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Review paper

The transformation mechanism from suspension to green body and the development of colloidal forming

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Abstract

Colloidal forming is a novel wet-processing way to prepare complex shaped ceramic parts with high reliability at low cost. In this article, the transformation mechanisms from suspension to green body and the development of colloidal forming are reviewed. The transformation from suspension to green body in colloidal forming is mainly dependent on the characteristics of suspension, and solidification is the key link in colloidal forming. Various colloidal forming methods are developed to produce ceramic parts, and these methods include slip casting, tape casting, direct coagulation casting, injection molding, gel-casting and so on. The study of defects during colloidal forming should be focused on the defects formation, inheritance and evolution during drying, de-binding and sintering processes. External free controllable technology of colloidal forming is an effective way to achieve ceramic fabrication industrialization, and stress-free colloidal forming is important for the future development of ceramic fabrication.

Keywords: A. Suspension; Colloidal forming; Coagulation mechanism

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1. Introduction

At present, high-performance ceramics are widely applied in many fields such as aerospace, energy, mechanics, biotechniques, etc. Critical factors in the commercialization of advanced ceramics are the starting materials and the way they are shaped. Typical defects in ceramic components are often introduced by the powder itself, and/or in the forming and sintering processes [1]. Reliability and product cost are two major considerations in the applications of advanced ceramics and ceramic composites, and both are directly or indirectly related to the micro-structural defects occurring in manufacturing process. Forming is the key link in the manufacturing process of ceramics, and the control of forming defects is very important. Forming defects can hardly be removed in the subsequent processes (drying, de-binding and sintering) and they become fracture origins which reduce the properties of the product or lead to a high rejection rate [2]. It is well known that the defects such as spallation, delamination, micro-cracks or large pores are often present in the green bodies formed by traditional forming processes (such as dry-pressing, isostatic pressing and injection molding).

Colloidal forming is one important forming technique, and it can significantly improve the micro-structure and uniformity of the ceramic green body [3]. Since 1990s, more attention has been paid to colloidal forming process. Colloidal forming includes slip casting, tape casting, direct coagulation casting, injection molding, gel-casting and so on [4–8]. The development of colloidal forming presents the hope of solving the reliability of advanced ceramics. Colloidal forming can accurately control the size and shape of the green body due to the *in situ* coagulation, and the sintered body basically does not need to be machined. Colloidal forming can not only reduce the production cost of advanced ceramics but also avoid the defects introduced during the processes of forming and machining, and thus it can improve the reliability of ceramic parts.

The nature of the colloidal forming is how to increase the viscosity of the suspension. Some studies showed that the distributions of ceramic powders in the green body influence the microstructure and play an important role in determining the reliability of the final product [9–12]. The control of dispersion and coagulation of ceramic powder particles in suspension is crucial for colloidal forming [12,13]. In order to take full understanding and develop a better system of the colloidal forming. In this article, the transformation mechanism from suspension to green body in colloidal forming and the development of colloidal forming are reviewed.

2. Suspension characteristics of colloidal forming

During colloidal forming, highly dispersed ceramic suspension can be converted into uniform structural green body through *in situ* curing in which ceramic powder particles still retain original uniform structures of the suspension [13]. Once shaped, the rheological properties of the as-formed body must be altered dramatically to permit demolding (when necessary) and subsequent handling without shape deformation. The transformation from suspension to green body in colloidal forming is mainly dependent on the characteristics of suspension.

All of the developed colloidal forming processes start with a suspension where the ceramic particles (ceramic powder particles, sintering aids, whiskers, platelets, etc.) are mixed with a liquid or a polymer melt, a proper dispersant, possibly further additives (such as organic binders, plasticizers, dispersant and other functional additives) [14], and ions (the soluble ions are introduced into suspension by the medium and ceramic powders). The rheological properties of the ceramic suspension are very important to the colloid forming process. It is critical to understand how to manipulate suspension properties to generate desired rheological behavior for the chosen forming technique [15]. Low viscosity and high solid loading are beneficial for both mixing and casting in ceramics suspension processing.

The rheological properties of the suspension affect the mechanical performance of the final sintered ceramic body. Recent research found that the highest flexural strength and the largest Weibull modulus were not achieved at the highest solid loading of the suspensions, and the mechanical performance deteriorated when the solid loading reached a certain high value [16,17]. The reasons for this phenomenon are as follows: the mechanical performance of the sintered bodies is mainly determined by the microstructure of the final sintered ceramic body, and the rheological behavior of the suspension influences the distributions of ceramic powder particles in green body and the microstructure of the final sintered ceramic body, and it plays an important role in determining the reliability of the final product due to the *in situ* occurring process of colloidal forming.

The study on the influence of various dispersants on the rheological properties of suspension is still exploring. Polyacrylic acids are frequently used to disperse oxide particles such as alumina [18,19], rutile, and hematite [20,21]. The investigation of the polymer conformation shows that the stretched polymer dangling into the liquid at the solid/liquid interface gives better flocculation than the coiled polymer sitting at the interface [22–26].

Pan et al. [27] investigated the adsorption and conformation of polymer in dispersion–flocculation of concentrated alumina suspensions, the results showed that the performance of polymer as stabilizer or flocculant for controlling the properties of concentrated suspensions depends upon both the extent of the polymer adsorption and the conformation at solid–liquid interfaces. Solid loading, polymer molecular weight, and the dissolved solid species, among others, are important factors that control the adsorption and conformation of polymer and the system behavior. The conformation of the adsorbed polymer is an important parameter for controlling flocculation/dispersion behavior of concentrated suspensions. Whether these results are applicable to the system of silicon nitride remains to be determined.

The effectiveness of acrylate-based polymers (such as polyacrylic acid and ammonium polymethacrylate) as dispersants for silicon nitride was demonstrated [28–36]. Shih and Hon [37] investigated the stability of colloidal silicon nitride suspension with poly-electrolyte, and the results showed that the conformation of ammonium poly(-acrylate) chain along with the electrostatic interactions was a major controlling factor in determining the stability of colloidal silicon nitride suspension. At the acidic pH range, polymer adsorption in the coiled form was demonstrated to have a positive contribution to the dispersion. Nevertheless, at the alkaline pH range, polymer adsorption in the stretched form was positive and the residual polymer in the stretched form was detrimental to the stability of colloidal silicon nitride suspension [37].

High solid loading is the basis for colloidal forming, and the solid loading of non-oxides (such as silicon nitride, silicon carbide, etc.) in suspension can be increased to about 50 vol% by the surface modification [38,39]. Zhou et al. [40] used Y_2O_3–Al_2O_3 as sintering aids which was coated on the surface of Si_3N_4 particles by precipitation of inorganic salts from a water-based solution containing $Al(NO_3)_3$, $Y(NO_3)_3$ and urea, and the electrokinetic and colloidal characteristics of Si_3N_4 powder were greatly changed by the coating layer. As a result, the dispersion of Y_2O_3–Al_2O_3 coated Si_3N_4 powder greatly increased as compared with that of the original powder, surface coating greatly improved the room-temperature flexural strength and Weibull modulus of the resulting Si_3N_4 ceramic bodies, and the solid loading in suspension would be increased to about 50 vol% by the surface modification.

However, for most of the current methods of surface modification, the surfaces of these non-oxides are coated with other oxides, which is not conducive to the precise control of phase composition in advanced ceramics. Therefore, the future research on the preparation of suspension should mainly focus on the influencing factors on rheological behavior of suspension and on the increase of solid loading of non-oxides in suspension without changing the phase composition of ceramic powders.

On the other hand, through careful control of interparticle forces, colloidal suspensions can be prepared in the dispersed, weakly flocculation, or strongly flocculated states. So far, although the theory of interaction between the ceramic powder particles seems to be more mature [41–47], the direct measurements of interparticle forces in ceramic systems are still lack and now commonly use the colloidal probe technique [48,49].

