth and acceptable final properties, narrowly dispersed submicron powders are used in the suspensions. In addition, high solids loading minimizes shrinkage and warpage during drying and enhances high sintered density. Therefore, in gelcasting, it is desirable to have a suspension with at least 50 vol% solids which is fluid and pourable. This necessitated several studies[17–20] on the rheology and characterization of gelcasting slurries. The dispersants for gelcasting slurries of alumina were evaluated,[21] and anionic polyelectrolytes were found to be the best. In all the studies, the organic monomers either had negligible effect on the dispersion or enhanced it slightly.

3.4 Drying of gelcast parts, binder burnout, and sintering

The drying of gelcast parts[22] was investigated in order to reduce the drying time, the slowest step

in the gelcasting process. There was no constant-rate drying period at any drying temperature. To avoid warpage and cracking caused by unrelieved stresses in the body, the drying of gelcast ceramics had to be at high relative humidities. Furthermore, it was found that shrinkage stopped early in the drying process when particle-to-particle contact had been established while the body continued to dry for a much longer time. Therefore, to decrease the drying time while minimizing unrelieved stresses, the initial drying is done at high relative humidities (> 90%) until shrinkage has stopped. Then the drying rate is increased either by raising the drying temperature, or decreasing the relative humidity, or a combination of both.

The drying is isotropic and the linear shrinkage for typical 50 vol% solids loading is about 3%. Shrinkage was much less for higher solids loading and is negligible at ~70 vol% solids loading. After drying, the binder left in the green body is typically less than 4 wt%.

The investigation of the binder burnout in air using thermogravimetric and differential thermal analyses (TGA/DTA) shows that all the binders come off primarily as complete combustion products, CO_2 and H_2O. The pyrolysis of the polymer is complete for Al_2O_3 green parts at below 600°C. Pyrolysis in N_2 leaves a residue of about 6 wt% of the polymer. Further studies which will be published later indicate that the burnout temperature depends on the ceramic involved. For example, gelcast nickel–zinc ferrite has a lower burnout temperature than Al_2O_3.

Gelcast parts were readily sintered to full density. The controlling parameter is the initial solids loading which should be high enough to produce an acceptable green density.

3.5 Mold materials and complex shapes

Molds for gelcasting have been made from several materials: metals, glass, wax, and plastics. This means that molds of very complex shapes can be made from inexpensive materials. The turbine wheels shown in Figs 2 and 6 were gelcast using wax molds. The wax molds were then melted or dissolved from the gelled wet body. The complexity of shape attainable by gelcasting is limited only by the ability to design the mold. In addition, because gelcasting produces an isotropic body, it is ideal for the preparation of near-net shapes.

3.6 Green strength of dried gelcast parts

A beneficial result of the gelcasting process is the high strength of the dried body. In a study[23] of green strengths, gelcast parts had tensile strengths of over 3 MPa, which was more than five times those of typical dry pressed powder. Gelcasting was
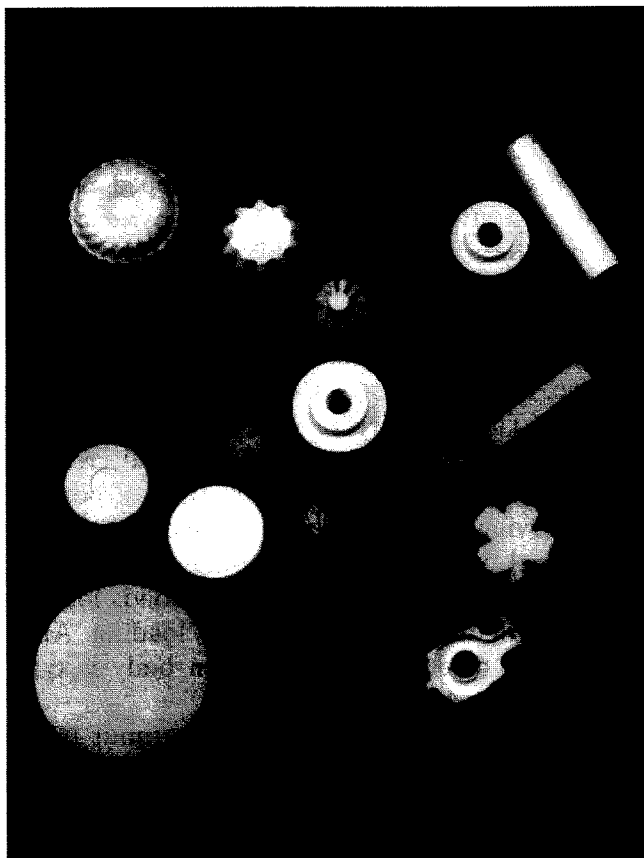
Fig. 2. Various ceramic shapes formed by gelcasting.

