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Journal of the European Ceramic Society 31 (2011) 2569–2591

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Recent developments in gelcasting of ceramics

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Abstract

Gelcasting is a well-established colloidal processing method with a short forming time, high yields, high green capacity and low-cost machining, and has been used to prepare high-quality and complex-shaped dense/porous ceramic parts. In this article, we reviewed recent developments in gelcasting technology for ceramic preparation. For environmental pollution reduction during ceramic preparation by gelcasting, the development of low-toxic and nontoxic gelcasting systems is discussed. The occurrence and control of inner stress and surface-exfoliation in ceramic green bodies prepared by gelcasting are analyzed, and then some methods to control and eliminate the inner stress and surface-exfoliation in ceramic gelcast green bodies, especially for colloidal injection molding of ceramics (CIMC) are proposed. Finally, the applications of gelcasting for the fabrication of porous ceramics and complex-shaped ceramics (e.g., microbeads, rutile capacitor, thin-wall rutile tube, refractory nozzle) are summarized.

Keywords: Gelcasting; Shaping; Suspension; Defects

1. Introduction

The wet-processing route is one of the most promising methods for producing high-quality ceramics. Compared to dry processing, wet processing can better control particle–particle interactions and increase the homogeneity of particle packing in the wet stage, and then less and smaller defects exist in the ceramic microstructures.[1] In past decades, many researchers have focused on the study of the process optimization for the increase of the ceramic reliability, and have demonstrated that colloidal processing was one of the most promising ways to increase the ceramic reliability.[2–6] Colloidal forming includes slip casting, tape casting, direct coagulation casting, injection molding, gel-casting and so on.[7–10] Colloidal forming can solidify fine particles to form ceramic green bodies, significantly improve the micro-structure and the uniformity of ceramic green bodies, and reduce the production costs for advanced ceramics,[11,12] thus the processing has been successfully applied to improve ceramic reliability.

Gelcasting is a well-established colloidal processing method for making high-quality, complex-shaped ceramic parts by means of in situ solidifying through which a macromolecular network is created to hold the ceramic particles together.[13] Gelcasting is a near-net-shape technology. During gelcasting, the macromolecular gel network results from the in situ polymerization of organic monomers added in the suspensions to hold the ceramic particles together, and the strong particle gel can develop sufficient strength to support their own weight and thus can be handled without shape distortion.[14–18] The typical route of the gelcasting process is preparing suspensions with high solid loading and low viscosity, and then solidifying the suspension cast in a pore-free mold. The green bodies prepared with the gelcasting process have a similar homogeneous microstructure like the precursor suspensions, such that the structure homogeneity and the reliability of ceramics are improved. In order to take full advantage of the gelcasting process, this paper primarily reviewed the development and applications of gelcasting.

2. Gelcasting principle

The gelcasting process was first developed in the Metals and Ceramics Division-Ceramic Processing Group at Oak Ridge National Laboratory (ORN), Oak Ridge, USA by Omatete and Janney during the 1990s.[17,19–22] The gelcasting process is based on a synthesis of ideas stemmed from traditional ceramics and from polymer-chemistry, and the generic principle is that monomers react to form polymers and create a 3D network that freezes the suspended particles in the desired shape. Gelcasting

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doi:10.1016/j.jeurceramsoc.2010.12.035

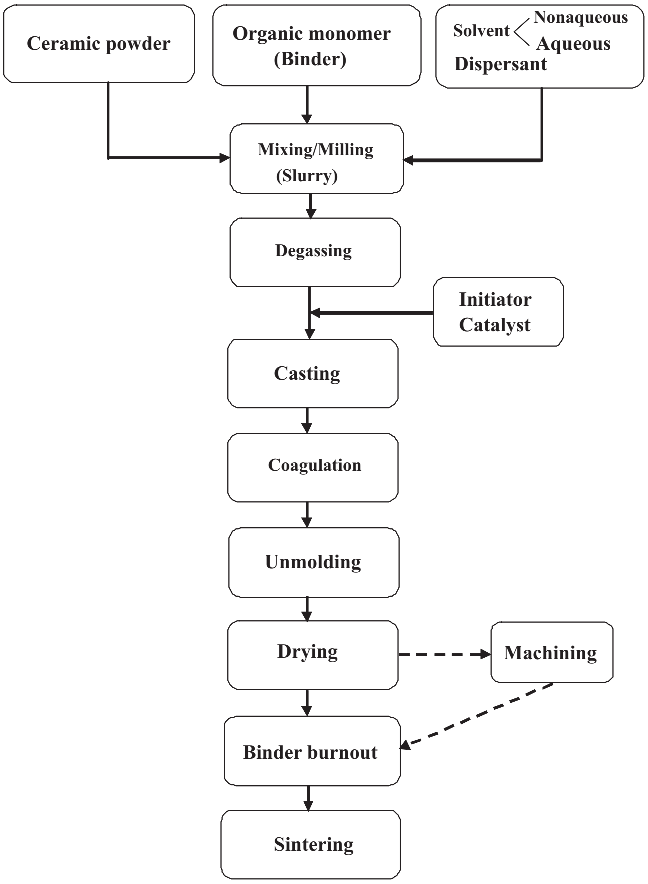

Fig. 1. Detailed flowchart of gelcasting process.

overcomes many limitations associated with forming methods, such as injection molding (e.g., long binder removal time and/or flaw generation during binder thermolysis) and slip casting (e.g., slow casting rates, inadequate strength for green machining) suitable for the complex shape fabrication by offering short forming times, high yields, high green capacity, and low-cost machining.[22–26]

During gelcasting, ceramic powders are dispersed in an aqueous solution containing a monomer, cross-linker, free radical initiator and catalyst to form a fluid and castable slurry; the slurry is poured into an appropriately designed mold and polymerized in situ to form a polymer–water gel that immobilizes the dispersed ceramic powder particles in the shape of the mold cavity. The gelled part with uniform chemistry and density is removed from the mold while still wet, and then the wet gelled part is dried in controlled conditions to the dried green body. The dried green body is strong enough to be machined.[24] Binder removal and sintering take place as in other ceramic processes. The detail of gelcasting process is shown in Fig. 1.

Like other polymer systems, some of the gelcasting components are reactive (e.g., oxidizer, corrosive, flammable, toxic) chemicals, and the environmental release of organic components and some monomers exhibit a capacity to sensitize exposed workers, and all are potentially irritating.[27] Therefore, gel system selection is very crucial.

During gelcasting, gelation and drying may induce the inner stress and microcracks in the green body, which influences the reliability of ceramic parts. The larger the ceramic part, the more harmful the stress. In the meantime, the polymerization of an acrylamide–*N*,*N*′-methylenebisacrylamide system is a free-radical reaction in which the surface-exfoliation phenomenon in gelcasting in air is unavoidable due to the inhibition of oxygen, and it influences the physical performance of the green body. Therefore, it is important to minimize the inner stress in the green bodies during the gelcasting of large ceramic parts and to avoid the surface-exfoliation phenomenon.

Gelcasting was mainly designed for the fabrication of dense ceramics since gelcasting was invented. Up to now, gelcasting is gradually applied to the fabrication of porous ceramics and complex-shaped ceramic parts.

The following sections will discuss the research progress of low-toxic/nontoxic gelcasting systems, the control methods for reducing defects in green bodies, and the application of gelcasting.

3. Development of the low-toxic/nontoxic gelcasting systems

In the forming process of gelcasting, two kinds of slurry were used – an aqueous and a non-aqueous slurry – by scientists at Oak Ridge National Laboratory (ORNL).[14] Both nonaqueous and aqueous solvents can be used for gelcasting, but the aqueous system is preferred because the water has many advantages (e.g., less departure from traditional ceramic processing and no environmental problems for disposal). In aqueous gelcasting, acrylic acid and acrylamide (AM) are commonly used to make monomer solutions. Since acrylic acid and water cannot completely dissolve in each other, a cosolvent needs to be added, the premixed solution may be partly gelated, and a high solid loading in acrylic acid system is difficult to be achieved. In the meantime, the main component of the commonly used monomer acrylamide system is a neurotoxin,[28] which limits the application of acrylamide system. At present, more and more researchers study low-toxicity or nontoxic gelcasting system other than acrylamide to reduce environmental pollution. However, a lot of experiments have demonstrated that the acrylamide–*N*,*N*′-methylenebisacrylamide (AM–MBAM) system can be more easily controlled during gelcasting due to its good gelation properties.

3.1. Low-toxic gelcasting system

Low-toxic/nontoxic gelcasting systems were developed with similar or superior properties to the previously used acrylamide–*N*,*N*′-methylenebisacrylamide (AM–MBAM) system.[28] Janney et al. (1998) reported that the system of methacrylamide–*N*,*N*′-methylenebisacrylamide (MAM–MBAM) monomers was suitable for aqueous gelcasting and was much lower in toxicity as compared to the original acrylamide (AM) system,[14,29] and that the green body possessed sufficient strength to permit machining.[30,31]

3.2. Nontoxic gelcasting system

Many nontoxic gelcasting systems were developed,[32–36] and the solidification mechanisms of these gelcasting systems can be categorized into two groups: the chemical effect mechanism of the dispersed medium and the physical effect mechanism of dispersed medium. All these systems include cross-linking of polymers by 2-hydroxyethyl methacrylate (HEMA),[37] cross-linking of polymers by metal ion complexation,[38,39] temperature activated cross-linking of polymers (e.g., agarose and carrageenans),[40–44] thermoreversible gelation of biopolymers[45] and freeze casting.[46]

3.2.1. Gelation by the chemical effect of a dispersed medium[47]

3.2.1.1. Cross-linking of polymers by 2-hydroxyethyl methacrylate (HEMA). 2-Hydroxyethyl methacrylate ($CH_2=C(CH_3)COOCH_2CH_2OH$, HEMA) is a water-soluble nontoxic reagent, and is prone to polymerization due to the vinyl bond in its molecule and the hydroxyl group that makes it possible to form a water-compatible polymer. Cai et al.[48] investigated the novel gelcasting system using HEMA as the monomer and ethylene dimethacrylate (EDMA) as a crosslinking agent for the preparation of alumina ceramics. The bending strength of the prepared green alumina body was as high as 18 MPa, and the microstructure of the green body was highly homogeneous. Dense complex-shaped ceramic parts were produced through the new gelcasting system, and it indicates that HEMA was a very promising monomer for gelcasting of ceramics. However, in this experiment, a small portion of the green bodies might show a much lower strength (~8 MPa as minimum) than the average strength value (18 MPa) because of the heterogeneity of the HEMA hydrogel network. Polyvinyl pyrrolidone (PVP) is a low-toxic organic reagent with the hydrophilic C=O group, and thus it is water soluble and can form hydrogel. Adoption of PVP as a synergistic gel-forming reagent can resolve the problem of wide strength distribution in green bodies formed by the HEMA system.[49] Additionally, the surface exfoliation phenomenon that seems inherent to the AM gelcasting system was also successfully eliminated in the HEMA–PVP system.[50] Analysis of the interaction between HEMA and PVP suggested that the improved microstructure and strength homogeneity, as well as the elimination of surface exfoliation in the new system, were mainly due to their ability to form intermolecular hydrogen bonding, which greatly improved the homogeneity of the entire poly-HEMA (PHEMA)–PVP co-gel and prevented phase separation and oxygen diffusion.

3.2.1.2. Cross-linking of polymers by metal ion complexation. Morissette and Lewis[38] investigated a harmless gelcasting system, poly(vinyl alcohol) (PVA) suspensions cross-linked by an organotitanate coupling agent. In the process, partially hydrolyzed PVA absorbed on the surface of the ceramic powders was used as the binder phase, and the chains of PVA were cross-linked by the incorporation of an organotitanate coupling agent containing 8.3% titanium by weight (Tyzor TE), which transformed the suspension into a rigid green body, as shown in Fig. 2.

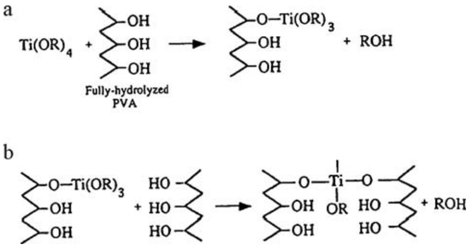

Fig. 2. Schematic illustrations of the proposed cross-linking reaction: (a) the representative chemical structure for the organotitanate coupling agent, Tyzor TE and (b) the proposed cross-linking reaction between Tyzor TE and PVA.