3. Colloidal coagulation

3.1. Colloidal coagulation mechanisms

Colloidal forming is desirable to form bodies directly from the slurry state with minimal process steps [12], and several colloidal forming methods are developed to produce ceramic parts of various geometric shapes. Representative colloidal forming methods and their salient features are shown in Table 1 [50].

3.1.1. Suspension coagulation by fluid medium removal

Suspension coagulation accompanies fluid removal in several forming methods [50] including pressure filtration [51–53], slip casting [54,55], osmotic coagulation [56,57], tape casting [58–60], and robocasting [61]. For pressure filtration, slip casting and osmotic coagulation, a portion of the liquid medium is removed to yield a saturated ceramic green body, and the green body is dried subsequently. For tape casting and robocasting, forming and drying occur simultaneously.

3.1.1.1. Slip casting. Slip casting is a well-known forming method for the fabrication of complex-shaped ceramics. The mechanism of slip casting was studied by many researchers and many theoretical formulae were proposed [53,55,62–64]. Furthermore, computer simulations based on these formulae have been attempted [65–69]. Slip casting is the process by which a porous mold (usually plaster of Paris: $2CaSO_4 \cdot H_2O$), is filled with a slip consisting of a suspension of a fine ceramic

Table 1
Representative colloidal forming routes classified by coagulation mechanism.

Forming method	Coagulation mechanism	Ceramic part shape
(A) Fluid removal		
Slip casting	Fluid flows into porous mold driven by capillary forces	Complex, 3D, thin walled
Pressure filtration	Fluid flows through porous filter an applied pressure	Simple, 3D
Osmotic coagulation	Fluid flows through a semipermeable membrane driven by osmotic pressure difference	Simple, 3D
Tape casting	Fluid removal by evaporation	Simple, 2D, thin layers
Robocasting[a]	Fluid removal by evaporation	Complex, 3D
(B) Particle flow		
Centrifugal coagulation	Particles flow due to applied gravitational force	Complex, 3D
Electrophoretic deposition	Particles flow due to applied electric field	Simple, 2D or 3D
(C) Gelation		
Aqueous injection molding (AIM)	Physical organic gel forms in response to a temperature change	Complex, 3D
Gelcasting	Cross-linked organic network forms by chemical reaction	Complex, 3D
Direct coagulation casting (DCC)	Colloidal gel forms by flocculation	Complex, 3D
Robocasting[a]	Colloidal gel forms by flocculation	Complex, 3D

[a] Solid freeform fabrication technique (coagulation can be induced via mechanism A or C).

powder in liquid [2,70]. Capillary action due to the pores in the mould withdraws the liquid medium from the slip, and a cast body is formed in the plaster mould as the liquid penetrates into the mould. Very high green densities are easily obtained with well dispersed slips, but slip-cast green bodies are very brittle [71,72], and constrained shrinkage often causes cracking during the drying of slip-cast bodies [73]. Organic binders can be added to increase the green strength, but they tend to cause other processing problems [71]. Addition of a water-soluble binder such as sodium carboxymethylcellulose (Na-CMC) or specially developed additives have been reported [74,75]. Most water-soluble additives negatively affect the viscosity, the long chains of dissolved molecules increase the viscosity of the water phase, and then the addition has to be minimized [71].

3.1.1.2. Tape casting. Tape casting technology first appeared in the 1940s during the Second World War when emerged serious shortages of the quartermaster materials to produce mica capacitors. Tape casting is the prominent technique to produce thin and plate ceramic green sheets [76–78] for substrates (Al_2O_3, AlN) or multilayer structures of various materials for various applications (such as $BaTiO_3$ multi-layer capacitors, laminar composites, etc.). Tape casting produces a thin layer of composite material by coating a carrier surface with a ceramic suspension using the doctor-blade technique [58–60,79,80]. The coating of ceramic suspension is dried to form a flexible film that consists of a particle-filled polymer matrix.

Tape-casting, as a processing method, is a multidisciplinary technique [81] involving ceramic technology, the physical chemistry of powder surface, gel chemistry, organic and polymer chemistry and others. According to the types of solvents used, the tape casting process can be divided into non-aqueous and aqueous systems [82–84]. Classical tape casting suspension consists of a mixture of the ceramic powder and various organic additives such as dispersant, solvent, binder and plasticizer. This suspension is deposited on a casting support, and the dried green tape with sufficient strength and flexibility can be demolded after evaporation of the solvent [85]. In order to avoid the high risk of shrinkage and cracking, the solvent evaporation is a critical stage in the tape casting process.

Non-aqueous solvents typically have lower boiling points and can avoid hydration of the ceramic powder, but they require special precautions concerning toxicity and inflammability [86]. Aqueous solvents have the advantages of incombustibility, non-toxicity and low cost, so are a substitute for non-aqueous solvents. However, the aqueous system is subject to high sensitivity to minor process variables changes such as drying conditions, low evaporation rate of water, casting composition and film thickness [87,79]. Therefore, cracks, bubbles and other defects usually appear in products. Due to these issues, aqueous systems are seldom used for industrial applications up to today. To overcome the drawbacks of tape casting above mentioned, some researchers have studied alternative routes to upgrade the process [78–94]. Based on the advantages and shortcomings of the traditional tape casting technology, the structural ceramic research team from Tsinghua University proposed a new aqueous gel tape casting process [95,96]. In the water-based gel tape casting process, ceramic powder and some additives are added into premixed solution that is prepared with organic monomer and cross-linker dissolved in deionized water. The ceramic slurry with a solid content of greater than 55 vol% containing initiator and catalyst takes on good liquidity and moderate viscosity. After tape casting, the casted slurry is heated at appropriate temperature, the organic monomer is polymerized due to existing initiator and catalyst, and thus the slurry is cured and formed to green tapes.

Gel tape casting technology can be applied for different ceramic powders. The green tapes have less organic content that can be removed through special de-binding process and then direct be sintered. The shaped green tapes are of smooth surface, high strength and good flexibility. However, oxygen can impede free radical polymerization of organic monomer in gel tape casting process. As a result, inert gas protection or other oxygen isolation devices is adopted in the gel tape casting process.

3.1.2. Suspension coagulation by shifting the pH of the suspension towards its isoelectric point (IEP)

In electrostatically stabilized slurries, the electrostatic stabilization relies on the repulsive potential between ceramic powder particles, and the surface charge of powder particles are caused by the protonation or deprotonation reaction of the hydroxyl ions in water [97]. According to Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [98,99], the total interaction potential of a ceramic powder particle in a suspension is the sum of the attractive potential and the electrostatic repulsion potential. The net force acting between the colloidal particles determines the stability of the colloidal system. A net attractive force leads to the aggregation or clustering of particles or for colloidal particles coalescence may occur. If the net force is repulsive, the system will remain stable [100,101].

Direct coagulation casting is a novel near-net-shape method for forming ceramic green bodies from homogenous high solids-loaded ceramic powder suspensions. It is based on the principle of the *in situ* coagulation of a powder suspension via a reaction-rate-controlled internal-enzyme(urease)-catalyzed reaction that produces the desired pH or salt change *in situ* after casting [7,102–104].

In the direct coagulation casting process, coagulation of the ceramic powder suspensions is carried out by shifting the force between the particles in the suspension from the repulsive to the attractive regime. The force between the particles is shifted from the repulsive to the attractive regime either by shifting the pH of the suspension towards its isoelectric point (IEP) or by compressing the electrical double layer [105–121], which thereby induces coagulation. The detailed flowchart of the direct coagulation casting process is shown in Fig. 1.