developed for near-net complex shapes. How-
ever, because of their high green strength, gelcast
parts can be green-machined inexpensively into
even more complex shapes. In addition, holes
~0·25 mm have been drilled through dried gelcast
parts.

The high green strength of gelcast parts has led
to interest in using gelcast parts in an aspect of
rapid prototyping. A block of dried gelcast part is
green-machined in a CNC (computer-numeric-
control) machine to a desired complex shape and
then sintered.

3.7 Gelcasting is simple, does not change material's properties

The flow chart of Fig. 1 shows the simplicity of
the process. It does not require any special equip-
ment and represents minimal departure from stan-
dard ceramic processing. Gelcasting does not
affect the properties of the sintered materials. Fig-
ures 3 and 4 show the fracture surfaces of gelcast
silicon nitride (Ube E10) and alumina (RC-HP
DBM), respectively. The silicon nitride has a
mean strength of 622 MPa and Weibull modulus
of 15 and shows uniform elongated grain struc-
ture. The alumina has strength of 450–525 MPa
and shows a mixed fracture mode. As in other slip
processes, efficient deairing of the slip and careful
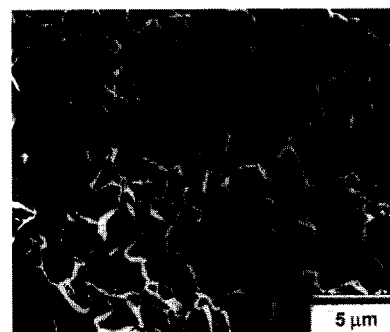mold filling are required to avoid the introduction

Fracture Surface
Ube E-10 Si₃N₄ 6 wt.% Y₂O₃/2 wt.% Al₂O₃
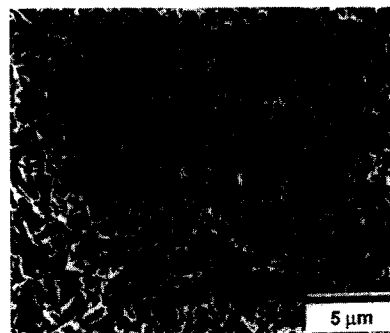
Four-Point Bend Strength = 622±49 MPa
Weibull Modulus = 15
Fracture Toughness = 7 MPa√m

Fig. 3. Fracture surface of sintered gelcast silicon nitride (Ube E10).

Fracture Surface
RC-HP DBM Al₂O₃

Four-Point Bend Strength = 450-525 MPa
Mixed fracture mode.

Fig. 4. Fracture surface of sintered gelcast alumina (RC-HP DBM).

of defects which may limit the strength and other
physical properties of sintered gelcast materials.

3.8 Gelcasting is a generic process

Monolithic ceramics that have been gelcast include:
Al_2O_3, ZrO_2, Si_3N_4, SiC, Si, Al_2TiO_5, SnO_2, NZP
(low thermal expansion ceramic), SiAlON, ferrites
and others, such as refractory mixtures. Nicalon
fiber-reinforced RBSN[24] (reaction bonded silicon
nitride), and Al_2O_3–ZrO_2[25] composites have been
gelcast. Recently, the process has been extended to
powder metallurgy. Figure 5 shows a variety of
parts which were gelcast from superalloy powders.