Alginate is a type of gelling polysaccharide, and schematic illustrations of the representative chemical structure for alginate are shown in Fig. 3(a). It can dissolve in water at room temperature and undergo chemical gelation to form a three-dimensional (3D) network in the presence of multivalent cations (e.g., calcium) at increased temperature after being cast.[51] The mechanism of cross-linking in alginate gels can be considered in terms of an "egg-box" model involving cooperative bonding of calcium ions between aligned polyguluronate ribbons (see Fig. 3(b)). Calcium iodate has been applied in this process. It has low solubility at room temperature and high solubility at increased temperatures above 60 °C. Thus, the gelcasting process can be controlled through the heating rate and the final temperature. Xie et al.[52–57] used the natural nontoxic polymer–sodium alginate (Na-alginate) to coagulate the alumina ceramic suspension. During the gelcasting process, calcium iodate was added into the alumina suspension that was dispersed in a sodium alginate solution. The suspension was stable at room

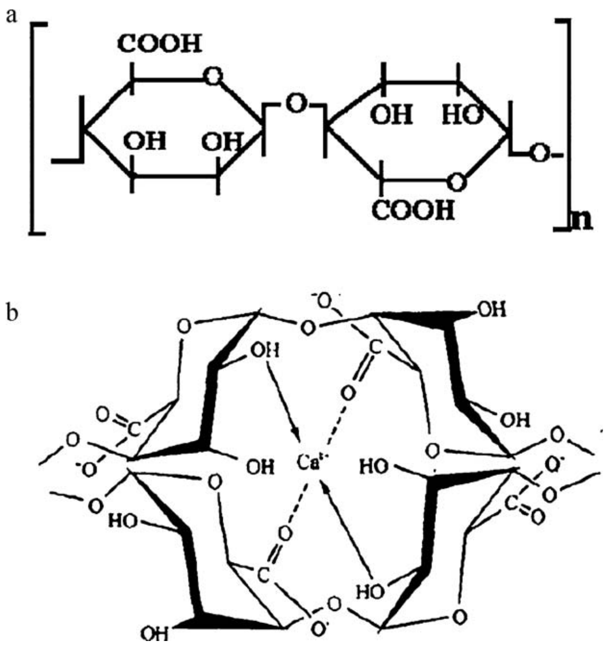

Fig. 3. Schematic illustrations of the representative chemical structure for alginate (a) and the "egg-box" model involving cooperative bonding of calcium ions between aligned polyguluronate ribbons (b).

temperature, but it solidified with increasing temperature. In the process, the released calcium ions bonded the alginate molecular chains after the mixture was heated three-dimensional network structure was formed, and then the alumina ceramic green body was fabricated by the proposed method.

Generally, when calcium salts are added into a sodium alginate solution, they will form gels very quickly through reaction between calcium ions and sodium alginate, as shown in Eq. (1). It is difficult to control the gelation rate between calcium salts and alginate, which makes it impossible to complete well casting processes at suitable period by adjusting the heating rate and the final temperature.[52] Gelation occurs during casting with a fast gelation rate and thus results in various cross-linking densities and heterogeneity within the gel. In order to complete the casting process under control, a controllable reaction of calcium salts with sodium alginate must be employed. Here, the reaction rate can be adjusted by sequestrant ($(\mathrm{(NaPO_3)_6})$) and hexanedioic acid ($C_6H_{10}O_4$).[53] In the process, if $Ca_3(PO_4)_2$ and $(NaPO_3)_6$ were added into the ceramic suspensions simultaneously, the gelation reaction between calcium salts and sodium alginate would be avoided because a stable complex is formed from the reaction between $(NaPO_3)_6$ and $Ca_3(PO_4)_2$. After hexanedioic acid ($C_6H_{10}O_4$) is added into the ceramic suspensions, the complex can decompose and free calcium ions are released slowly, and the released free calcium ions react with sodium alginate and form a 3D network, thus leading to gelation.

$$2\text{Na-alginate} + \mathrm{Ca}^{2+} \leftrightarrow \text{Ca-alginate} + 2\mathrm{Na}^{+} \qquad (1)$$

Hydroxyaluminum diacetate (HADA), because of its low solubility in water, is able to gradually release acetate ions and aluminum in aqueous media, which decreases the pH and increases the ionic strength of the solution. In order to induce the gelation of alginate molecules initially introduced in the aqueous suspension, some researchers[57] took advantage of the gradual release of aluminum ions from the coagulation agent hydroxyaluminum diacetate (HADA) in water, where the ceramic particle network was coagulated by compressing the electrical double layer.

3.2.1.3. Thermoreversible gelation of biopolymers. The chain conformation of some types of globular proteins (e.g., bovine serum albumin (BSA), albumen (egg white powder) and whey protein concentrate (WPC)) in water can be changed when heated/cooled to a certain temperature.[58,59] This process can be used to solidify water-based ceramic suspensions into rigid bodies. Lyckefldt et al.[60] found that the denaturation of globular proteins could be accomplished by heating, that the peptide chain in globular proteins was in its unfolded state after denaturation (see Fig. 4), and that the polypeptide chains became tangled to form a three-dimensional and thermo-irreversible gel network (coagulation) through the formation of new hydrogen bonds between the unfolded peptide chains (see Fig. 4).

Chitosan is biocompatible and the solubility in acidic media has been found to be useful for avoiding toxic organic solvents during the processing. Bengisu and Yilmaz[32] fabricated alumina and zirconia ceramics using the biopolymer chitosan. The gel forming system is based on the reaction between a solution of 1% chitosan in diluted acetic acid and glutaraldehyde. At ambient temperatures, chitosan as a binder was added into the dispersed suspension, dissolved in acetic acid, and then was crosslinked when heated to a certain temperature.

3.2.2. Gelation by the physical effect of dispersed medium

The methods mentioned above involve the immobilization of the ceramic powders by the chemical reaction of the dispersed medium in a suspension to form a strong gel network. Slurries can also be solidified by the physical effect of the dispersed medium in a suspension to form a network.

3.2.2.1. Temperature activated cross-linking of polymers. Many nontoxic natural polymers (e.g., agarose and agar,[61–63] gelatine[64] and carrageenans[41,65]) are soluble in hot water and gel on cooling,[66–68] which can solidify the slurry in situ to form a ceramic green body.

Xie et al.[69,70] reported that a ceramic suspension was gelled to a green body using agarose/gelatine. In the work, a well-dispersed ceramic suspension containing agarose/gelatine was heated at 80/40 °C to dissolve them completely, and then cast in a non-porous mold. When cooling down to room temperature, the suspension gelled and formed a wet ceramic green body with the desired shape. However, the high cost of agarose and the difficulty in controlling the rheological properties restricted its large-scale application.

Millan et al.[41,71] proposed the use of carrageenans as gelling agents for silicon nitride powder processing. Carrageenans are nonagaroid polysaccharides with high gel strength, and it has a cost of at least 1 order of magnitude lower[41] less than agarose. Carrageenan binder also has a lower melting temperature (normally about 40 °C) than that of agarose (normally higher than 80 °C).

The problem of a temperature activated cross-linking polymer process is that the suspension has to be heated to a certain temperature before casting, and may increase the viscosity of the slurry due to water vaporization during the heating process.

Gelatine is a protein polymer composed of various amino acids, and can be dissolved quickly at a rather low temperature (about 40 °C), and gel at 15–20 °C. A gelation process using gelatine and enzyme catalysis for forming a ceramic green body was developed.[72] The forming method is based on the process in which gelatin, urea and urease are used. Urea can prohibit a hydrogen bond from forming between gelatin molecules when the hot gelatine solution cools down. As urease is added into the suspension, gelatine molecules attract each other and change to a three-dimensional network structure through hydrogen bonding due to urea decomposition by urease. Thus the suspension containing ceramic powders and gelatine will be solidified in situ by the gelatine at ambient conditions. This process can avoid an increase in viscosity before casting. Also the process is more easily controlled for obtaining homogeneous microstructures in the green body.

3.2.2.2. Freeze casting technique. The freeze casting technique[73–80] is a novel environmentally friendly form-

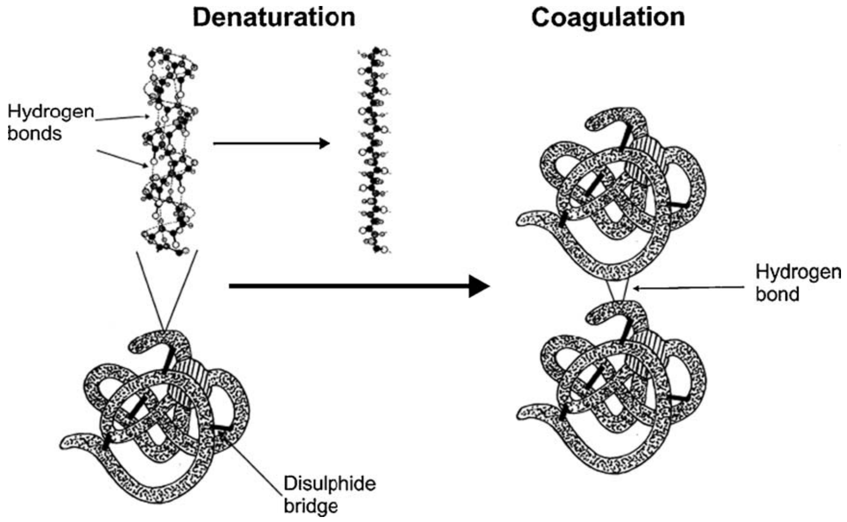

Fig. 4. Schematic illustration of the denaturation of globular proteins.

ing method, and it draws much attention due to its simplicity and the absence of organic substances. In the forming process, the ceramic suspension is poured into a mold, then frozen and subjected to sublimative drying of the solvent (water) under vacuum. This method allows the frozen solvent to temporarily act as a binder to hold the parts together for unmolding. The sublimation of the solvent (water) is made to eliminate the drying stress, and to avoid shrinkage, cracks and warpage of the green body that generally existing in the normal drying.[81]

The freeze casting technique is often used for the preparation of porous ceramics with widely controllable porosity,[76,79–81] and by controlling the freezing direction and temperature gradient, aligned pore channels and a porous gradient can be achieved. A major problem of freeze-casting is the low strength of green body, when the frozen suspension is volatilized, the green body becomes very fragile and difficult to handle, and further efforts are underway to improve the strength of green body.[82]

4. Development of control method for reducing defects in green body

During gelcasting, asynchronous solidification of the suspensions caused by various reasons, such as the gradient of temperature or initiator distribution, has always been present in most gelcasting process. The asynchronous solidification makes the suspension shrink non-uniformly, and then the inner stress in the ceramic green body develops, which possibly makes it an origin of cracks during subsequent handling. At the same time, the polymerization of acrylamide–*N*,*N*′-methylenebisacrylamide system is a free-radical reaction in which the surface-exfoliation phenomenon of green body in air is unavoidable, thus influencing the performance of green body (e.g., the strength, the size). Therefore, it is important to minimize the inner stress and the surface-exfoliation phenomenon in the green body during the gelcasting process, which includes the addition of special composition and improving the forming method. In this section, the occurrence and transformation of inner stress and surface-exfoliation in ceramic green body prepared by gelcasting are analyzed, and some methods to control and eliminate the inner stress and surface-exfoliation in ceramic gelcasting green body are proposed.

4.1. The release and control of the inner stress in ceramic green body

The inner stress in ceramic green bodies is usually caused at the forming or drying stage.[83] In a practical gelcasting process, the solidification speed of slurry is controlled by temperature induction or adjusting the additional contents of the initiator and catalyst. Inner stress in ceramic green bodies originates mainly from the non-uniform shrinkage during the solidification of the precursor suspension (the gradients of temperature, initiator concentration) and the drying of the green bodies (temperature, humidity). Huang et al.[84] found that the inner stress could be traced back to the forming stage due to the gradient of the initial temperature or the concentrations of solidification agents. In the subsequent drying stage, the inner stress was inherited and magnified due to further contraction. The control of the inner stress developed in the forming process was critical to the success of the subsequent drying and de-binding processes after gelcasting.

4.1.1. The release and control of the inner stress at the forming stage[85]

The inner stress caused by the concentration gradient of the initiator in the suspension results in an uneven distribution of free radicals, after which the asynchronous solidification occurs. Yang et al.[86] designed and fabricated a cantilever beam sensor to record changes in the inner stress during solidification of the suspension from liquid to solid. The results indicate that the relatively rapid solidification rate makes inner stress low, thus shortening the reaction time conducive to effectively reducing inner stress in ceramic green bodies.