In the direct coagulation casting process, the typical time-delayed enzyme-catalyzed hydrolysis of urea (NH_2CONH_2) reaction that is used to change the pH and the electrolyte concentration of ceramic powder suspensions is urea decom-

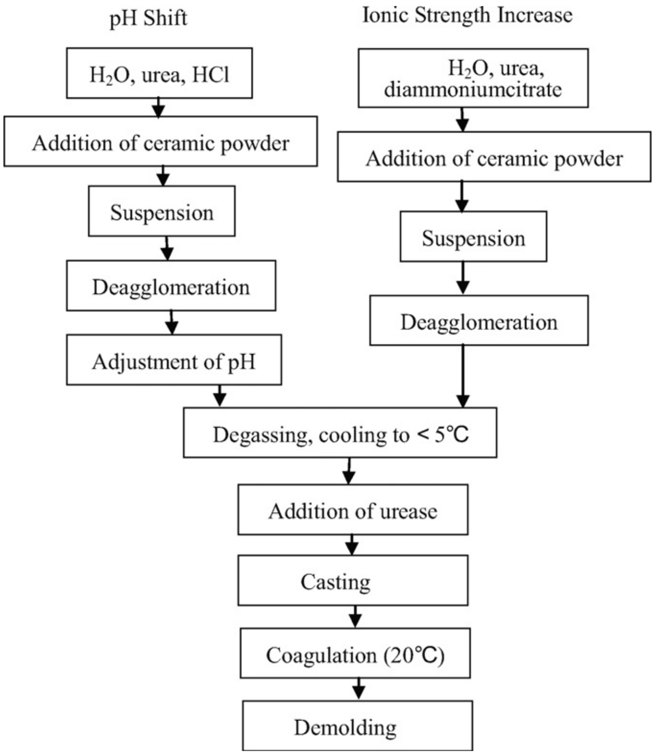

Fig. 1. Detailed flowchart of the direct coagulation casting process [104].

position catalyzed by urease [7]. In aqueous medium, the reactions are:

$$CO(NH_2)_2 + 2H_2O \xrightarrow{\text{urease}} 2NH_3 + H_2CO_3 \tag{1}$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{2}$$

$$H_2CO_3 \rightarrow HCO_3^- + H^+ \tag{3}$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \tag{4}$$

where the buffer pH is 9 and the main reaction products are NH_4^+ and CO_3^{2-}. The reaction causes two effects in the suspension: the pH is buffered at ~9.2; and, because of the production of ions, the ionic strength is increased. In electrostatically stabilized alumina suspensions containing urea, both effects can be used to induce coagulation. Here, we will concentrate on suspension coagulation by shifting the pH of the suspension towards its isoelectric point (IEP). A detailed description on direct coagulation casting by compressing the electrical double layer will be in Section 3.1.3.

3.1.2.1. Urease-catalyzed reactions (DCC-ΔpH mechanism). In DCC, ammonia generated by *in situ* hydrolysis of the urea increases the pH of the suspensions prepared in acidic range only by pH adjustment towards its isoelectric point [122]. At isoelectric point (IEP), ceramic particles that are noncharged (zeta = 0) will strongly attract each other, because of their large Hamaker constant [123], to form a stiff ceramic particles network at high solid loading (generally, >50 vol%). In this case, alumina particles in pure water have an isoelectric point (IEP) of pH ~ 9, If the particles are stabilized at pH ~ 4 using

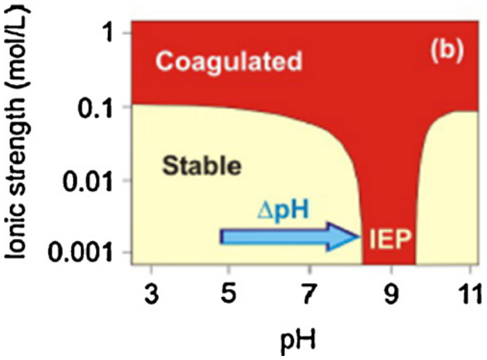

Fig. 2. Stability diagram for an Al_2O_3 suspension as a function of pH [102,124].

an acid, the urea decomposition can be used to shift the pH toward 9 and, thus, lead to coagulation of the alumina suspensions.

Gauckler and co-workers [102,124] utilized enzymatic reactions to shift pH toward the IEP of the colloidal system, thereby inducing coagulation of suspensions, as shown in Fig. 2.

The microstructure of green body produced by pH-shift to the IEP is always very dense and homogeneous without cracks in the green body, and the wet green strength is rather moderate by pH shift due to that the number of ‘‘bonds’’ per particle is low [104]. The coagulation time of the suspensions is usually about 0.5–2 h [4,5], depending on temperature and urease concentration. For pH shift slurries, urea and urease amounts are referred to the alumina weight because the particle surface has to be neutralized. For the coagulation method, no syneresis or sedimentation occurs, which means that the particle network is not contracted during coagulation, although the separation distances between neighboring particles are decreased [125].

3.1.2.2. The combination of physical and chemical gelling mechanisms. Gauckler [126] proposed a method for the direct casting of alumina suspensions that combined the chemical and physical gelling mechanisms. In the chemical and physical gelling, an alginic acid salt is used as the chemical gel precursor, and hydroxyaluminum diacetate (HADA) is used as a time-delayed coagulating/gelling agent. HADA has low solubility in water and can gradually release acetate and aluminum ions into the solution, the released acetate ions lower the pH of the suspension accounted for physical gelation, but it is insufficient to reach the IEP of alumina particles dispersed with diammonium citrate (~5). However, the released aluminum ions in solution can increase the ionic strength, which plays an essential role in the coagulation of suspensions accounted for chemical gelation.

The method utilizes the benefits of each individual gelling mechanism by the addition of HADA. In the process, the physical gel is formed by the gradual release of aluminum and acetate ions from the HADA in water, while the chemical gel originates from the cross-linking of alginate molecules by the polyvalent aluminum ions. Suspension can be coagulated through the above the mentioned chemical and physical gelling mechanisms.

3.1.2.3. Hydrolysis assisted solidification (HAS).

At almost same time that Gauckler proposed DCC, Kosmac et al. [127] proposed the similar approach, hydrolysis assisted solidification (HAS). Hydrolysis assisted solidification (HAS) is a novel ceramic wet-forming technique, in which a small amount (1–5 wt%) of inorganic aluminum nitride (AlN) powder is added as a setting agent to consume the dispersing media [127–129]. In hydrolysis assisted solidification, the pH of suspension is changed only by thermally induced decomposition of AlN not by enzymatic hydrolysis of organic matter. The hydrolysis rate of AlN is temperature dependent, it is low at near room temperature, but higher temperature can greatly accelerate the hydrolysis of AlN. The reactions in water are introduced by Bowen et al. [130] as follows:

$$\mathrm{AlN} + 2\mathrm{H_2O} \rightarrow \mathrm{AlOOH_{amorph}} + \mathrm{NH_3} \quad (5)$$

$$\mathrm{AlOOH_{amorph}} + \mathrm{H_2O} \rightarrow \mathrm{Al(OH)_{3gel}} \quad (6)$$

$$\mathrm{NH_3} + \mathrm{H_2O} \rightarrow \mathrm{NH_4}^+ + \mathrm{OH}^- \quad (7)$$

During hydrolysis assisted solidification (HAS), slurry coagulation mainly depends on the formation of the stiff aluminium hydroxide ($Al(OH)_3$) gel network. During hydrolysis of AlN, water is consumed, and ammonia is formed, both of which increase the pH of the suspension to the IEP of a certain ceramic powder [131–133]. Each of these mechanisms can be used to increase the viscosity and to solidify the slurry.

On the other hand, Kosmac et al. [134] proposed that a thin layer of non-crystalline aluminum hydroxide containing nanocrystals was formed on ceramic powder particle surfaces. The non-crystalline phase plays an important role in suspension solidification, the precipitation formed in suspension of non-crystalline phase may increase suspension viscosity, or the non-crystalline phase selectively precipitates on particle surfaces and thus neck binding is formed between ceramic particles. In low-solid loading suspension, the role of non-crystalline phase in suspension solidification is noticeable. Ceramics based on alumina [135], zirconia [134], and silicon nitride [136], have been prepared by this technique. However, HAS process is not suitable for high purity ceramics fabrication due to the alumina formed.