4 Development toward Industrial Production

4.1 Cooperative research and development agreements (CRADA)

Gelcasting technology transfer workshops were held
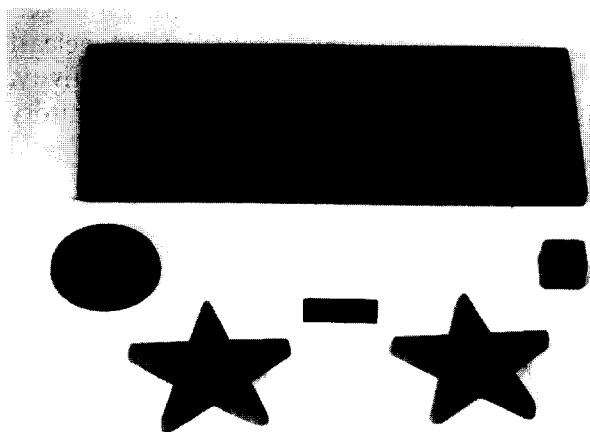at ORNL in 1990 and 1991, to which US-based

Fig. 5. A variety of shapes gelcast from superalloy powder.

companies were invited. Meanwhile, a modus operandi for collaborative research between companies and ORNL for technologies developed at ORNL was introduced. It was called a Cooperative Research and Development Agreement (CRADA), in which the participating company shared research efforts with ORNL and each provided matching financial outlay to support its activities. In addition, the company could license and use the technology.

Several companies have signed CRADAs to evaluate the gelcasting process, and some of them have now been completed. At this time, ORNL is working on other gelcasting CRADAs. These include the following activities: gelcasting of ferrite powders for soft magnets, fabrication of complex ceramic shapes to be infiltrated with molten metal for ceramic-reinforced metal composites, production of complex-shaped SiC parts for Si wafer processing, production of Al_2TiO_5 parts for exhaust portliners, and rapid prototyping using gelcasting slurries in an injection stereolithography process.

4.2 Collaborative work with AlliedSignal Ceramic Components (ASCC)

AlliedSignal Ceramic Components (ASCC) in California fabricates Si_3N_4 components for turbomachinery in aerospace, industrial and automotive gas turbine applications. ORNL has had a long and continuing collaborative investigation with ASCC in the gelcasting of Si_3N_4 powder for the fabrication of turbine parts. The initial cooperative research was for the gelcasting of their GN10 Si_3N_4 formulations. ASCC used those studies to evaluate gelcasting and to compare it to slip casting which they were using to fabricate large Si_3N_4 turbine wheels. They showed that the two processes produced parts with similar strength (σ) and Weibull moduli (m), (slipcast: $\sigma = 954$ MPa,

$m = 18.9$, gelcast: $\sigma = 1017$ MPa, $m = 15.5$). However, gelcast parts have significantly less density variation, a major advantage. Over 50 mm $\times$ 76 mm $\times$ 38 mm (2" $\times$ 3" $\times$ 1.5") Si_3N_4 plates, the density variation for slipcasting was 2.8% compared to just 0.8% for gelcasting. These results heightened their interest in gelcasting.

In 1992, a three-year project funded by the National Institute of Science and Technology's (NIST) Advanced Technology Program (ATP) began between ORNL and ASCC to work toward commercialization of gelcasting. This project involved the investigation of all aspects of gelcasting including finding low-toxicity monomers. As part of the project and in anticipation of industrial-level production of ceramic parts by gelcasting, ASCC invited one of the researchers in gelcasting at ORNL to spend three months at their company. The researcher became involved in the scale-up study at ASCC.

A major undertaking during the researcher's visit was to optimize the gelcasting of large batches of Si_3N_4 formulations.[26] A Taguchi statistical $L_8(4^1 \times 2^4)$ design was used in the optimization. The factors at two levels were: the total monomer concentration, the monomer/crosslinker ratio, the initiator concentration, and the initiator/catalyst ratio; the factor at four levels was the initiator concentration per mass of the slip. The primary criterion used to determine optimum design was the green strength of the dried parts which was shown to have increased by 80% at the optimum (4.3 MPa versus 2.4 MPa, the initial value). Also, during the three months' interaction, it was shown that the dried gelcast Si_3N_4 part was strong enough to withstand green-machining.