The soluble ions introduced into gelation system by impurities influences the decomposition of the initiator ammonium persulfate (APS), which affects the gelation process. For exam-

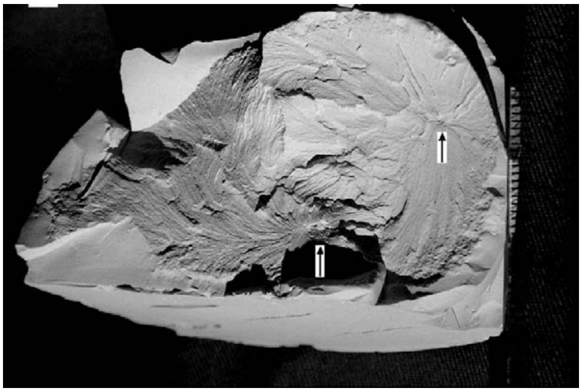

Fig. 5. The micro-cracks appeared in the green body during debinding caused by the gradient of free radicals.

ple, Zhao et al.[87] found that Cu^+ ions could accelerate the decomposition of ammonium persulfate (APS) due to the following reaction:

$$S_2O_8^{2-} + Cu^+ \rightarrow SO_4^{2-} + SO_4^{\bullet -} + Cu^{2+} \tag{2}$$

Thus, a gradient of free radicals occurs in a suspension when a copper beaker is used. When the suspension containing initiator was cast into the copper beaker, Cu^+ diffused from the beaker wall to the center of the suspension, and a concentration gradient of Cu^+ ions was formed and a gradient of the free radicals appeared. In the enrichment zones, the suspensions solidify in the first instance and become centers for contraction, such that the shrinkage of the subsequent solidifying zones is constrained. As a result, a complex distribution of inner stress occurs. To analyze the effect of the enrichment of initiator in a suspension of the green body, an initiator (APS) and catalyst (TEMED) were added into suspension, and then the suspension was cast without sufficient stirring to prepare a green body. The macro-cracks appeared in the green body during de-binding, and are shown in Fig. 5. From the orientation of the cracks, it could be determined that there exist at least two origins within the green body. The reason for the random cracks is the non-homogeneous distribution of initiator or free radicals, which yields multi centers of contraction and causes stress concentration.

Inner stress caused by the temperature gradient during solidification, for all the solidification methods associate with heating, heating results in a gelation reaction that starts at the outer skin of the component and progresses towards the inner parts of the body, and the solidification speed increases with increasing temperature for a given composition. Non-uniform solidification occurs due to the temperature gradient in the ceramic suspension, and the existence of the temperature gradient makes a microstructure non-uniform due to asynchronous solidification, resulting in inner stress at the gelcasting process and microcracks or damage in the green body on subsequent drying and de-binding process. Theoretical analysis indicates that the magnitude of the inner stress increases with the stiffness of the green body. Based on this finding, a fraction of the monomers was replaced by a moderator-hydroxylethyl acrylate (HEA)[88] in the suspension to control the stiffness of the gel network during gelcasting.

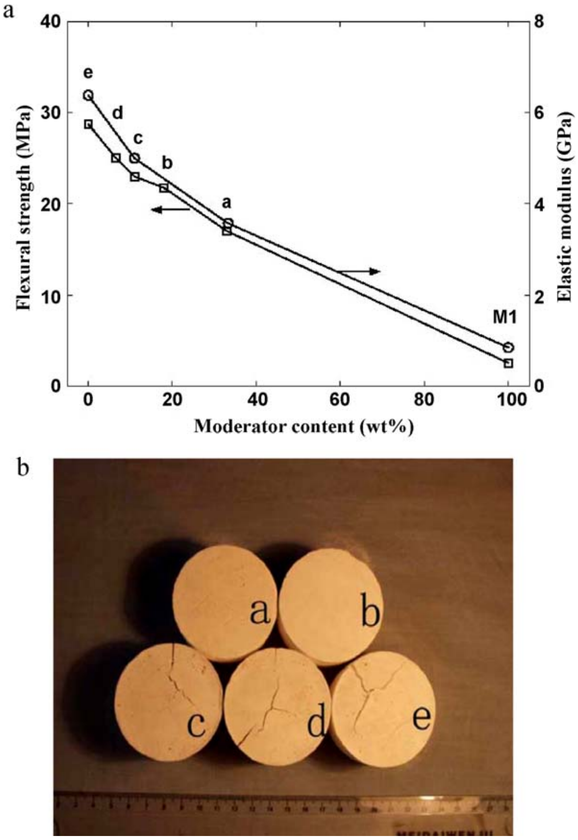

Fig. 6. The influence of the amount of moderator on the performance of Al_2O_3 green bodies. (a) Strength and elastic modulus of alumina green bodies versus and (b) surface patterns of the Al_2O_3 green bodies after debindering.

Yang et al.[88,89] found that the inner stress could be successfully reduced by the addition of a proper plasticizer or a moderator (hydroxyethyl acrylate (HEA)) in the suspension, which could adjust the polymer network structure (soften the polymer network) and thus control the stiffness of the gel network. Five alumina discs, a–e, were produced under the same conditions, Fig. 6(a) shows the strength and elastic modulus of alumina green bodies versus the amount of moderator, and the identifiers of the disc samples are marked on top of the corresponding amount of the moderator. It indicates that both the flexural strength and elastic modulus of green bodies decrease simultaneously with the amount of the moderator. This reveals that the strength of polymer network is reduced when the harder polymer chain is relaxed by the incorporation of the shorter chain molecules of the moderator, while the gel network with no moderator is very stiff. Fig. 6(b) shows the surface patterns of the alumina green bodies after drying and de-binding to remove all the water and organic binders. Radial cracks are found on samples (c, d and e) after de-binding when the amount of the moderator is not sufficient to soften the polymer network, while the samples (a and b) with higher amount of moderator (the concentration of moderator > 20 wt%, the concentration is based on the whole suspension) are free of visible cracks after de-binding because the inner stress is effectively reduced and cracking is suppressed, and is believed that the inner stress is initiated at the

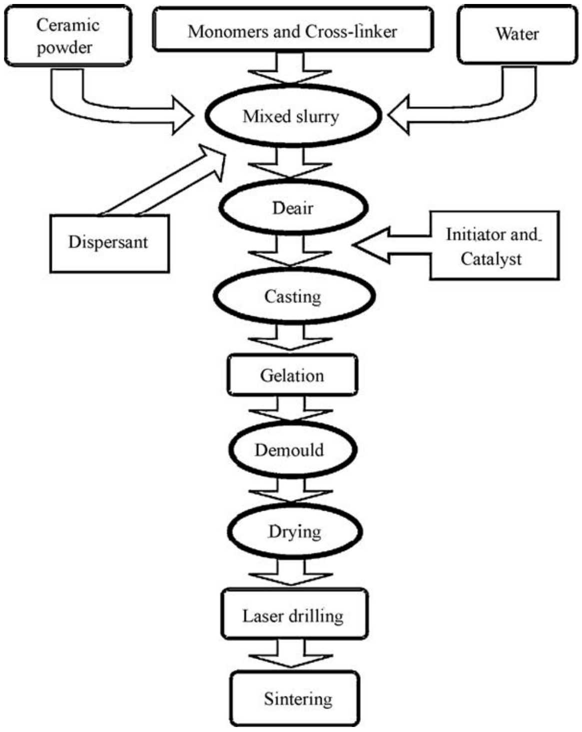

Fig. 7. Detailed flowchart of the laser green machining technology.

forming stage and magnified during drying process when the preform becomes harder.

The initiation and evolution of inner stress in the green body formed by gelcasting were discussed above. It can be concluded that the important factors responsible for inner stress were the temperature gradient and the distribution of solidification agents. Adding a proper amount of HEA into the concentrated suspension improves the flexibility of the polymer network and thus reduces the inner stress in the green body.

Another reason for the inner stress caused in the green body is the differential contraction due to nonsymmetrical shrinkage and warpage during drying.

4.1.2. The release and control of the inner stress at the drying stage

Inner stress caused by the moisture gradient in a green body during drying, although the moisture-distribution in a wet green body is homogeneous, the moisture gradient exists in the green body during drying because the moisture drains at different rates at the surface and the center of the wet green body. The moisture gradient makes the green body shrink unevenly, and then inner stress occurs. In order to control the shrinkage rate, the wet green body is usually dried slowly under controlled temperature and humidity. This is not favorable in practice because it leads to a prolonged operation time and high production cost.

Generally, at the drying stage, there is a relatively short constant-rate drying period (CRP) in the initial part of the drying cycle. In this stage, the process undergoes a rearrangement of particles on surface and the shrinkage of the surface. Subsequently, the interface between solid and liquid water withdraws from the surface to the interior of the green body, and the remained moisture in the green body is removed by diffusion through capillaries.[90] The "dried" superficial layer constrains the shrinkage of the interior part of the green body, and thus the inner stress appears in the drying green body. During debinding, the radial and annular cracks appear in the disc. The influence of temperature gradient can be ignored because of the suspension solidifying at room temperature. It is believed that the non-uniform shrinkage during drying is an origin of the inner stress in a green body.

Ghosal et al.[90] proposed a physical model for gelcast drying that used experimental data to estimate key model parameters. This model predicted the instantaneous moisture content of a gelcast sample with an accuracy better than 10% when the dryer humidity, dryer temperature, and sample thickness were specified.

Yu et al.[91] investigated the influences of the monomer content (AM and MBAM) and the ratio of monomers (AM/MBAM) on the warpage rate, shrinkage rate, and the flexural strength of Si_3N_4 ceramics green body. The results showed the warpage and shrinkage could be minimized during drying by adjusting the monomer content and the ratio of monomers, and then the inner stress in the green bodies could be reduced. In the drying process of green bodies, the moisture is transported primarily by capillary forces to the part surface and evaporates to the atmosphere at a constant rate, thus the large compressive stress sets up in the green parts by the capillary forces, the ceramic particles attached to the polymer network move towards each other when the network collapses, and it causes a bulk shrinkage of the green body. When the intensity of the macromolecular network gel is sufficient to choke back the capillary forces an increase in the monomer content and the ratio of monomers, thus controlling the warpage and shrinkage, the inner stresses in the green bodies are minimized.

In the meantime, the malformation and shrinkage of the green body can also be minimized or completely eliminated by using the liquid desiccant drying method (aqueous/non-aqueous solution of PEG1000).[83,92,93] The wet green body is brought into contact with an appropriate liquid desiccant by immersion, and the reason for the drying effect of the liquid desiccant on a gelcast part is the osmotic difference between the liquid desiccant and the gelled polymer in the part. The advantages using the liquid desiccant are as follows[83,94]:

1. Liquid desiccant provides a more uniform medium in comparison with conventional air drying methods.
2. In this method, the part loses safely about 20–30 wt% of interior solvent (water) in a very short time, which is considered a breakthrough in the critical stage of the drying.
3. By providing buoyant support on the part, malformations such as bending, warping, cracking and other defects can be minimized or completely eliminated during drying.
4. Using liquid desiccant allows no region of the part to dry too quickly, so the reduction of the residual stress is developed during drying.

Here, the drying speed of a whole region of the green body is identical because of the used liquid desiccant drying method

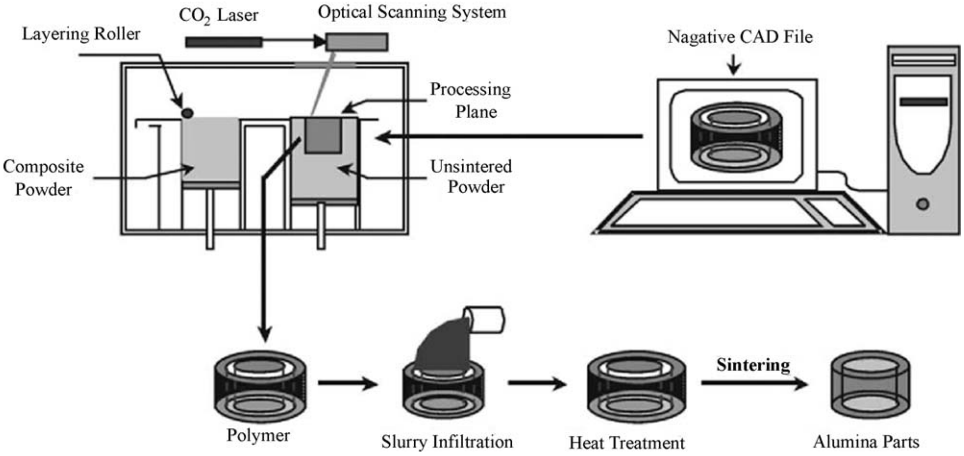

Fig. 8. Schematic chart of the steps in the lost mold approach for fabricating alumina ceramics.

used, and thus the inner stress is reduced during drying. By reducing the inner stress in the green body, the de-binding time of large ceramic parts can be significantly shortened.