3.1.3. Suspension solidification by increasing ionic strength (DCC-ΔI mechanism)

3.1.3.1. Urease-catalyzed reactions (DCC-ΔI mechanism).

The electrical double layer is developed by the surface charge on the powder particles that arises from the reaction of the potential determining ions H^+ and OH^- of the water with the ceramic powder surface or by other charged ions that specifically adsorb on the particle surface [137,8]. Ions and polar molecules in the solution surrounding a particle will respond to the charged surface. Electrostatic forces will repel like-charged ions, but attract unlike-charged ions into a region near the surface, increasing their concentration relative to that in the bulk. A diffused electrical double layer is formed around each particle [138,8]. The double-layer thickness is compressed with increasing ionic strength. That is with increasing concentration of counter ions and their valance in the solution, the repulsive forces can be minimized and thereby the suspension destabilized.

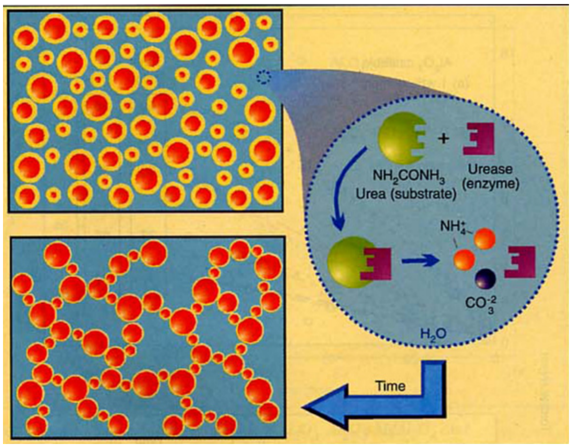

Fig. 3. Schematic illustration of the coagulation mechanism based on the time-delayed increase of ionic strength in the interparticle aqueous medium [140].

Schematic illustration of the coagulation mechanism based on the time-delayed increase of ionic strength in the interparticle aqueous medium is shown in Fig. 3. This coagulation mechanism decreases the magnitude of the electrostatic repulsive forces among particles by increasing the ionic strength of the liquid medium. In direct coagulation casting process, owing to the time-delayed enzyme-catalyzed hydrolysis of urea (NH_2CONH_2) in water, the NH_4^+ and CO_3^{2-} ions produced by hydrolysis reaction ((1)–(4)), and the ionic strength of the suspension increases. It is well known that electrostatically stabilized colloids often coagulate when the ionic strength of the medium is increased sufficiently. The ions of $NH_4^+$and CO_3^{2-} shield the surface charges on the particle surfaces on a short distance, which leads to the compression of the electric double layer around the particles, promotes the formation of a cohesive network of particles and induces the coagulation of suspensions. Velamakanni et al. [139] found that the strength of the particle networks coagulated by increasing the ionic strength of the suspension was much higher than that of suspensions flocked by adjusting the pH to the IEP.

In ionic-strength slurries, the important parameter is the ionic strength which is constant throughout the liquid, and urea and urease concentrations are referred to the liquid volume. Because of ionic-strength slurries containing much more urea, the coagulation time by increasing ionic strength is longer than that of by pH-shift [140]. In general, for the coagulation by increasing ionic strength, several hours or up to 3 days are necessary to get a maximum strength of the wet green bodies. Its compressive wet strength is higher by a factor of up to 10 compared to that of the pH-shift method, but it strongly depends on the coagulation time. This is explained by particles network aging during which the number of particle contacts is increased, thereby improving the strength of the particles network [141].

3.1.3.2. Colloidal vibration molding method.

In order to suppress the composition segregation of colloidal forming (particularly in multiphase system), in 1999, Franks [139] proposed the colloidal vibration molding method: the addition of the independent electrolyte in the uniform dispersed suspension increases the suspension ionic strength and forms weak flocculation, and the flocculation of the suspension does not produce the material segregation and uneven density during centrifugal sedimentation or concentrate filter press. Owing to the decrease of the distance between particles after the concentration, the ''third'' role of a short-range hydration repulsion between particles provides the lubrication of particle rearrangement. Concentrated and water-saturated compacts show flowability under vibration condition, and the suspension can be injected into the mold by vibration method, and then heat curing (95 °C), demolding. During the preparation of composite materials containing the coarse particle, fiber, whisker and the composite crystal panels, the colloidal vibration molding can prevent the composition segregation caused by the sedimentation of reinforcement composition, and it also can overcome the problem of solid volume fraction constrained resulted from double-layer when nano-powder is used.

3.1.4. Suspension solidification by MgO as coagulating agent

The innovation of the present direct coagulation casting process is that the coagulation is neither by pH shift towards the isoelectric point of the suspension nor by an increase in ionic strength to compress the electric double layer. Recently, Prabhakaran et al. [142–144] reported a novel near-net-shape direct coagulation casting method using ammonium poly(-acrylate) as dispersant, and the generation of Mg^{2+} ions from sparingly soluble MgO. The coagulation reactions of the alumina suspension are as follows: [142]

$$\text{Ammonium poly(acrylate)}_{\text{(aqueous)}} \Leftrightarrow \text{ammonium poly(acrylate)}_{\text{(adsorbed on alumina)}} \qquad (8)$$

$$MgO + H_2O \Leftrightarrow Mg^{2+} + 2OH^- \qquad (9)$$

$$\text{Ammonium poly(acrylate)}_{\text{(aqueous)}} + Mg^{2+} \rightarrow \text{Mg-poly(acrylate)} + NH_4{}^+ \qquad (10)$$

In this process, Mg^{2+} ion reacts with the un-adsorbed ammonium poly(acrylate) in the dispersion medium to form precipitate of Mg-poly(acrylate), and it induces the desorption of dispersant (ammonium poly(acrylate)) from the alumina particle surfaces, which leads to insufficient dispersant surface coverage and the coagulation of suspension. The coagulation of the suspension and the structure of the wet-coagulated body are shown in Fig. 4.

A flowchart of the DCC process using MgO-coagulating agent is given in Fig. 5. In the process, the wet-coagulated body with high yield strength and Young's modulus achieved at high MgO concentrations is easily demolded.

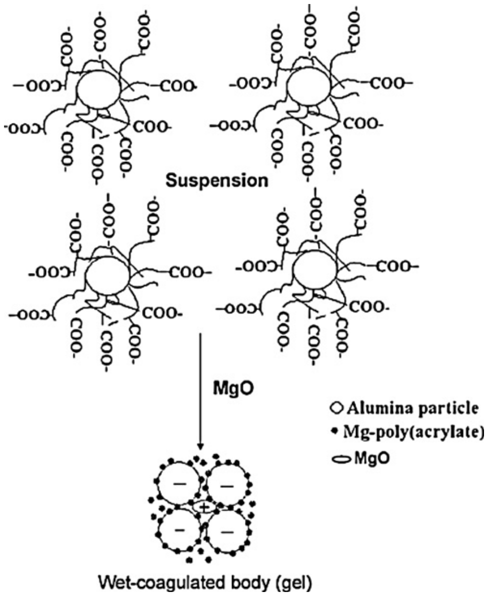

Fig. 4. Schematic sketch of the coagulation process and the structure of the wet-coagulated alumina body (gel) [143].