ASCC has been impressed with the simplicity and robustness of the gelcasting process[27] and continues to work with it. Figure 6 shows silicon nitride turbine components that ASCC has formed by gelcasting. ASCC has now licensed the process to fabricate Si_3N_4 components for different

Fig. 6. Silicon nitride turbine components formed by AlliedSignal Ceramic Components using the gelcasting process.

applications by gelcasting. They plan to use gelcast parts in some of their initial tests, preparatory to trials for more rigorous applications.

A follow-up project has been initiated by ASCC to commercialize the manufacturing of silicon nitride turbomachinery parts by gelcasting. It involves the creation of a consortium of federal and state governments, a producer of the powder, manufacturers and consumers of turbomachinery components, university and private interests, and ORNL which will act as consultants on gelcasting. At the end of the two-year project, the feasibility of the commercialization of the gelcasting of silicon nitride turbomachinery parts should have been determined.

4.3 Other licenses

Several CRADAs are in place. If the results of these investigations satisfy the companies, they may decide to license the process for their use. LoTEC, Inc. of Salt Lake City, Utah was so impressed after only a brief trial of the gelcasting process using sodium zirconium phosphate (NZP), a low thermal-expansion ceramic, that they have signed a license to produce gelcast NZP components. Currently, only US-based companies may license inventions from the Department of Energy National Laboratories.

5 Conclusions

Gelcasting is a ceramic process developed at the Oak Ridge National Laboratory in an effort to reduce the cost of shaping advanced ceramic parts. Because it replaces the polymer binders in processes such as injection molding, slip casting or dry pressing with monomers which are polymerized *in situ* after casting, it has separated the mold filling step from the setting step. Thus gelcasting has several advantages.

The process is generic and has been adapted to a variety of monolithic and composite ceramic parts and is now being extended to powder metallurgy. It produces not only near-net-shaped parts, but also complex shapes limited only by the mold design. Gelcasting uses a variety of mold materials: wax, plastic, glass or metals, which facilitates the production of complex shapes. It represents a minimal departure from standard ceramic processing. Dried gelcast parts are durable and are readily machinable to even more complex shapes.

Because gelcasting is simple and inexpensive, many companies are investigating its usefulness in their ceramic-forming process. Two companies have licensed the technology and six are participating in CRADAs with ORNL. Others are exploring rapid prototyping using either the gelcasting slurry or the machinable, dried gelcast parts. As a result of this interest and activity, gelcasting is gradually moving from the laboratory development toward industrial applications and production.