4.2. *The improvement of forming method*

As a precondition to materials design and realization of the high performance ceramic products of desired shapes, the ceramic forming process usually plays a crucial role in determining the reliability and the cost of the products. The traditional methods of forming the ceramic products have been widely used in the field of fine ceramics, but are not sufficient to meet the requirements of high performance ceramics due to the defects mentioned above. Therefore, much efforts have been directed to devise new methods for the ceramic forming process. In the section, some new methods and new techniques based on gelation are introduced, such as gelation by ultrasonic effects, laser machining technology, and solid freeform fabrication.

4.2.1. *Gelation by ultrasonic effect*

Ceramic scientists have paid great attention to the gelcasting technique since its ineption. The controllability of the gelcasting process is not ideal since the amounts of initiator and catalyst added into ceramic suspensions are restricted within a narrow range, because ceramic suspensions can solidify too fast to cast with slightly more initiator and catalyst, whereas slightly less initiator and catalyst result in an incomplete solidification of the suspensions. In most cases, initiator and catalyst are added into cooled ceramic suspensions to prolong the processing time, and then initiate the polymerization of the monomers to solidify the suspensions by ultrasonic waves or increasing the temperature of the mold.

Both temperature and ultrasonic waves can promote the decomposition of initiator (ammonium persulphate), and thus accelerate the solidification of suspension for gelcasting. However, ultrasonic waves result in superoxide anionic free radicals greatly than that caused by raising temperature. Therefore the suspension can be solidified with less initiator, so the controllability of suspension solidification and the flexibility of gelcasting process can be improved through the ultrasonic effect. At the same time, the asynchronous solidification of the suspension, which is caused by the temperature gradient and led to potential crack during drying and de-binding of the green body, can be suppressed with ultrasonic activation because the suspension is uniformly heated. Additionally, a suspension with less initiator yields green bodies with high strength after ultrasonic activated solidification. This indicates that suspension with less monomer can be solidified by ultrasonic waves.

4.2.2. *Laser green machining technology*

The machining of ceramics to their final dimensions and shapes by conventional methods is extremely laborious and time-consuming. A new laser green machining method is proposed to produce ceramics. Laser green machining is a non-contacting, abrasionless technique, which eliminates tool wear, machine-tool deflection, vibration and cutting forces, and reduces limitations to shape formation and inflicts less subsurface damage. As an advanced manufacturing method, it is used in different areas such as electronics, aerospace, and material processing.[95,96]

Laser green machining of a ceramic green body combines laser green machining and gelcasting techniques together to machine complex-shaped ceramic parts. Detailed flowcharts of the laser green machining technology is shown in Fig. 7. The main principle is to ablate the organic matter of the gelcasted green body, after which the ceramic powder will shed naturally. This method builds parts by selective removal of materials, layer by layer, as specified by a computer program to generate geometrical objects directly from a three-dimensional computer image without part-specific tooling or human intervention.

The basic mechanism of laser green machining is based on the thermal action of the light. When high intensity light from an ultrasonic head strikes the material surface, the photons of the beam are absorbed and converted into thermal energy. The temperature rises locally and a combination of melting and vaporization occurs. Under the continuous effect of the laser beam, the molten material is ejected by the material vapor (washer) and ceramics with different shapes and sizes are formed.

At present, this study has attempted to discuss the laser green machining mechanism by means of laser-material interaction parameters and the laser green machining of Al_2O_3 green body by changing the laser parameters. Additionally, a novel anti-spatter and anti-crack laser drilling method based on the gelcasting technique was developed.[97,98] Laser drilling of a gelcast alumina green body proved to be highly effective in preventing spatter and microcracks during laser percussion drilling. Micro-holes with regular and uniform shapes, without cracks were successfully obtained by this technique. From the thermal nature of the drilling process and from inspections of the microstructure, it was deduced that the absence of cracks in the gelcast green body might be attributed to the lower heats of evaporation and melting, as well as the relatively loose microstructure of the green body compared to sintered ceramics. What should be pointed out is that gelcasting is a highly versatile fabrication process. It is not limited to use with any particular ceramic powder. It can be quickly adapted for use with new materials and new applications and works as well for metal powder forming as for ceramic powders. Therefore, the laser processing method used here may be applied to the laser green machining of a variety of materials.

In our research group, the laser green machining of Al_2O_3 and ZrO_2 ceramic bodies prepared by different forming methods (including dry pressing, tape casting, gel casting, injection molding) and the relationship between laser machining parameters and green bodies prepared by different forming methods were studied.[99–101] The results showed that machined depth increased with the increase of electric current and decreased with the increase of machining speed and scanning gap for the green bodies prepared by the same forming method. Under the same machining parameters, the injection molding ceramic bodies was machined easier. ZrO_2 sintered bodies with different shapes and sizes were fabricated by laser green machining technology.

4.2.3. Solid freeform fabrication (SFF)

Solid freeform fabrication (SFF), which appears in the 1980s, is the near-net-shape approach to produce parts or prototypes directly from a computer aided design (CAD) file without hard tooling, dies or molds. It has triggered a huge change in the approaches to manufacturing technology and production efficiency. Many countries recognize the importance of this new forming technology, which was considered to be a major breakthrough in the field of manufacturing.

Solid freeform fabrication is a comprehensive embodiment of multidisciplinary and technology, the emergence of which accompanied the high-speed development of computer, laser, digital control and material technology as well as the cross-cutting of various disciplines. It is an advanced manufacturing technique which generates accurate geometrical objects directly from a three-dimensional computer image without part-specific tooling or human intervention. This means that designers have the freedom to produce physical models of their drawings more frequently, allowing them to check the assembly and function of the design as well as discussing downstream manufacturing issues with an easy-to-interpret, unambiguous prototype. Consequently, errors are minimized and product development costs and lead time are substantially reduced. With the emergence of SFF technology, a bright future of the industrialization of advanced ceramics can be envisioned.

To date, several SFF techniques have been developed. Laminated object manufacturing (LOM) process uses tape-cast ceramic sheets to fabricate ceramic parts.[102] Ceramic-binder extruded filaments are being used as feedstock in fused deposition of ceramics (FDC) processing.[103,104] Stereo lithographic (SLA) techniques are being developed to produce ceramic parts via ultraviolet curing of a highly concentrated suspension of ceramic particles in a photo-polymerizable liquid.[105,106]

A novel lost mold method was successfully designed by combining the SLS and gelcasting techniques. Fig. 8 shows a graphic depiction of the process. First, a composite polymer powder is developed for SLS to fabricate sacrificial molds having a die of the desired structure for gelcasting. Then, a homogeneous alumina gelcasting slurry with high solids loading and low viscosity is poured into the mold. During the sintering of the ceramic parts the polymer mold is removed entirely. Because the solidified green bodies have high strength even at elevated temperature, the desired geometry of the ceramic parts is successfully retained after sintering. Through this means, many complex alumina parts are produced successfully.

4.3. Avoiding the surface-exfoliation[107,108]

The Oak Ridge National Laboratory (USA)[109] first reported flaws and spallation on the surface of dried green body prepared by gelcasting in air. Their study concluded that the surface spallation phenomenon was due to the presence of oxygen hindering polymerization and gelation of the monomers in gelcasting systems.[110,111] Surface spallation could result in a green body with a powdery surface that could be a few millimeters thick. This would reduce the strength and make it difficult to control the dimension of the final products, and thus must be avoided in production. It was found that gelcasting in a nitrogen atmosphere could suppress the effect of oxygen inhibition and hence prevent surface spallation from occurring.[112,113] In industrial production, however, a technical operation under nitrogen introduces complexity with significant increases in the cost of the production.

Ma et al.[112,114,115] attempted to resolve the surface spallation problem by introducing a water-soluble polymer (e.g., polymer polyethylene glycol (PEG), polyacrylamide (PAM), or polyvinylpyrrolidone (PVP)) into the acrylamide based gelcasting system. The effects of the polymers on gelcasting and the surface spallation phenomenon of green body were investigated.

A proper amount of PAM may eliminate the surface spallation phenomenon of green bodies cast in air, but increases the fluidity of the suspension. The results showed that the suspension with 2.8 wt% PAM (based on alumina) had good fluidity and exhibited no surface spallation phenomenon. The flexural strength of the green body prepared from the suspension with the addition of PAM is higher than that without PAM. Previous studies indicated that the strength of green body formed by gelcasting was provided by the polymer gel.[116] As the polymerization proceeds for the monomer solution with 2.8 wt% PAM, the native

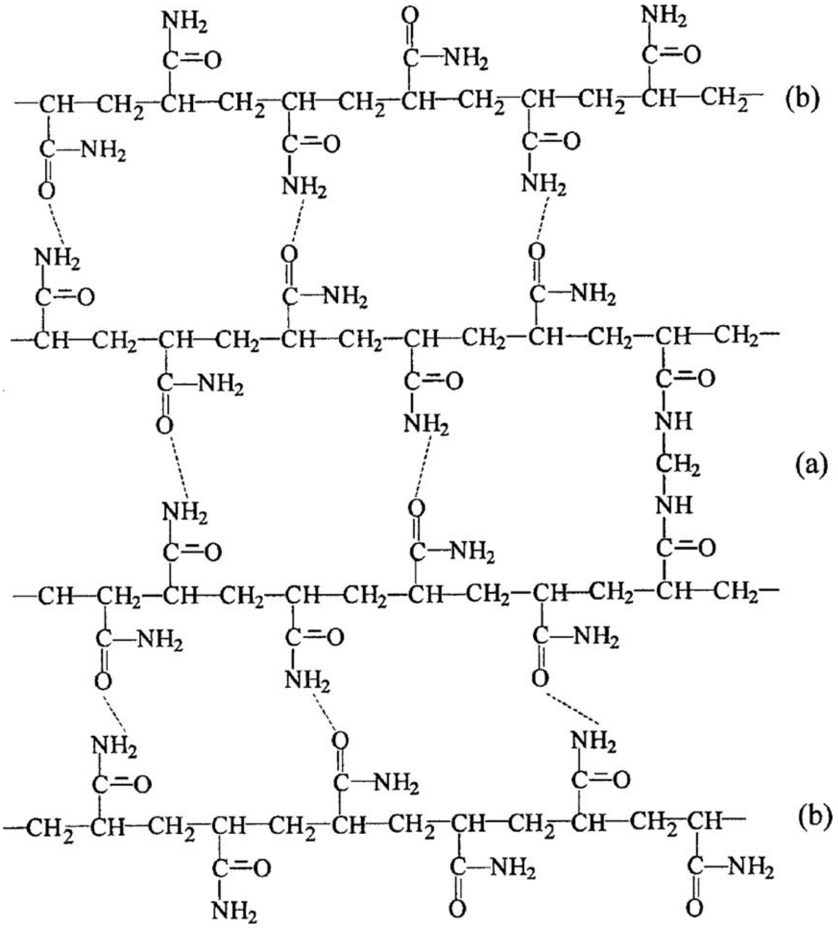

Fig. 9. The proposed structure of cross-linked PAM (a) gel after an addition of native PAM (b).

PAM with free amino and keto groups are likely to form a more complicated network structure through hydrogen bonding with the keto groups of the PAM polymerized by monomers, resulting in an intimate mix of polymer chains (see Fig. 9). At the same time, the sintered ceramic bodies have a high density and uniform microstructure without developing a huge grain growth with the addition of 2.8 wt% PAM.

Polyethylene glycol (PEG) with a molecular weight of 10,000 is a white waxy solid and a non-ionized water-soluble polymer. The suspension with 1.3 wt% PEG (based on alumina) has a good fluidity and has no surface-exfoliation phenomenon. The storage modulus of the slurry with PEG is lower than that of the slurry without PEG (see Fig. 10), which indicates that the strength of green body with PEG is less than that of the green body without PEG.

4.4. Avoiding the prepolymerization of the slurry

The activity of acrylamide is so strong that it can self-polymerize before casting. The slurries often are polymerized even if without initiator and catalyst during ball milling with large balls or storage in summer. In order to avoid this problem, inhibitors for gelcasting were studied. Many kinds of inhibitors, such as ferric chloride, phenol, diphenylamine, and so on, have been investigated. Compound inhibitors of phenothiazine and catechol have the best effect among these inhibitors at room temperature. The best mixture ratio for phenothiazine and catechol was about 1:5. Table 1 shows the inhibition effect of this compound inhibitor on acrylamide polymerization.[116] It indicates that idle time is extended greatly after the compound inhibitor is added into slurry. Thus, the ceramic slurry can be

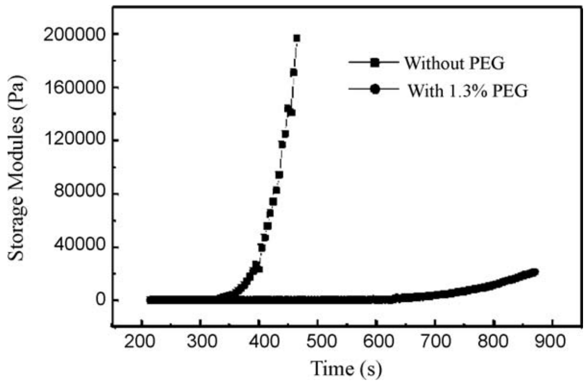

Fig. 10. Relationship of the storage modulus of alumina suspension versus solidified time.