3.1.5. Suspension coagulation by the reaction of organic binder-gelcasting

Ceramic gelcasting is one of the important colloidal forming processes. Compared with other casting methods, gelcasting can produce green body with higher flexural strength to permit machining in the green state [145–147] and can fabricate much more homogeneous materials with little density differences in ceramic parts. It has been rapidly developed in the past decade

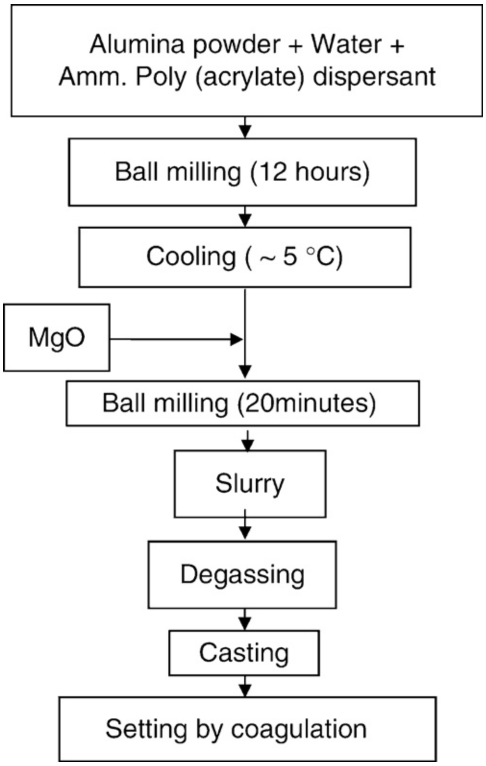

Fig. 5. Flowchart of the direct coagulation casting process using an MgO coagulating agent [144].

due to its capability of near-net-shape forming of fine ceramic pieces, as well as it can be used for a wide range of ceramic and metallic powders. The advantages of the technique include dimensional accuracy, complex shaping capabilities and reducing the cost of manufacturing. Young et al. [148] and Omatete et al. [149–151] investigated the general feasibility of the process and its advantages in comparison with other wet forming processes. In gelcasting process, monomer (acrylamide), crosslinker (*N*,*N*′-methylenebisacrylamide), initiator, catalyst and ceramic powder are mixed in water to form a homogeneous suspension with high solids loading and low viscosity, then monomer is polymerized to form a polymer–solvent gel, and the macromolecular gel network resulting from the in-situ polymerization of dispersed medium holds the ceramic particles in the shape defined by the mold [36,152]. The detail of gelcasting process is shown in Fig. 6.

In addition to acrylamide, many polymer solutions can also gelate in suitable conditions [153], such as agarose [154–156], gelatin [157], carrageenan [158,159], and sodium algaecide [160–164].

So far, most of the researches on gelcasting have been focused on the preparation of suspensions and the process control of gelcasting, the effect of dispersants and pH on the rheological behaviors of suspensions and the effects of concentration of monomer and usage of catalysts and initiators on gelation have been widely studied [148–151,165,166].

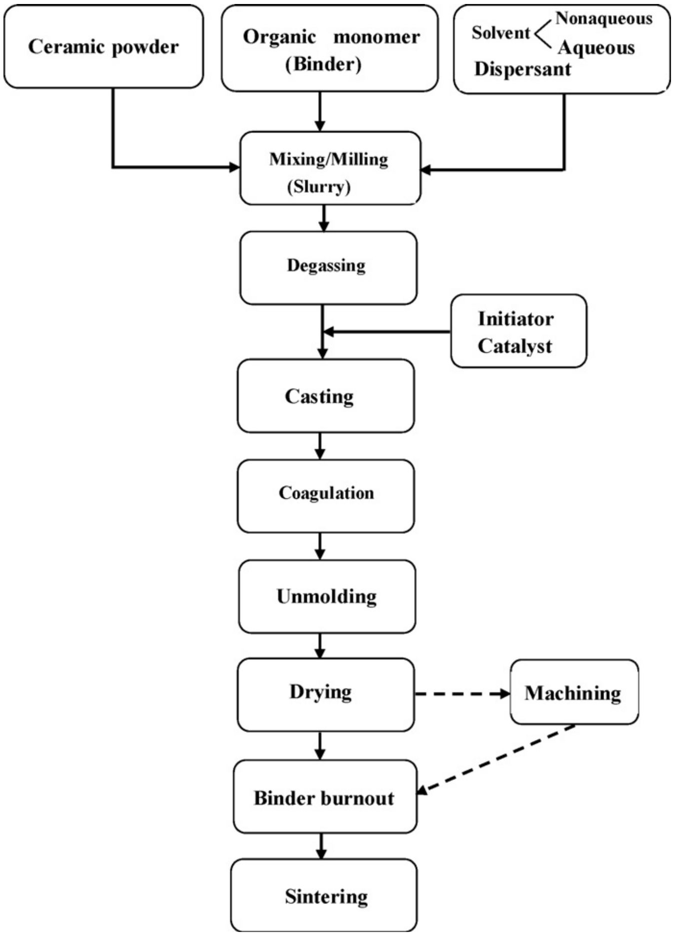

Fig. 6. Detailed flowchart of gelcasting process.

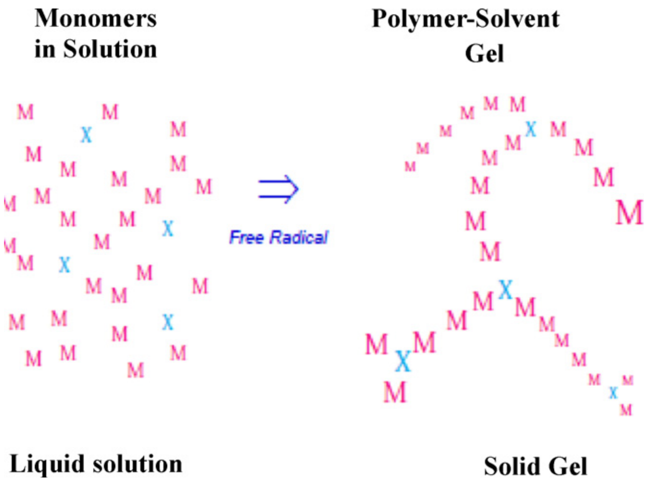

Fig. 7. Monomer solution polymerizes to form a polymer–solvent gel [169].

Omatete et al. [166] discussed the key aspects of gelcasting process: premix solution, rheology of gelcasting slurries, drying process of gelcast parts, binder burnout, strength of dried gel-casting green body, etc. Waesche and Steinborn [167] investigated the effects of slip viscosity on the mechanical properties of high purity alumina by gelcasting. They revealed that the interaction of rheological behavior of the suspension and the generation of defects in the green body were of crucial importance for the optimization of ceramic microstructure in gelcasting process.

In gelcasting, the monomer solution consists of the solvent (typically water), a chain forming monomer, a chain branching (crosslinking) monomer, and a free radical initiator. The polymerization or gelation can be induced by UV radiation [89], applying heat [168] and a catalyst [147]. Gel formation is shown schematically in Fig. 7 [169], the chain building monomer is depicted as ‘‘M’’, and the chain branching or crosslinking monomer is depicted as ‘‘X’’. Upon the addition of free radicals to the solution, the ‘‘M’’ monomers react to form long chains that are occasionally caused to branch by the incorporation of the ‘‘X’’ monomers, and the polymerization result is that a very high molecular weight polymer fills space and traps the solvent molecules among its branches. The network structure will determine whether the water will be firmly held or whether the gel will behave more like a sponge, where water is easily squeezed out. The gel structure will also have a major impact on the texture as well as diffusion of water and soluble compounds [170].

In gelcasting, a monomer solution containing ceramic particles polymerizes to form a polymer–solvent gel, and the macromolecular gel network resulting from the *in situ* polymerization of dispersed monomers medium immobilizes the particles in the gel [152,171]. After removal from mold, the gelled part contains about one-fourth of its mass as moisture, and the moisture is then removed by drying. A microscopic cross-section of wet and dried gelcast parts is shown in Fig. 8.