References

1. Pujari, V. K., Tracey, D. M., Foley, M. R., Paille, N. I., Pelletier, P. J., Sales, L. C., Wilkens, C. A. & Yeckley, R. S., Reliable ceramic for advanced heat engines. *Am. Ceram. Soc. Bull.* 74(4) (1995) 86–90.
2. Sheppard, L. M., Cost-effective manufacturing of advanced ceramics. *Am. Ceram. Soc. Bull.*, 70(4) (1991) 692–701.
3. Das, S. & Randall Curlee, T., The cost of silicon nitride powder and the economic viability of advanced ceramics. *Am. Ceram. Soc. Bull.*, 71(7) (1992) 1103–1111.
4. Omatete, O. O., Janney M. A. & Strehlow R. A., Gelcasting — A new ceramic forming process. *Am. Ceram. Soc. Bull.*, 70(10) (1991) 1641–1649.
5. Young, A. C., Omatete, O. O., Janney M. A. & Menchhofer, P. A., Gelcasting of alumina. *J. Am. Ceram. Soc.*, 74(3) (1991) 612–618.
6. Terpstra, R. A., ed., *Ceramic Processing.* Chapman & Hall, London, 1995.
7. White, J. L. & Dee, H. B., Flow visualization for injection molding of polyethylene and polystyrene melts. *Poly. Eng. Sci.*, 14 (1974) 212–222.
8. Novich, B. E., Sundback, C. A. & Adams, R. W., Quickset injection molding of high performance ceramics. *Ceram. Trans.*, 26 (1992) 157–164.
9. Rivers, R. D., Method of injection molding powder metal parts. *U.S. Patent* 4113480 (1976).
10. Fanelli, A. J., Silvers, R. D., Frei, W. S., Burlew, J. V. & Marsh, G. B., New aqueous injection molding process for ceramic powders. *J. Am. Ceram. Soc.*, 72 (1989) 1833–1836.
11. Blanchard, E. G., Pressure casting improves productivity. *Am. Ceram. Soc. Bull.*, 70 (1991) 1294.
12. Crutchfield, M. M., Reversible deflocculation of clay slurries. *US Patent* 4327189 (1982).
13. Graule, T. J., Baader, F. H. & Gauckler, L. J., Shaping of ceramic green compacts direct from suspensions by enzyme catalyzed reactions. *Ceram. Forum Intl. DKG.* 71(6) (1994) 317–323.
14. Janney, M. A., Method for forming ceramic powders into complex shapes. *US Patent* 4894194, 1990.

15. Janney, M. A. & Omatete. O. O., Method for molding ceramic powders using water-based gel casting. *US Patent* 5028362, 1991.

16. Janney, M. A. & Omatete, O. O., Method for molding ceramic powder using a water-based gelcasting process, *US Patent* 5145908, 1992.

17. Omatete. O. O., Young, A. C., Janney, M. A. & Adair, J. H., Investigation of dilute gelcasting alumina suspension. *Am. Ceram. Soc. Trans.* **12** — *Ceramic Powder Science III* (1990) 537–544.

18. Bleier, A., Omatete, O. O. & Westmoreland, C. G., Rheology of zirconia–alumina gelcasting slurries. *Mat. Res. Soc. Symp. Proc.*, **271** (1992) 269–275.

19. Bleier, A., Omatete, O. O. & Westmoreland, C. G., Rheology and microstructure of concentrated zirconia–alumina suspensions for gelcasting composites. *Mat. Res. Soc. Symp. Proc.*, **289** (1993) 109–115.

20. Omatete, O. O. & Bleier, A., Tailoring suspension flow for the gelcasting of oxide and nonoxide ceramics. *Mat. Res. Soc. Symp. Proc.*, **346** (1994) 357–363.

21. Omatete, O. O. & Bleier, A., Evaluation of dispersants for gelcasting alumina. In *Dispersion and Aggregation: Fundamentals and Applications*, eds B. M. Moudgil & P. Somasundaran. Engineering Foundation, New York, 1994.

22. Omatete, O. O., Strehlow, R. A. & Walls, C. A., Drying of gelcast ceramics. *Trans. Am. Ceram Soc.*, **26** (1992) 101–117.

23. Nunn, S. D., Omatete, O. O., Walls, C. A. & Barker, D. L., Tensile strength of dried gelcast green bodies. *Ceram. Eng. & Sci. Proc.*, **15** (1994) 493–498.

24. Omatete, O. O., Tiegs, T. N. & Young A. C., Gelcast reaction-bonded silicon nitride composites. *Ceram. Eng. & Sci. Proc.*, **12** (1991) 1257–1264.

25. Omatete, O. O., Bleier, A., Westmoreland, C. G. & Young, A. C., Gelcast zirconia–alumina composites. *Ceram. Eng. & Sci. Proc.*, **12** (1991) 2084–2094.

26. Omatete, O. O., Pollinger, J. P. & O'Young, K., Optimization of the gelcasting of a silicon nitride formulation. *Ceram. Trans.*, **56** (1995) 337–343.

27. Pollinger, J. P., Improved silicon nitride materials and component fabrication processes for aerospace and industrial gas turbine applications. ASME Paper 95-GT-159, American Society of Mechanical Engineers, 1995.