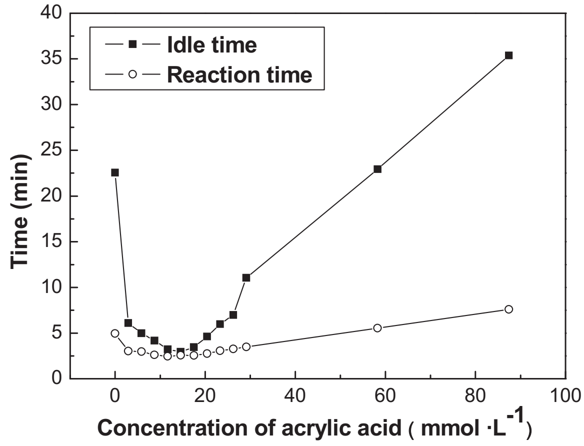

Fig. 11. The influence of acrylic acid on acrylamide polymerization.

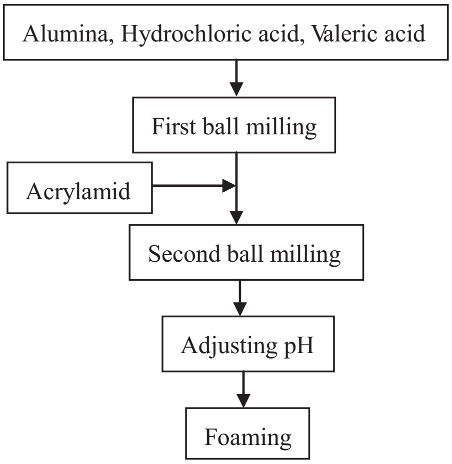

Fig. 12. The flowchart of generation of particle-stabilized foams containing organic monomers for gelcasting.

stored for a long time even at higher temperature. Because both phenothiazine and catechol are organic substances, no impurity is left in the ceramic components after sintering. The viscosity of slurry decreases with the addition of phenothiazine and catechol. Therefore, this compound inhibitor does not influence the viscosity of ceramic slurry, and is suitable for gelcasting.

In addition, acrylamide in the slurry can hydrolyze, and acrylic acid is generated.[117] When slurry is stored under strong light or there are some impurities in the slurry, the process of hydrolysis would be accelerated. In our research, it is found that acrylic acid had a great effect on the solidification of the ceramic slurry, and the influence of minute acrylic acid on idle time and reaction time of acrylamide polymerization is shown in Fig. 11. It shows that the solidification process is accelerated under a very low concentration of acrylic acid in Fig. 11. However, the reaction is slowed down when acrylic acid concentration is over 15 mmol L^{-1}. The mechanisms can be achieved as follows: acrylic acid is a weak acid, an even if there is only a small amount of acrylic acid in the slurry, the acidity of slurry still rises. The pH of slurry has great effect on acrylamide polymerization initiated with ammonium persulphate (APS) and tetramethylethylenediamine (TEMED). Hydrogen ions act as a catalyst for the decomposition of APS, and hydrogen ion can react with TEMED generating a stable ammonium and retarding the decomposition speed rate of APS. Thus, when the concentration of acrylic acid is greater than a certain value, 15 mmol L^{-1}, the rate of acrylamide polymerization is decreased and the idle time becomes longer. Thereby, ceramic slurry for gelcasting should protect from light.

Table 1
Inhibition effect of phenothiazine–catechol on acrylamide polymerization [AM] = 4 wt%, [APS] = 2.76 mmol L^{-1}, [TEMED] = 40 mmol L^{-1}.

No.	Temperature (°C)	Phenothiazine (mmol L^{-1})	Catechol (mmol L^{-1})	Idle time τ (min)
1	30	0	0	2.6
2	30	0.025	0.125	5.8
3	30	0.05	0.25	7.2
4	30	0.075	0.375	12

5. The application of gelcasting

5.1. *The preparation of porous ceramics by gelcasting*

Gelcasting has been mainly used for the fabrication of dense ceramics since gelcasting was invented, and is gradually applied to the fabrication of porous ceramics due to its homogeneous structure.[118,119]

5.1.1. *Fabrication of porous ceramic from particle-stabilized foams based on gelcasting*

Ceramic foams are innovative materials with characteristics like high specific surface area, high specific strength, low thermal conductivity, high thermal shock resistance, etc. They are becoming more and more useful in many fields of engineering applications, including filtration of high-temperature gases, filtration of molten metals, and biomedical devices. The manufacturing methods of ceramic foams have been reported in more and more papers. They are typically classified into replication, burn-out of pore formers and direct foaming.[120] With direct foaming techniques, it is easy to produce porous ceramics, especially those with high porosity and high specific strength.[121]

In the fabrication process of porous ceramics from particle-stabilized foams, the short chain amphiphiles (usually carboxylic acids) were used to generate the bubbles, which were different from the long chain surfactants used previously. Short chain carboxylic acids were adsorbed onto the surface of ceramic particles due to the electrostatic interactions. By this surface modification, the particles were lyophobic and tended to attach themselves to the liquid–gas interfaces to stabilize the bubbles. The particle-stabilized wet foams are much more stable than the ones prepared with long chain surfactants. Porous ceramics were fabricated by particle-stabilized foams, which could avoid the influence of intervals between foam generation and foam setting. The microstructures of these porous ceramics are different from the porous ceramics reported before.[122,123] Fig. 12 shows a the flowchart outlining the generation of particle-stabilized foams containing organic monomers for gelcasting.

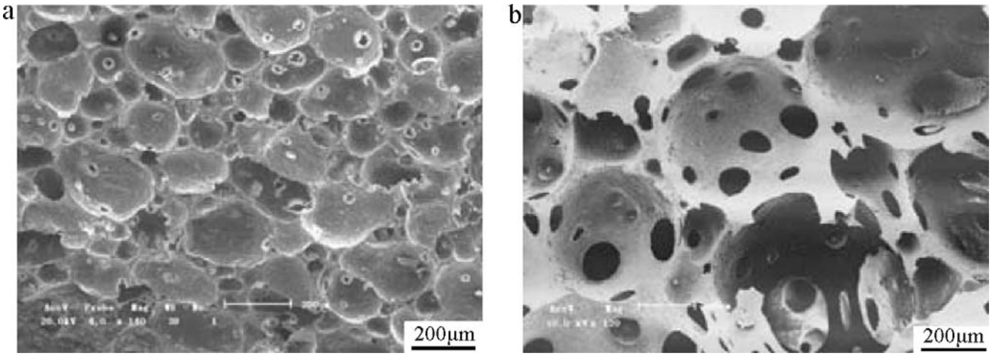

Fig. 13. SEM photos of two kinds of porous ceramics: (a) porous ceramic from particle-stabilized foams with 0.73 open porosity and (b) conventional porous ceramics with 0.73 open porosity.

Authors studied the fabrication of porous ceramics from particle-stabilized foams,[124] and the SEM images of the prepared porous ceramics are shown in Fig. 13. The results show that the morphologies of the windows of two kinds of porous ceramic were evidently different. For porous ceramic from particle-stabilized foams, the porous ceramics contained closed and open-cell pores, and most of them were open, with a typical microstructure, cell-window mode. There were one or more windows in the shells of open cells (pores), which connected the cells. These open cells give permeability for the porous ceramic. So the open porosity of ceramics fabricated from the particle-stabilized foams usually is more stable. The borders of the windows were indistinct unlike the trim borders of windows of conventional porous ceramics.

5.1.2. Fabrication of porous ceramics with small pores

Up to now, there have been three main ways (combining gelcasting with foaming technique, sponge method, and the addition of sacrificial phase) to prepare porous ceramics through the gelcasting technique.[125–131] The foaming technique and sponge method can prepare the ceramics with high porosity and large pores even up to several hundred micrometers. During porous ceramic fabrication by addition of a sacrificial phase where the pore size[132–134] depends on the diameter of the sacrificial phase, the porosity is usually lower than 50%, and the distribution of pores in the ceramics body is not homogeneous. The ceramics with small pores and high porosity are difficult to obtain by the three ways of porous ceramics fabrication above. Porous ceramics with smaller pores show better flexural strength than ceramics with larger pores at an equivalent porosity. Gu et al.[135] fabricated porous YSZ ceramics with an open porosity of 33.1–50.3%, a mean pore size of 0.66–0.98 mm and a nitrogen permeability of 215–438 m^3 $(m^2\,bar\,h)^{-1}$ by changing the sintering temperature from 1300 to 1650 °C. Additionally, the amount of carbon powder was 5–10 wt% as a pore-forming agent and the amount of organic monomers, acrylamide and *N*,*N*′-methylenebis-acrylamide, were 5 wt% of the dried solids during gelcasting.

Organic monomers (e.g., acrylamide and urea–formaldehyde) are widely used for gelcasting of

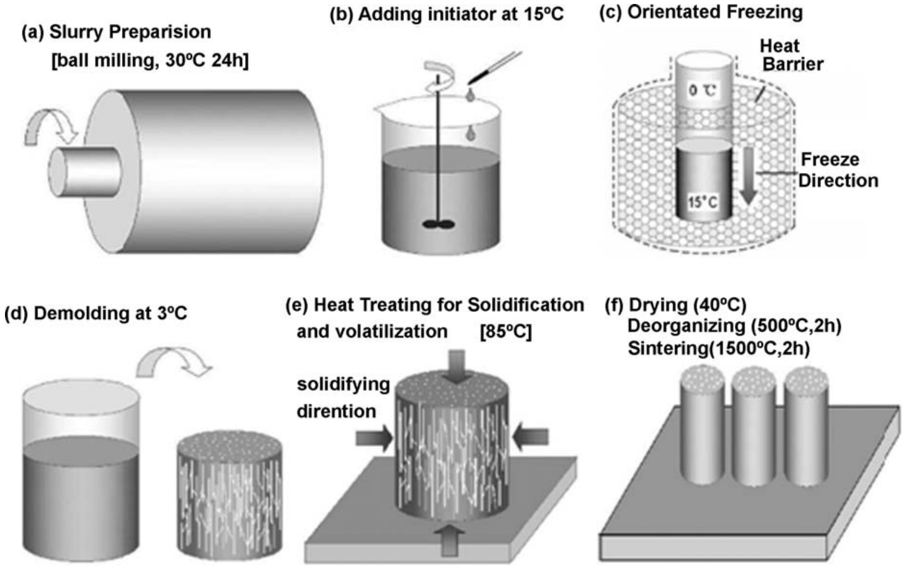

Fig. 14. Full process for fabricating ceramics with long-range ordered porous structure by freeze-gelcasting technique: (a) slurry preparation (ball milling, 24 h); (b) adding initiator at 15 °C; (c) orientated freezing; (d) demolding at 3 °C; (e) heat treating for solidification and volatilization (85 °C); (f) drying (40 °C), de-binding (500 °C, 2 h) and sintering (1500 °C, 2 h).

Table 2
Selected physical properties of TBA (compared with water).

	Liquid density (g mL^{-1})	Boiling temperature (°C)	Saturated vapor pressure at 40 °C (kPa)	Freezing temperature (°C)	Volume increase during freezing (%)	Morphological characteristics after freezing
Water	1	100	3.4	0	10	Dendritic crystal
TAB	0.79	82.5	6.4	25.3	2	Straight prisms

aqueous ceramic powder particles.[136,137] In order to obtain porous ceramics with fine pores, Yu et al.[138–141] fabricated porous Si_3N_4 ceramics by merely increasing monomers content (acrylamide and *N*,*N*′-methylenebis-acrylamide) in the ceramic suspension without other organic additives during acrylamide-based gelcasting. High performance of porous Si_3N_4 ceramics was formed. The flexural strength and porosity of porous Si_3N_4 ceramics could reach 54.5–234.2 MPa and 49.5–62%, and the pore size was less than 1 μm. In the gelcasting process, the pores of porous ceramics mainly originated from the residual microspace of the organic polymers in the green body during organic binder burnout. The additive organic polymers can disperse and dissolve in the aqueous medium of suspension, and thus makes the distribution of pores in the ceramic body homogeneous and the pore size fine in ceramic body.

Prabhakaran et al.[137] fabricated porous alumina ceramics by increasing monomer content (urea–formaldehyde) in the ceramic suspension during urea–formaldehyde-based gelcasting, and the results showed that porosity and the average pore size of the porous alumina ceramics were 27–62.5% and 2.0–4.3 μm, respectively.