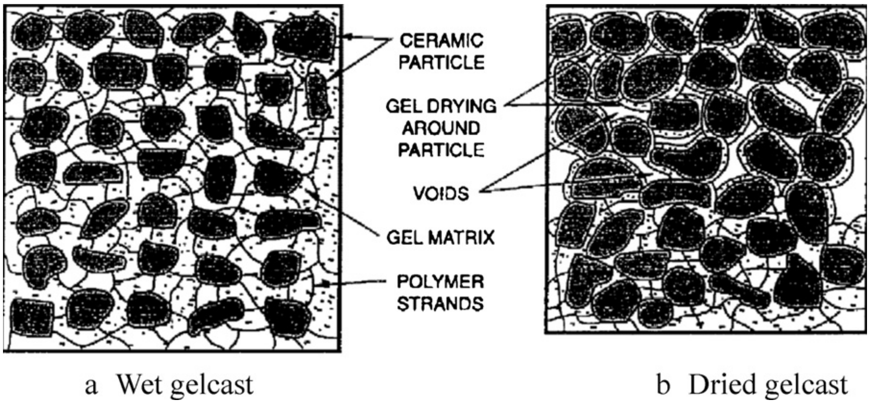

Fig. 8. Magnified schematic representation of a microscopic cross-section of wet and dried gelcast parts [171].

3.1.6. Suspension coagulation by changing the characteristics of dispersant

The most important forces which determine the stability of colloidal dispersions are van der Waals dispersion forces, electrostatic and steric forces due to polymers adsorbed at the interface. The term electrosteric stabilization is often used to describe how polyelectrolytes act as dispersants to make ceramic powder particles stabilized in suspension. Electrosteric stabilization is a combination of a pure electrostatic repulsion and polymer steric repulsion [172], where the relative importance of the respective contributions is closely related to the segment density profile at the interface. If the polyelectrolyte adsorbs in a flat conformation, the polymeric repulsion is short-range in nature, and the stabilization mechanism is mainly electrostatic. Usually, when the polyelectrolyte is highly charged, the polyelectrolyte has an extended conformation, and the ceramic particle surface is oppositely charged. With thicker adsorbed layers, the chains of polyelectrolyte easily protrude into the solution, and the polymeric contribution will become more important. In addition to the steric contribution, there is always an electrostatic contribution since the adsorption of a highly charged polyelectrolyte on a weakly charged amphoteric oxide surface usually results in an increase of the net surface charge density [173]. Therefore, polyelectrolytes acting as dispersants can make ceramic powder particles electrosterically stabilized in suspension.

Temperature induced forming (TIF) [174–176], a novel near-net shape forming method by changing polymer conformation with temperature to initiate gelation, has been recently developed at the Max-Planck-Institut für Metallforschung (Stuttgart, Germany). In TIF, the change of polymer conformation with temperature makes the interparticle potential change, and then particles start to connect each other to form flocculation (a so-called physical gel) [177]. The slurry is gelled and can be demolded when the flocculation size reaches the dimensions of the mold.

Bergstrom and Sjostrom [178] made use of the change of dispersant configuration in suspension by adjusting temperature to realize the colloidal forming of ceramic powder particles under Van der Waals force dominated condition, and they prepared Al_2O_3, Al_2O_3/SiC suspension (amphoteric surface-active agent polymer as dispersant, amyl alcohol as the medium). In the stable suspension, the dispersant has good solubility and stretches in linear at relative high temperature (30 °C). When the temperature is reduced to a certain degree, the dissolve effects of dispersant and medium decrease, and the configuration of dispersant transfers from stretch to coil (see Fig. 9). The repulsion forces between the particles decrease because of the decrease of dispersant thickness on the surface of powder particles, and particles flocculate by the dominated attraction. Compared to the irreversible temperature-induced solidification of the electrostatic stabilization suspension, the temperature-induced solidification of the spatial stable suspen-

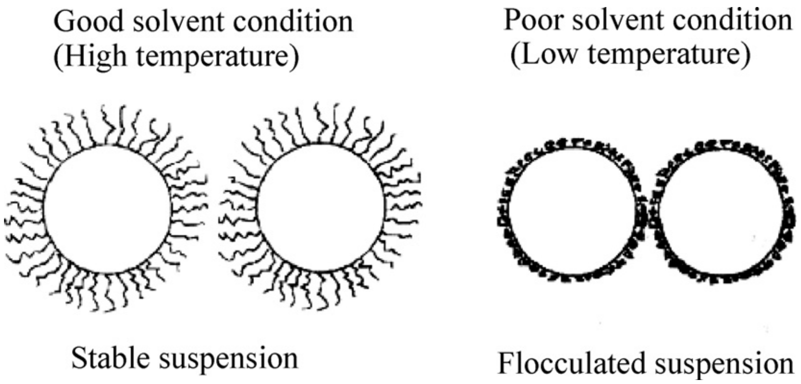

Fig. 9. The change of configuration of dispersant in suspension with temperature.

sion is reversible: with the decrease of temperature, suspension flocculates; with the increase of temperature, the dispersant configuration stretches, the dispersant thickness on the surfaces of powder particles increases, the repulsion between the particles increases, and the flocculated suspension is redispersed.

In TIF, when a low molecular weight dispersant for stabilization at room temperature is employed to obtain highly concentrated stabilized ceramic suspensions, the added macromolecules of the polymer exchanges the low molecular weight dispersant adsorbed when temperature increases, and the drive for dissolution makes the suspensions flocculate. In the process, the gelation is initiated by the change of materials' solubility with temperature [179], which makes suspensions transform from ''fluidlike'' to ''solidlike'', and it leads to the gelation of TIF slurries. As an example, Al_2O_3 powders are dispersed by the adsorption of ammonium citrate (TAC) to form high solid loading suspension. During the preparation of high concentration Al_2O_3 ceramic suspension, firstly dispersant (TAC) is added to make the adsorption of powder surface saturated. At room temperature, the added dispersant is adsorbed on the surface of powder particles, which makes the surfaces of powder particle have the same kind of charges and makes the powder particles in suspension electrostatically stabilized due to the repulsive potential between powder particles. When a very small amount of macromolecule (e.g. poly(acrylic acid) (PAA)) is added into the suspension at room temperature, PAA adsorption cannot occur due to its equivalent surface charge and the physical obstruction of the adsorbed TAC molecules. When the temperature of suspension is raised, the solubility of Al_2O_3 increased, and TAC molecules are replaced with PAA molecules from the surfaces of powder particles (see Fig. 10). The chain of PAA macromolecules extends far into ceramic suspension, the free end of PAA macromolecules can adsorb other particles and create a bridged network, the bridged flocculation network constrains the solvent and increase the viscosity, and finally the suspension is solidified.

3.1.7. Suspension coagulation by freezing liquid medium

Freeze casting technique [180–189] is a novel environmental friendly forming method, and it draws much attention because of its simple operation and no addition of natural polymers. In the preparation process, ceramic suspension is poured into a mold, then frozen and subjected to sublimative drying of the solvent (water) under vacuum. Particular features of this technique are the steps of freezing a slip in a mold, demolding in the frozen state, followed by freeze drying and sintering. The frozen suspension liquid acts as not only a binder to hold the part together for demolding but also the template of the pore channels. Sublimation of the solvent (water) is made to eliminate the drying stress, avoiding shrinkage, cracks and warpage of the green body that generally exist in the normal drying [190]. Freeze casting technique is often used for the preparation of porous ceramics with widely controllable porosity [184,188–190], and aligned pore channels and a porous gradient can be achieved by controlling the freezing direction and temperature gradient. A major problem of freeze-casting is the low strength of green body, the green body becomes very frangible and difficult to handle when the frozen suspension liquid is volatilized, and further efforts are underway to improve the strength of green body [191].

3.2. Study on the defects during colloidal forming

Colloidal forming is a new multidisciplinary process, and it still has some practical problems during the large-scale industrial production. Colloidal forming technology can make a highly dispersed ceramic suspension be converted into uniform structural green bodies and products through *in situ* curing, but 40 vol% of the solvent is left in green body, in which temperature and humidity must be properly controlled, or it may result in the stress and crack in green body in the drying process.

In order to obtain high-quality ceramic green body and sintered parts, these defects must be eliminated. So far, more attention should be given for the study on the defects formation, inheritance and evolution during drying, de-binding and sintering processes.

Since 1990, many new colloidal forming routes have been developed, and many papers about colloidal forming were published, but it has been neglected the shrinkage from liquid to green body during colloidal forming. The inner stress in the ceramic green body originates from the non-uniform shrinkage during the suspension solidification and the drying of green body, the magnitude of the inner stress increases with the

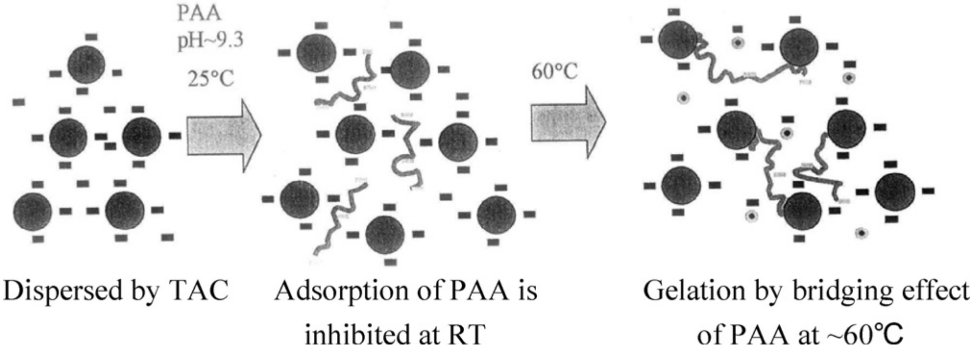

Fig. 10. Bridging flocculation of Al_2O_3 slurry by exchange of TAC and PAA with increasing temperature.

shrinkage rate and the elastic modulus, and the temperature gradient, initiator concentration and moisture are also the important original factors causing the inner stress. The inner stress in green body is often responsible for the initiation of microcracks on subsequent drying and de-binding processes, and thus colloidal forming process without shrinkage is very important for the fabrication of high-quality ceramic parts.

4. Controllable colloidal forming and its industrialization

Since colloidal forming is a new forming process, taking into account of the differences with the traditional process, we must pay attention to the research and development of special equipment. From the powder pretreatment, slurry preparation, molding, solidification, demolding, drying, de-binding and sintering, the systematic and complete sets of equipment must be considered to ensure that the stress, deformation, cracking and other defects are not introduced specially in those stages from the powder pretreatment to the demolding.

In the industrialization of high performance ceramics, forming has become a bottleneck not to overstep. External controllable technology of colloidal forming is an effective way to achieve industrialization. Among the above-mentioned techniques, gel-casting and injection molding are considered as the two possible solutions to the industrialization of high performance ceramics. Traditional injection molding can be used to form complex ceramic parts with high dimension-precision, so that can be applied to realize the automation of large-scale production of ceramic products in industries. The problem of this technique is that, due to the high content of organics, it is very difficult for de-binding. The colloidal forming processes such as gelcasting and DCC can avoid this disadvantage, and these approaches can improve the uniformity of green bodies and the reliability of the ceramics products. These approaches, however, have other shortcoming, for example, they need manual operation and thus are difficult to be applied in the ceramic industries where automation is a necessity. An optimal approach would be a combination of both injection molding and colloidal forming processes, bringing together their advantages.

According to the situation, a new forming technique meets the requests of industrialization. The new technique is defined as colloidal injection molding of ceramics (CIMC) [190–195]. The idea for colloidal injection molding of ceramics is shown in Fig. 11. The process may be the hope of industrialization of advanced ceramics.

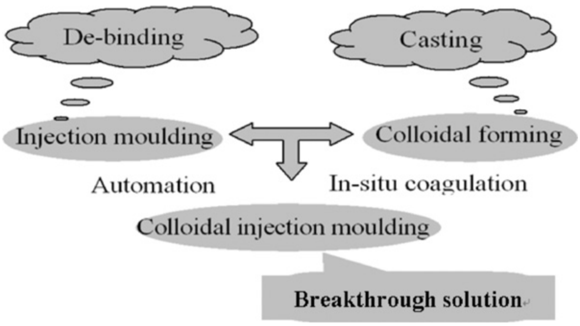

Fig. 11. The idea for colloidal injection molding of ceramics.

4.1. Colloidal injection molding of ceramics (CIMC)

Colloidal injection molding of ceramics combines the advantages of the conventional injection molding and gelcasting. Fig. 12 shows the schematic graph of this process. The fast uniform mixing and controllable colloidal forming process of ceramics suspension is divided into two components A and B. The monomers are added into A, and the initiator is added into B. In this case, there is no reaction in separate A or B because of segregation of the monomers and the initiator. The suspensions can keep good fluidity until they are mixed quickly and uniformly. Once A and B were mixed together, the encounter of monomers and initiator resulted in gel reaction in the suspension. The initiator quantity and the applied pressure are the dominative factors of the solidification reaction. By the way, the catalyst in suspension A cannot generate reaction with monomers, and its main function is to accelerate the reaction when the monomers and initiator encounter.

In colloidal injection molding of ceramics (CIMC), pressure is used to induce a gel reaction, and it is different from gelcasting, in which gelation is induced by higher temperature. The pressure-induced solidification has distinct advantages over temperature-induced solidification. The mold temperature and the temperature gradient can be reduced owing to the pressure-induced solidification mechanism. By adjusting initiator volume and injection pressure in the process, the solidification speed of the suspension in the mold can be effectively controlled, the pressure can be controlled precisely to optimize the speed of solidification and minimize the structural defects, and this is the meaning of controllable colloidal forming. In the process, the crucial impact of temperature on gel reaction is completely avoided, and it can avoid the effect of the temperature gradient on gelcasting process.

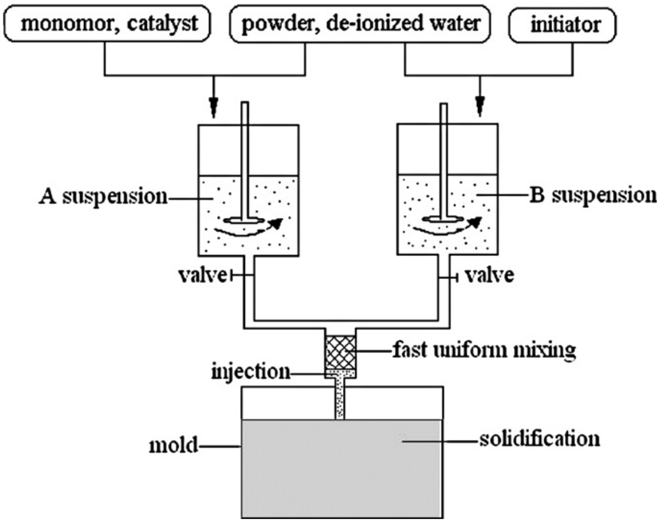

Fig. 12. Schematic graph of colloidal injection molding of ceramics [196].

Table 2
The characteristics of dry pressing, traditional colloidal forming and stress-free colloidal forming.

Performance	Dry pressing	Traditional colloidal forming	Stress-free colloidal forming
Body stress	Little	With stress	Stress relief
Body density	Non-uniform	Uniform	Uniform
Drying stress	Little	With stress	Controlling the drying, eliminating stress
Debinding stage	–	May lead to cracking	No cracking
Sintering stage	May lead to cracking	May lead to cracking	No cracking

The efficiency and reliability of the product are greatly improved due to more homogeneous solidification that reduces the inner stress at the colloidal-forming process and avoids the microcracks in green bodies owing to the pressure-induced solidification.

The colloidal injection moulding process is a promising inner-stress free colloidal forming solution. Inner-stress free colloidal forming has the following characteristics (as shown in Table 2): (1) stress is released in green body; (2) body density is uniform; (3) stress can be controlled or eliminated during drying; (4) no cracking occurs during de-binding and sintering stages. And thus stress-free colloidal forming is important for the future development of the ceramic fabrication.

4.2. 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, the design is shown in Fig. 13.