Inspired by the aerogel conception, Wu et al.[132] prepared porous ceramics by gelcasting technology. Low concentrated suspensions were employed to make the solvent occupy more spaces, and gelation resulted in ceramic particles being partitioned into many "rooms" in a "multi-storey building". After heat treatment and sintering, the loosely immobilized particles directly formed into porous ceramics with a fine pore (pore size <3 μm) in the absence of any pore-forming agents, and pores were induced by evaporation of solvent.

Tert-butyl alcohol (TBA) and *N*,*N*-dimethylformamide (DMF) have high saturation vapor pressure and low surface tension force, and thus can evaporate easily under relatively low temperatures and cause minimal shrinkage during green body drying. The idea of ceramics with ultra low density fabricated by gelcasting was proposed by Chen et al.[142] and some important conclusions were obtained. Selected physical properties of TBA are shown in Table 2.

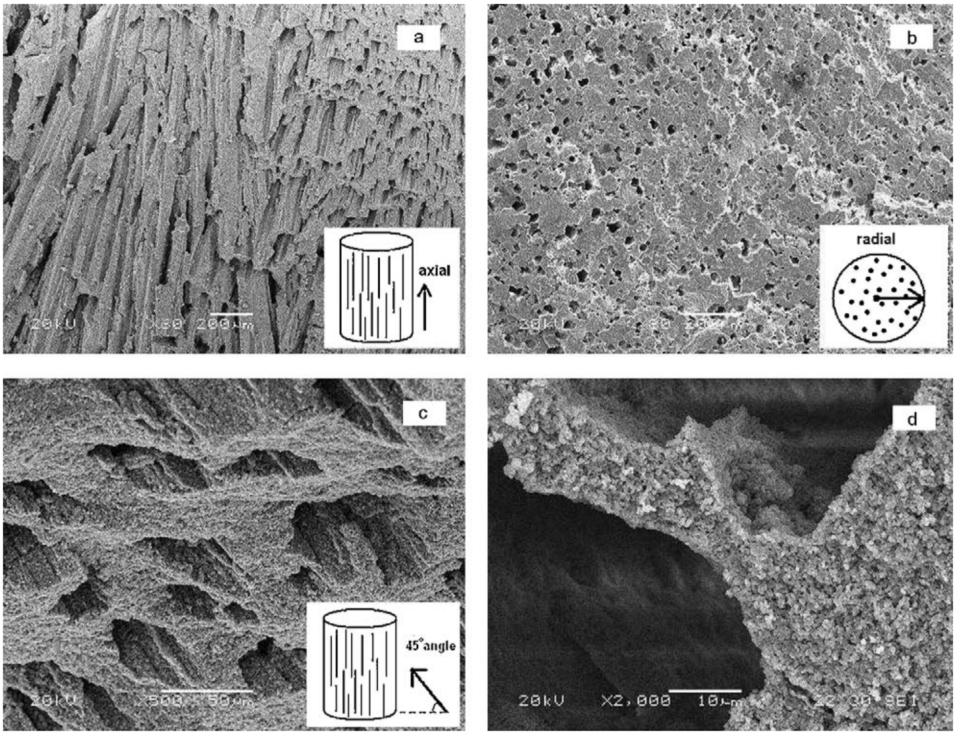

Fig. 15. Microstructures of porous ceramics with long-range unidirectional pore channels fabricated by the freeze-gelcasting method observed in different orientations: (a) vertical to freezing direction, (b) parallel to freezing direction, (c) at 45° angle direction and the dense walls formed between pores (d).

Table 3
Open porosity, pore size and specific surface area of alumina with low density acquired by TBA-based gelcasting.

Slurry solid loading (vol.%)	Sintering temperature (°C)	Open porosity (%)	Mean pore size (μm)	Specific surface area ($m^2\,g^{-1}$)
5	1400	92	0.1	14.82
5	1600	80	2.2	6.52
10	1400	85	0.8	8.75
10	1500	75	1.0	4.97
15	1400	77	0.6	5.2
15	1500	64	0.8	4.00

Chen et al.[142] applied the gelcasting technique to TBA-based ceramic slurries and to fabricate ceramic green bodies with ultra-low density, where the shrinkage of green body ($\leq$0.5%) during drying was successfully reduced, and the sintered Al_2O_3 with high open porosity (90%), high compression strength ($\geq$10 MPa) and mean pore size ($\leq$2 μm) was obtained, as shown in Table 3. The choice of dispersant in the TBA system was proposed[143] by the addition of the citric acid and acetic acid that can produce stable Al_2O_3 suspensions in liquid tert-butyl alcohol.

Wu et al.[132] choosed DMF as solvent to prepare porous Al_2O_3 ceramics, and the porosity could be controlled between 82% and 29%, and the compressive strength varied from 3.8 to 79 MPa.

5.1.3. The fabrication of porous ceramics with special porous structures based on freeze-gelcasting technique

5.1.3.1. Fabrication of porous ceramics with unidirectional pore channels. Porous ceramics with unidirectional pore channels are fabricated by the TBA-based freeze-gelcasting method, and the process is shown in Fig. 14: (a) slurry preparation (ball milling, 24 h); (b) adding initiator at 15 °C; (c) orientated freezing; (d) demolding at 3 °C; (e) heat treating for solidification and volatilization (85 °C); (f) drying (40 °C), de-binding (500 °C, 2 h) and sintering (1500 °C, 2 h).

In the process, TBA is frozen from top to bottom, forming complete unidirectional crystalline prisms penetrating the whole body as the template of pore channels (see Fig. 14(c)). The frozen bulks were easily removed from the molds at a low temperature 3 °C (see Fig. 14(d)), and then heat-treated at 85 °C (see Fig. 14(e)). Green ceramic bodies with high strength could be obtained by these freeze and gelation steps, and the final ceramic parts were fabricated by the following processes of drying, de-binding and sintering (see Fig. 14(f)). In our research group, the porous ceramics with unidirectional pore channels were fabricated by the freeze-gelcasting technique, as shown in Fig. 15.

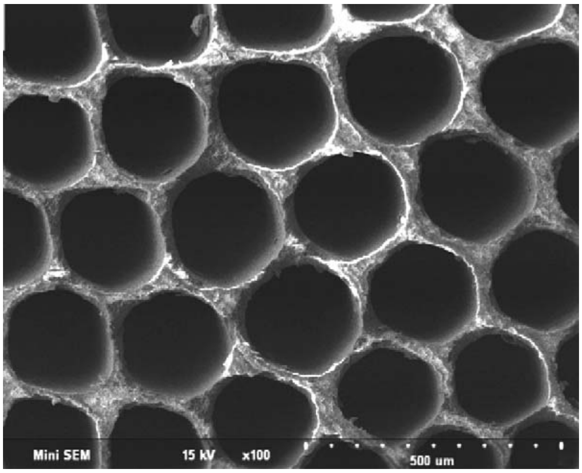

Fig. 16. The ceramics with very well unidirectional pore channels structure.

Huang et al.[144] fabricated porous ceramics with unidirectional pore channels by combining the gelcasting and the freeze drying technologies, and porous ceramics with very well unidirectional pore channels structure were fabricated, as shown in Fig. 16.

5.1.3.2. Fabrication of gradient porous ceramics. The freeze-gelcasting of alumina/TBA/AM slurry was also used to fabricate gradient porous ceramics. The process for fabricating gradient porous ceramics is similar to the process described above, with the main difference being in the freezing step. Molds containing slurry and packed by heat barrier layers were placed under conditions with a temperature gradient. One end was set below the freezing point of TBA and the other end was exposed to air at the temperature in its melting range. Therefore, the slurry froze from the cold bottom with crystals of TBA. On the other end, solidification and volatilization occurred near the hot surface. These two procedures proceeded simultaneously in opposite directions and formed a novel pore gradient structure. The steps to fabricate gradient frozen parts are illustrated in Fig. 17, in which two different temperature conditions are put into effect, about 12 °C mm^{-1} and 5 °C mm^{-1} in (a) and (b), respectively. Sintered parts showed almost full densification without any noticeable defects, either in the dense region near the top surface or in the alumina walls in the porous region near the bottom (see Fig. 18(d)). Using TBA as a template in its frozen state, a green body with pore channels was fabricated, unlike the circular cross-sections in aqueous or camphene based freeze casting.[73]

5.2. The preparation of ceramic parts with complex shapes

Gelcasting was a well-established colloidal processing method for making high-quality, complex-shaped ceramic parts, and was applied for preparing microbeads of ceramics, improving the breakdown strength of a rutile capacitor, developing a thin-wall rutile tube for ozone generators, producing a refractory nozzle of zirconia (ZrO_2) and lead zirconate titanate (PZT), which was discussed in this section.

5.2.1. The preparation of microbeads of ceramics based on gelcasting

According to the interfacial tension principle, the gel-beads forming is a process that uses the rapidly solidifying slurry with water-soluble monomer. By adjusting the ball forming media and these job parameters of slurry characteristics, the key processes of forming, shape dressing and shape maintenance can be

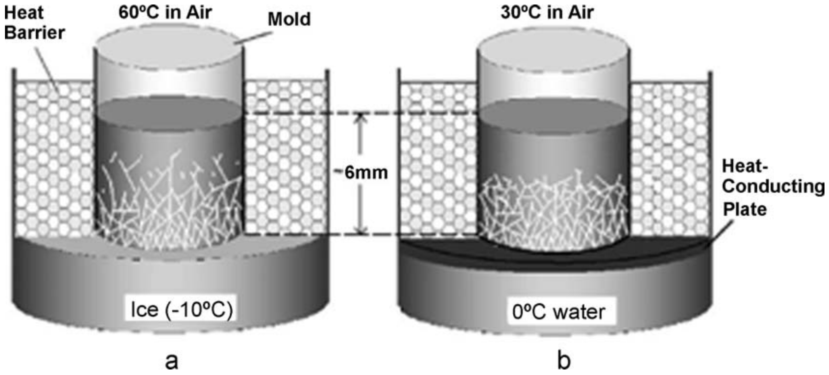

Fig. 17. Freezing step controlled with different temperature conditions to achieve novel gradient porous structures, with higher temperature gradient of ∼12 °C/mm (a), and with lower temperature gradient of ∼5 °C/mm (b).

accomplished. In this work, a new gel-beads forming of ceramics microbeads is proposed by Yang and Huang[145] at State Key Lab of New Ceramics and Fine Processing, Tsinghua University.

The forming principle of ceramic microbeads is based on the interface tension between two different surfaces. When the slurry is dropped into the oil medium, solidification occurs and beads are formed. The interface tension can be described by the surface tensions difference when two kinds of liquids have been mutually saturated, that is $\gamma_{12} = \gamma_1 - \gamma_1$. According to this formula, without the influence of the external force, the bead can always be formed when the γ_{12} is large and the time is long enough. The larger the γ_{12} is, the shorter the required forming time of the beads.

In preparation process, there are two kinds of mediums. One is water-based ceramic slurry ($\gamma_1 \approx 50\,\mathrm{mN\,m^{-1}}$), the other is oil-based medium ($\gamma_2 \approx 20\,\mathrm{mN\,m^{-1}}$). When the interfacial tension γ_{12} is about $30\,\mathrm{mN\,m^{-1}}$, the slurry droplet can rapidly become a bead in the oil medium. The technical route of gel-beads forming for microbeads is presented in Fig. 19. The process can be more specially described as follows:

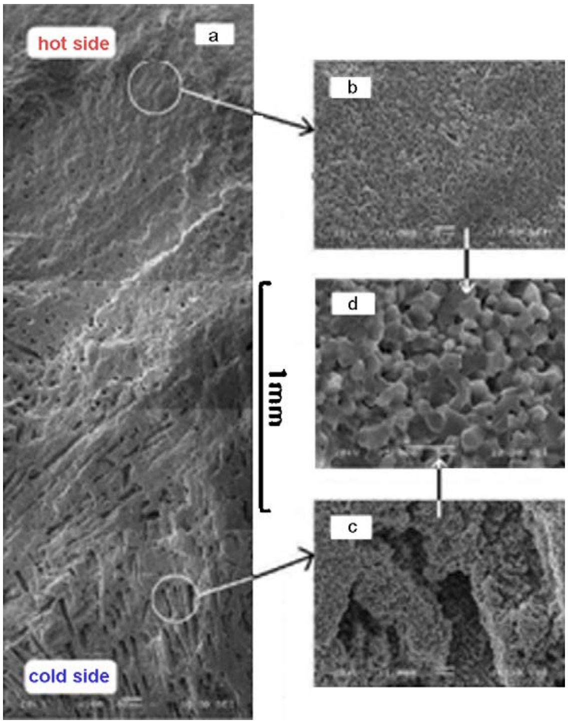

Fig. 18. Gradient pore alumina ceramics fabricated by the freeze-gelcasting technique under the freezing temperature gradient of 12 °C/mm.

Step 1: the preparation of high concentrated ceramic suspension with low viscosity and high solid loading. The ceramic powders, organic additives, and dispersants are mixed in the

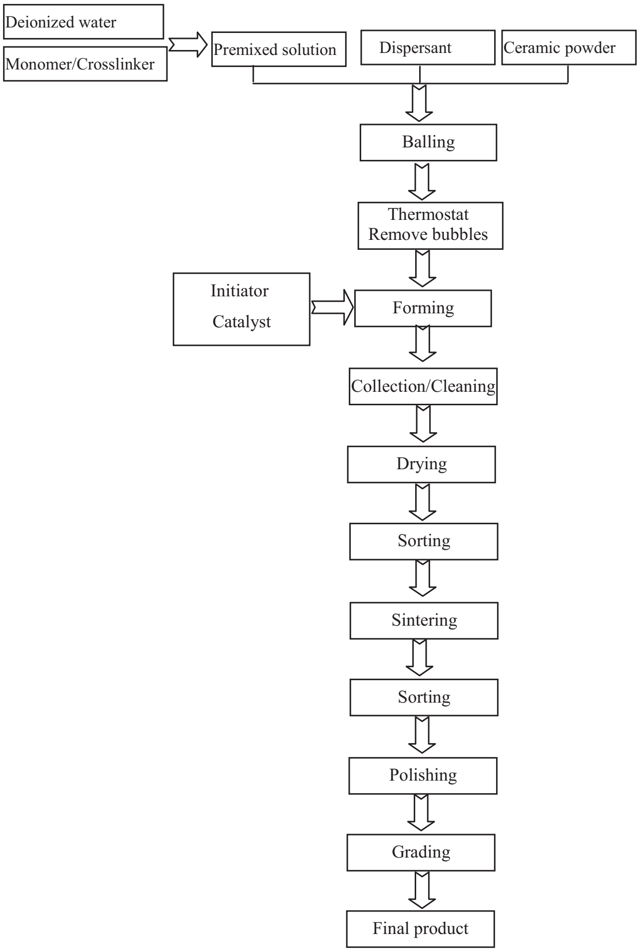

Fig. 19. The technical route of gel-bead forming technique.

Fig. 20. ZrO_2 microbeads of ceramics prepared by gel-bead forming technique.

Table 4
The application fields of ceramic beads with high-performance.

No.	Diameters (mm)	Applications
1	ϕ0.4–0.8	Sandblasting, derusting, surface treatment
2	ϕ0.4–3.0	Ultrafine grinding of non-metallic minerals, paint, dope, printing ink, food, pharmacy
3	ϕ0.38, ϕ0.5, ϕ0.7, ϕ1.0	Ball-pen beads
4	>ϕ3.0	Bearing (hybrid and complete), decorations, ball screw, bike ball
5	>ϕ10	Grinding media, ball valve with acid and alkali resistant and high temperature resistance

aqueous solution uniformly. Generally speaking, the solid loading of ceramic powders in the aqueous suspension is greater than 50 vol.%.
Step 2: by adding the curing agents, the suspension is dropped into the oil-based medium through the necessary instrument, and then is solidified into a microbead through the synthetic effect of curing agents and temperature.
Step 3: after forming, cleaning and drying, the microbeads are sintered.
Step 4: by using the centrifugal rotation type polishing machine, the surface of the sintered ceramic ball can be polished.
Step 5: after cleaning, the balls are sieved into the final products with different diameters.

The gel-beads forming is suitable for various ceramic materials with different sizes (the diameter of microbeads is between 0.1 and 3 mm), such as for the forming of ceramic microbeads of Al_2O_3, ZrO_2, Si_3N_4, SiC and so on. Fig. 20 shows the microbeads of ceramics prepared by gel-bead forming technique. These methods can be carried out just by adjusting process parameters, and would not need new equipment. Compared with other forming methods for ceramic microbeads, the gel-beads forming method has a shorter production cycle and a higher forming efficiency. The microstructure of the products is uniform and dense, and the decortications and fragmentations which occurrerd in traditional rolling method of beads are overcome. The hollow microbeads produced by the melting method are solved, and it is easy to adjust the process parameters, and to carry out automatic and continuous production. At present, the ceramic microbeads are being used for grinding media, ball pen, and far infrared function for health care. According to the diameter distinction of high-performance ceramic beads, the application fields of them are listed in Table 4.

5.2.2. The preparation of rutile capacitor of ceramics based on gelcasting[146]

Rutile possesses excellent mechanical and electrical characteristics, a high dielectric constant, a low loss angle and large breakdown strength. It is an important material especially when applied as a high power capacitor. It has been widely used in high frequency appliances, such as broadcast emitters, radar, high frequency welding machines, and smelting furnaces. For these applications, the most important properties are dielectric constant, loss angel and breakdown strength.[147,148] Generally, the dielectric constant of rutile ceramics is 60–80 ranging from 0.5 Hz to 5 MHz at room temperature. For rutile ceramics, the tangent of loss angle under 1 MHz is about $4–5 \times 10^{-4}$ (testing temperature is $20 \pm 5\,°C$), as such low loss angle is beneficial for decreasing the energy loss of the rutile ceramics under high frequency. Another important property of dielectric materials is the ability to withstand large field strengths without electrical breakdown. According to the national standard of the People's Republic of China, the breakdown strength of the rutile ceramics applied under DC field should be above $10\,kV\,mm^{-1}$.

In the past decades, rutile capacitors with complex shapes and large sizes were mainly fabricated by extrusion forming and subsequent machining.[149] However, the whole procedure is too long (about 2.5 months), and the machining of dried green bodies will result in a great deal of pollution and waste of raw materials. It is difficult to produce rutile capacitors with a large size, complex shape or containing numerous additives in the raw materials by using the traditional process. To overcome these disadvantages, the present authors[146] developed a new route based on gelcasting.

The gelcasting process of the rutile mixture is described in Fig. 21. First, the calcined rutile mixture was dispersed into a premix solution, which was prepared by dissolving AM and MBAM in deionized water. With the aid of a dispersant, the concentrated slurry with low viscosity was formed after balling for 24 h. The slurry was then degassed in vacuum for 10 min after the initiator and catalyst were added. All the above steps were operated at room temperature. Afterwards, the slurry was cast into a steel mold that has been heated in an oven at 70 °C. After coagulation, the demolded green bodies were dried, de-binded and sintered. The production cycle can be decreased to three weeks, and the dust caused by machining can be eliminated. Therefore, both production costs and the pollution can be reduced greatly, while the functional property can be improved greatly, especially the breakdown strength. Compared to extrusion forming,

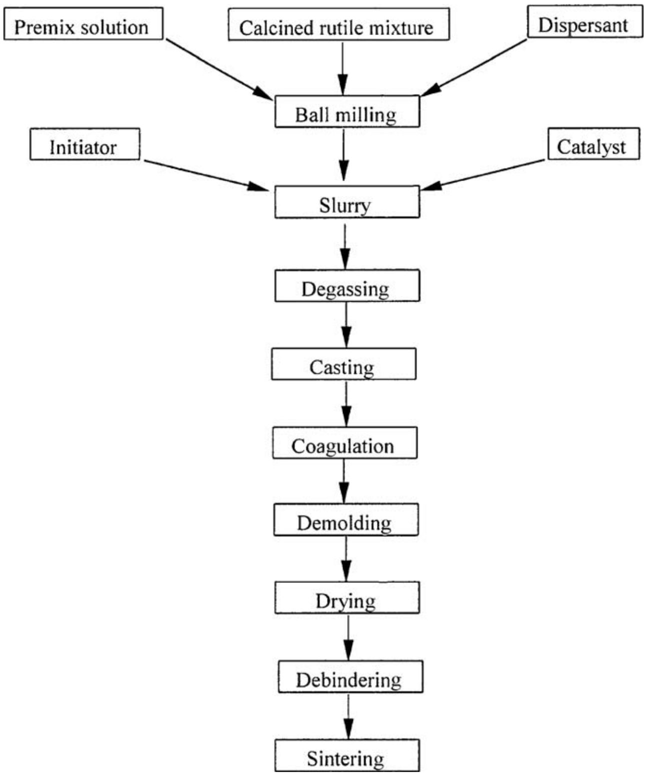

Fig. 21. The flow chart of gelcasting of calcined rutile mixture.

the breakdown strength of rutile capacitor prepared by gelcasting is improved greatly due to the homogeneous microstructure of gelcast parts. Because it is well known that the dielectric breakdown phenomenon of dielectrics is structure-sensitive, the breakdown strength values vary widely according to the characteristics of the microstructure of dielectric materials.[150] By gelcasting, since the microstructure of the sintered bodies of ruitle mixture can be improved, the breakdown can be improved greatly.

5.2.3. The preparation of thin-wall rutile tube for ozone generator based on gelcasting

Ozone is one of the strongest oxidants, which are extensively applied in water treatment, chemical oxidation, food protection and medical treatment and so on. In recent years the requirement for high capacity ozone generators has rapidly increased. Previous studies indicated that the yield of ozone directly related to the dielectric constant and wall thickness of the dielectric body in the ozone generator.[151–153] The dielectric constant of rutile ceramic is about 80–100 which is 15–30 times greater than that of glass and enamel. Furthermore, the rutile ceramics possess a high breakdown voltage. These two characteristics indicate that the rutile ceramics are the optimal material for the dielectric body of ozone generators. However, the forming process of large size thin-wall ceramic tube is very complicated. Technical difficulties and high costs are the main reasons for restricting rutile application in ozone generators.

A stainless steel mold was used to form the thin-wall ceramic tubes. A nonstick agent was pre-coated on the inwall of the mold, which was preheated to about 80–100 °C. The large thin-wall rutile tubes were prepared by colloidal injection molding of ceramics (CIMC), and the processing parameters are as follows: injection speed 15–20 mm s^{-1}, injection pressure 0.3 MPa, pressure holding time 1–2 min.

The ozone generator requires a dielectric body with high dimensional precision. The thin-wall rutile tubes prepared through colloidal injection molding of ceramics (CIMC) can meet this demand. The wall thickness of the sintered tube is 1.5–2 mm and its inner diameter is about 26 mm, and length can reach about 300 mm. The largest eccentricity of the tubes is 0.15.

5.2.4. The preparation of refractory nozzle of zirconia based on gelcasting

A refractory nozzle for precision casting of a 50%Cu–50%Cr molten alloy is required with a high melting point above 2200 °C and a good thermal shock resistance to withstand a temperature rise from the room temperature to 2200 °C in several seconds. In order to control the molten alloy flux accurately, the nozzle should also possess a precise dimension that remains unchanged during casting.

Ziconia, melting at 2680 °C, is usually used as a refractory material at an extremely high temperature. Due to microcracks induced by martensitic phase transformation, ZrO_2 materials have high toughness and good resistance to thermal shock and flux scour. So, it is a suitable material to make the nozzle for precision casting of Cu–Cr molten alloy. To avoid the deformation caused by the shrinkage of the green body during sintering, some coarse particles in the ingredient are useful.

Gelcasting is a near-net-shaping technique to manufacture homogeneous ceramic green bodies due to its in situ consolidation of suspension, but very little research about the gelcasting of suspensions with coarse particles have been reported. For these suspensions with coarse particles, settlement stability should be paid attention to as well as aggregation stability. The effects of various kinds of dispersants (TAC, APA, Gum) on the rheological behavior and the settlement stability of zirconia suspension with coarse particles were investigated, and utilizing such a suspension, a refractory nozzle for precision casting of Cu–Cr molten alloy was prepared by gelcasting. Considering both fluidity and settlement stability, ammonium polyacrylate (APA) was chosen as the dispersant to prepare 69 vol.% ZrO_2 suspensions to make a refractory nozzle for precision casting of Cu–Cr alloy by gelcasting. The nozzle has negligible density difference between different parts, and a good resistance to thermal shock and flux scouring.

5.2.5. The preparation of lead zirconate titanate based on gelcasting[154–158]

In the last several decades, piezoelectric materials such as lead zirconate titanate (PZT) have received an increased demand in a wide field of applications including actuators, sensors, and transducers. The colloidal chemistry of PZT powders in an aqueous solvent, the rheological behavior of the PZT suspension, microstructures and piezoelectric properties of gelcast samples from suspensions with different solids loading were also investigated in comparison with those that were die pressed. It was found that the gelcast samples exhibited stronger piezoelectric effects than die pressed ones using the same sintering method. This may be due to their microstructural difference. After developing concentrated PZT suspension with low viscosity, complex shaped PZT objects are successfully fabricated by gelcasting.