In the process, the uniform mixing direct coagulation casting (DCC) of ceramic powder suspensions is divided into two components A and B. The 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 reaction in separate A or B because of segregation of the urea and the urease. The suspensions can keep good fluidity until they are mixed quickly and uniformly. Once A and B were mixed together, the encounter of urea and urease resulted in direct coagulation reaction in the suspension. By the way, it is unnecessary to cool the suspension before the urease is added because of the segregation of urea and urease used for the catalyst decomposition of urea, and thus this simplifies the direct coagulation casting (DCC) of ceramic suspensions process. In addition, the colloidal injection molding makes the direct coagulation casting (DCC) controllable, and its application can realize DCC industrialization.

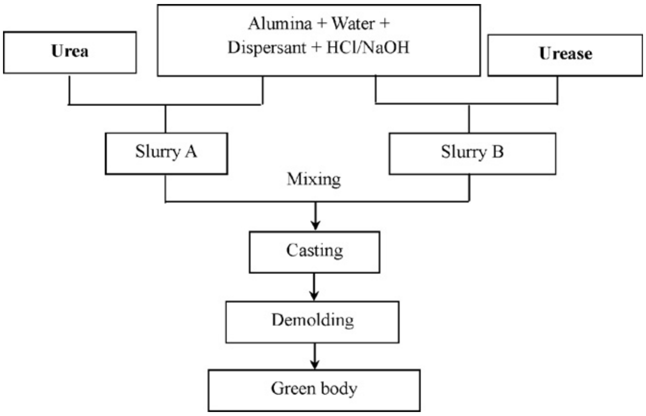

Fig. 13. Flow chart of direct coagulation casting of ceramics.

4.3. The industrialization of colloidal injection molding

A special equipment for the colloidal injection molding of ceramics process was manufactured by Yang et al. as show in Fig. 14.

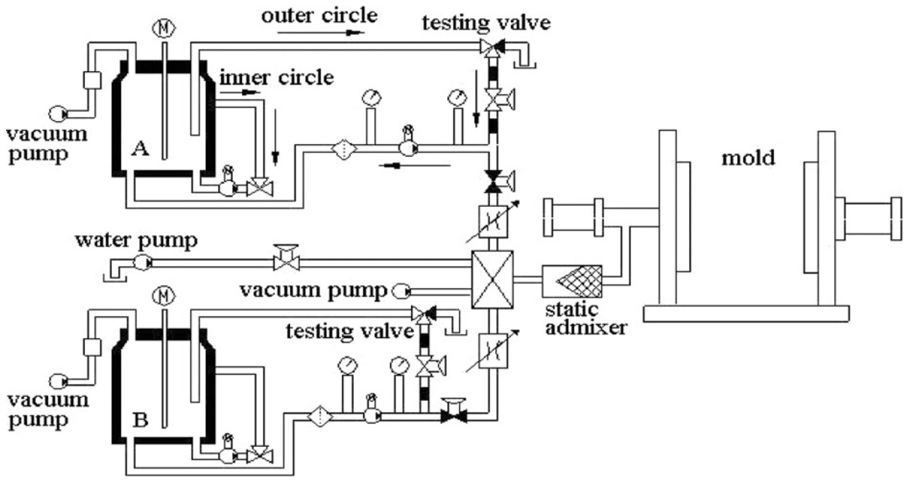

Fig. 14. The equipment for colloidal injection molding of ceramics.

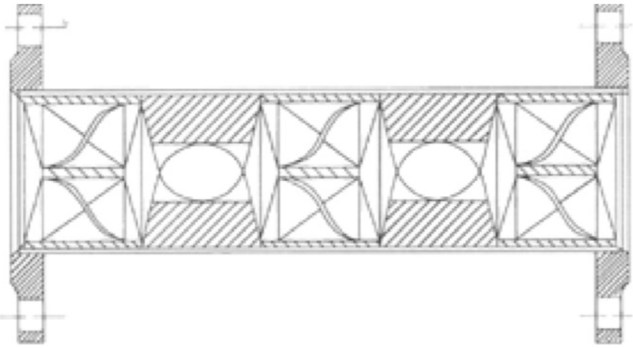

Fig. 15. Inner structure of the static admixer.

Fig. 14 shows the flow chart of the machine working. The characteristics of this equipment for the colloidal injection molding of ceramics process are as following: firstly, the prepared suspensions are transferred into A and B container respectively, in the containers, the suspensions can be vacuumized through the vacuum pumps to completely remove the gas solved in them; to avoid the suspension deposition, a stirring paddle is applied in each of the containers to continuously intermix the slurries; furthermore, with the function of bellows pumps, the slurries can circulate by two routes (inner circle and outer circle), this circle transportation plus stirring action on the slurries can thoroughly prevent the occurrence of deposition; the suspension state can be monitored through the testing valves, which is positioned on the outer circle line.

Before injection molding, the metering pumps quantify two same volume slurries. The two slurries are simultaneously and quickly injected into the static admixer with a high pressure 5–8 MPa. The core status of the static admixer can be seen in Fig. 14. It is just like a bridge connecting the machine and the mold. Its main function is to realize fast uniform mixing of A and B suspensions. The inner structure of the device can be seen in Fig. 15. From this chart, it is known that the mixing process is realized by a series of mixing units with different shapes in the hollow tube. These units make the penetrating slurries fast levo-rotate and dextral-rotate alternately. These frequent changes of the slurries' flowing directions can help us obtain good mixing effect that is so called fast uniform mixing.

The above mixed suspensions are injected into the mold under the pressure of 3–8 MPa. The antisticking agent is usually pre-coated in the in-wall of the stainless steel mold. Initiator volume and injection pressure are the dominative factors to control the solidification process. In conclusion, the separation of monomer and initiator guarantees no reaction in separated suspensions, which gains enough operating time for the process. When the injections of the suspensions are completed, these tubes in the equipment for the colloidal injection molding of ceramics can be washed in time by water pump.

5. Summary and conclusions

Colloidal forming can accurately control the size and shape of the green body due to the *in situ* coagulation, and it can significantly improve the micro-structure and uniformity of the ceramic green body and increase the reliability of ceramic parts. Colloidal forming technology can make a highly dispersed ceramic suspension be converted into uniform structural green bodies and products through *in situ* curing, the transformation mechanisms from suspension to green body and the development of colloidal forming are reviewed.

The transformation from suspension to green body in colloidal forming is mainly dependent on the characteristics of suspension, low viscosity and high solid loading are beneficial for both mixing and casting in ceramics suspension processing, and the rheological properties of the suspension affect the mechanical strength of the final sintered ceramic body.

Coagulation is the key link in colloidal forming, various colloidal forming methods are developed to produce ceramic parts, and these novel methods include slip casting, tape casting, direct coagulation casting, injection molding, gelcasting and so on. The coagulation mechanisms of colloidal forming include fluid medium removal, changing the electrical properties of ceramic particles, changing ion strength of suspension, the reaction of organic binder-gelcasting, changing the characteristics of dispersant, and freezing liquid medium.

In colloidal forming, more attention should be given for the study on the defects formation, inheritance and evolution during drying, de-binding and sintering processes. Colloidal forming process without shrinkage is very important for the fabrication of high-quality ceramic parts.

Colloidal injection molding combines the advantages of the conventional injection molding and gelcasting. The colloidal injection molding process is a promising inner-stress free colloidal forming solution. External free controllable technology of colloidal forming is an effective way to achieve industrialization, and stress-free colloidal forming is important for the future development of the ceramic fabrication.

6. Prospects of colloidal forming

The process of colloidal forming is essentially to increase viscosity of suspension to form a wet green body with enough strength which can be demolded. Exactly, colloidal forming *in situ* should be no shrinkage from liquid to solid. However, most of colloidal forming processes have some shrinkage, many defects produced by shrinkage during forming would go into next steps, such as drying, de-binding, sintering and machining, by heredity, aberrance and rebirth of these defects, and thus the colloidal forming without shrinkage and internal stress is one of future direction for colloidal forming.

Acknowledgements

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