5.2.6. The preparation of ceramics substrates based on gel-tape-casting[159–161]

Ceramics substrates (ceramic sheets) are important electrical component materials that possess many outstanding characteristics such as high temperature resistance, wear resistance, corrosion resistance, anti-oxidation, lightness, and insulation. Thus, they are widely applied in integrated circuits, ceramic capacitors, piezoelectric ceramic devices, and layered composite material.

Generally, ceramic green sheets can be produced through various forming methods[161] such as extrusion forming, dry-pressing, rolling film forming, screen printing forming, tape casting and so on. However, all of the methods available at present have their limitations for ceramic sheets mass production even though some new forming methods and technologies will be further developed and perfected. The gel-tape-casting is considered the main manufacturing method for large-scale ceramic sheet production, and ceramic thin sheets of 0.1–1 mm are successfully formed by gel-tape-casting process.

The gel-tape-casting was proposed by structural ceramic research group from Tsinghua University[159,161,162] which combined the techniques of gelcasting and tape-casting. Gel-tape-casting with a water-based ceramic slurry was achieved through water-soluble organic monomer polymerizing and curing under certain conditions. In the water-based gel-tape-casting process, ceramic powders and some additives are added into premixed solution that is prepared with organic monomer and cross-linkers dissolved in deionized water. The ceramic slurry with a solid loading of greater than 55 vol.% or 60 vol.% containing initiator and catalyst takes on good liquidity and moderate viscosity. After tape casting, the casted slurry is heated at appropriate temperature, and the organic monomer is polymerized due to existing initiator and catalyst. Therefore, the slurry is cured and formed to green tape.

6. Colloidal injection molding of ceramics (CIMC)

6.1. The basic principle of colloidal injection molding of ceramics (CIMC)

Colloidal forming is one important forming technique. It includes slip casting, tape casting, direct coagulation casting, injection molding, and gelcasting. Among these techniques, gelcasting and injection molding are considered as two possible solutions to the industrialization of high performance ceramics. Though they both have many advantages, there are still several problems to solve in the industrialization process. Since the above-mentioned application of gelcasting indicated that there were still some disadvantages, carrying out industrialization by gelcasting is difficult. Most important of all, low automation prevented gelcasting to be utilized in the industrialization of high performance ceramics.[14,22]

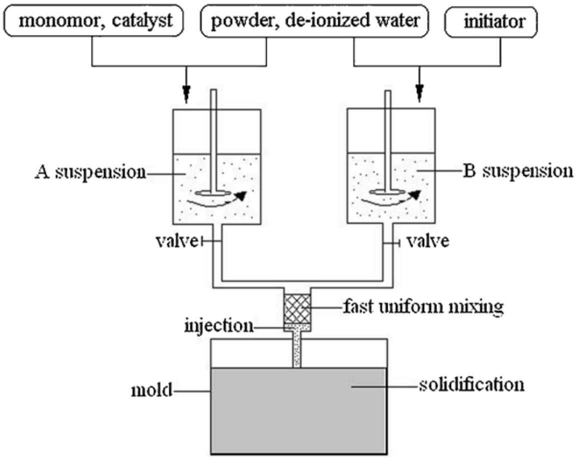

Fig. 22. Schematic graph of colloidal injection molding of ceramics.

Injection molding has been used in the ceramic industry for several years for its high automation capacity. It is a well-established ceramic shaping technique, which involves the mixing of ceramic powder with a large concentration of polymer (up to 50–60 vol.%). The carrier polymer provides very high viscosity, and very high pressures (10–150 MPa) and temperatures (120–200 °C) are needed for injection molding. In addition to the high cost derived from the use of organics the major problem arises from the de-binding step, which can easily lead to defects and failure of the sintered body. In the preparation of products with a complex shape and a big cross section, the problem is more obvious. These disadvantages prevent injection molding from being utilized in the industrialization of high performance ceramics.[158–160,85]

According to the literature, a new forming technique meets the requests of industrialization. The new technique is defined as colloidal injection molding of ceramics (CIMC).[84,158,161,163–168] The process combines the advantages of the conventional injection molding and gelcasting.

The process may promise leaps for the industrialization of advanced ceramics. Fig. 22 shows the schematic graph of this process. The fast uniform mixing and controllable colloidal forming process of ceramics suspension was divided into two components A and B. The monomer and catalyst was added into A, and the initiator was added into B. In this case, there was no separate reaction in A or B because of segregation of the monomer and the initiator. The suspensions could keep good fluidity until they were mixed quickly and uniformly. Once A and B were mixed together, the mixture of monomer and initiator resulted in gel reaction in the suspension. As a sidenote, the catalyst in suspension A could not generate reaction with monomer, and its main function was to accelerate the reaction when the monomers, catalyst and initiator encountered.

6.2. The pressure-induced solidification of colloidal injection molding of ceramics

In colloidal injection molding of ceramics (CIMC), pressure is used to induce a gel reaction, which is different from gel-

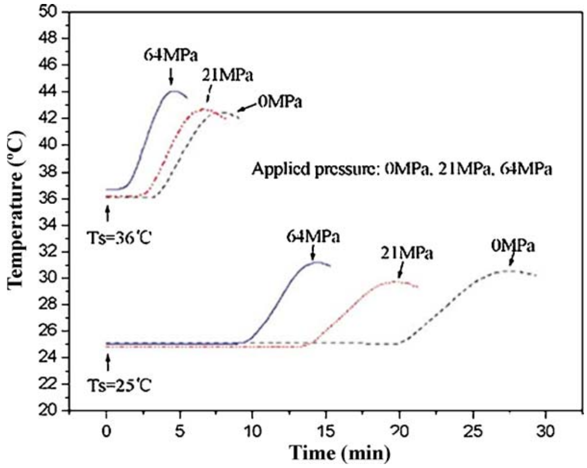

Fig. 23. Influences of pressure on acrylamide gelcasting system.

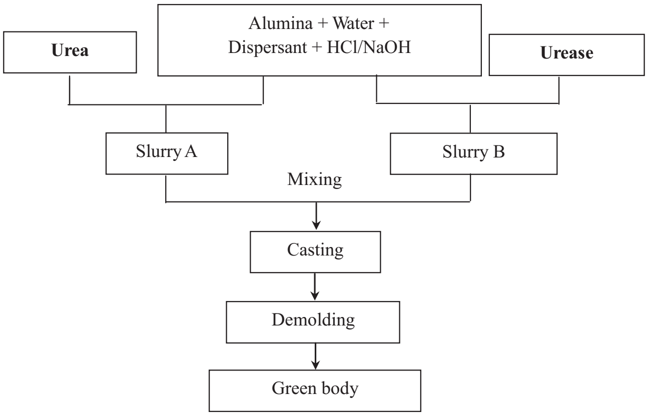

Fig. 24. Flow chart of the application of colloidal injection molding in direct coagulation casting.

casting, in which gelation is induced by higher temperature. The pressure-induced solidification has distinct advantages over temperature-induced solidification. The mold temperature and hence the temperature gradient can be reduced owing to the pressure-induced solidification mechanism. The initiator quantity and the applied pressure are the dominant factors of the solidification reaction in colloidal injection molding. By adjusting initiator quantity and injection pressure in the process, the solidification speed of the suspension in the mold can be effectively controlled, and the pressure can be controlled precisely to optimize the speed of solidification and minimize the structural defects. In the process, the effect of the temperature gradient in the gelcasting process was completely avoided, and the efficiency and reliability of the product were greatly improved due to more homogeneous solidification that reduced the inner stress at the colloidal-forming process and avoided microcracks in green bodies owing to pressure-induced solidification.

The influences of pressure with a mold temperature of 25 and 36 °C on an acrylamide gelcasting system are shown in Fig. 23. The onset time of gelation becomes shorter and the gelation speed increases significantly with the increase of the pressures. At higher temperatures, the influence of the pressure becomes more significant and the gelation finishes almost immediately.

The distribution of pressure in flowing suspensions is homogenous, and fast uniform mixing aided the physical uniformity in the suspensions. The combination of these two techniques ensured simultaneous solidification in different parts of the suspensions. The synchronous solidification decreased the inner stress in the green bodies.

6.3. The application of colloidal injection molding in direct coagulation casting

Colloidal injection molding can also be used for direct coagulation casting (DCC) of ceramic powder suspensions, and the design is shown in Fig. 24.

In the process, the uniform mixing direct coagulation casting (DCC) of ceramic powder suspensions is divided into two components: A and B. Urea is added into A, and the urease used for the catalyst decomposition of urea is added into B. In this case, there is no separate reaction in A or B because of the segregation of the urea and the urease. The suspensions can keep good fluidity until they are mixed quickly and uniformly. When A and B are mixed together, the reaction between urea and urease results in direct coagulation reaction in the suspension. It is unnecessary to cool the suspension before the urease is added because of the segregation of urea and urease used for the catalytic decomposition of urea, and thus simplifies the direct coagulation casting (DCC) of ceramic suspensions process. In addition, colloidal injection molding makes the direct coagulation casting (DCC) controllable, and its application can aid DCC industrialization.

7. Summary and conclusions

Gelcasting is a well-established colloidal processing method for the fabrication of near-net complex-shaped ceramic parts. At present, the studies on gelcasting are mainly focused on the following aspects: (1) the development of low-toxic/nontoxic gelcasting system; (2) the development of control methods for reducing defects in the green body; (3) gelcasting applications for porous ceramics and complex-shaped ceramics (e.g., microbeads, rutile capacitor, thin-wall rutile tube, refractory nozzle and so on); (4) colloidal injection molding of ceramics (CIMC).

The main component of the commonly used monomer acrylamide system in gelcasting is a neurotoxin, which limits the application of acrylamide system. Many low-toxic or nontoxic gelcasting systems were developed. The methacrylamide system is much lower in toxicity as compared to the previously used acrylamide system. Among nontoxic gelcasting systems, the cross-linking of polymers by metal ion complexation, thermoreversible gelation of biopolymers, temperature activated cross-linking of polymers and freeze casting technique are efficient ways to reduce environmental pollution caused by toxic polymers in the gelcasting process. But the experiment demonstrated that the acrylamide–*N*,*N*′-methylenebisacrylamide (AM–MBAM) system was easier to control during gelcasting due to its good gelation properties.

The inner stress in the ceramic green body is usually caused during transformation from suspension to a green body or during the drying stage. The asynchronous solidification of the suspensions caused by various reasons (e.g., the gradient of temperature or initiator distribution) and the surface-exfoliation phenomenon of the green body under air influences the performances of green body (e.g., the strength, the size), and thus it is important to minimize the inner stress and the surface-exfoliation phenomenon in the green body during gelcasting.

The addition of a proper plasticizer or a moderator (hydroxyethyl acrylate (HEA)) in the suspension can adjust the polymer network structure (soften the polymer network) and can control the stiffness of the gel network, thus reducing the inner stress. Adjusting the monomer content (AM and MBAM) and the ratio of monomers (AM/MBAM) can minimize the warpage and shrinkage of a ceramics green body during drying. In the meantime, the malformations and shrinkage of a green body can also be minimized or completely eliminated by using the liquid desiccant drying method. The surface spallation problem can be resolved by introducing a water-soluble polymer (e.g., polymer polyethylene glycol (PEG), polyacrylamide (PAM), or polyvinylpyrrolidone (PVP)) into the acrylamide-based system. Some new methods and new techniques based on gelation are developed to overcome the defects of ceramic parts, such as gelation by ultrasonic effects, laser machining technology, and solid freeform fabrication.

Gelcasting is a well-established colloidal processing method for making ceramics green body with short forming time, high yields, high green strength and low-cost machining, and has been used to prepare high-quality and complex-shaped dense/porous ceramic parts. Gelcasting is widely applied to the fabrication of porous ceramics and complex-shaped ceramics (e.g., microbeads, rutile capacitor, thin-wall rutile tube, refractory nozzle).

Colloidal injection molding of ceramics (CIMC) combines the advantages of the conventional injection molding and gelcasting. In CIMC, pressure is used to induce a gel reaction, which can avoid the effects of the temperature gradient on the gelcasting process. The efficiency and reliability of the product were greatly improved due to more homogeneous solidification that reduced the inner stress at the colloidal-forming process and avoided microcracks in the green body owing to the pressure-induced solidification, and its application can aid DCC industrialization.

Acknowledgements

Our research work in this paper is supported by the National Basic Research Program (Grant No. 2006CB605207-2), the National High Technology Research and Development Program (Grant No. 2008AA03Z507), and Shanxi Provincial Key Scientific and Technological Program of China (Grant No. 20080321027). The authors are grateful for these grants.

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