

Alumina Casting Based on Gelation of Gelatine

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Abstract

A new colloidal in-situ forming technique based on the gelling property of gelatine is discussed in this paper. A warm slurry containing more than 50 vol% alumina powder and a small amount of gelatine (~1 wt% of powder weight) is cast into a nonporous mould, and a rigid green body can be produced upon cooling below the so-called gel point of gelatine (15–20°C). The mixed slurry is a pseudo plasticity fluid with an apparent viscosity lower than 1 Pa·s. After drying, ceramic compacts can be sintered without special debinding operations due to the small amount of binder © 1998 Elsevier Science Limited. All rights reserved

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1 Introduction

Gelcasting is a near-net-shape forming method combining polymer physical chemistry, colloidal chemistry and ceramic technology.^{1,2} Aqueous gelcasting has been studied and used widely in recent years.^{3–8} In the process, ceramic powders are dispersed in the pre-mixed monomer solution and then cast in a nonporous mould. At the temperature of 60°C or so, by acting with a cross-link agent, initiator and catalyst, the monomer polymerizes to form a strong, cross-linked polymer-solvent gel and permanently immobilizes the ceramic slurry in the desired shape. Besides the common properties of colloidal forming methods, such as reducing agglomerates and impurities, improving the reproducibility and reliability of ceramics,^{9–11} gelcasting has a notable merit—the dried green body is very strong and can be machined easily, which can decrease the demands to moulds and cut down greatly the cost of ceramic fabricating.

However, this process is not perfect in that the polymerization of monomer is difficult to control in the ceramic suspension. Reductive agents usually restrain the free-radical polymerization of commonly used acrylamide. In addition, acrylamide is harm to the nervous system of people.¹²

In fact, many polymer solutions can gelate under suitable condition,^{13–16} such as agarose, gelatine, sodium alginate, and so on. When the polymer is dissolved in solvents, the molecular chains attract each other to form a three-dimensional network by Van der Waals forces and hydrogen bonds. The gelation property of agarose has been used in the water-based injection moulding^{17,18} and gelcasting¹⁹ of alumina. In these cases, a well-dispersed suspension of alumina and agarose powder was heated at 85–90°C to dissolve the agarose completely and then cast into a nonporous mould. At about 35°C, the agarose gelled, enclosing ceramic powder and water in its gel network to form a green body with the desired shape.

The problem of agarose is that the solving temperature is fairly high (~85°C). During the process of heating, water vaporized heavily, resulting in agglomerates and flocculation, which increased the viscosity of the slurry.

Compared with agarose, gelatine (protein polymer composed of various amino acids) has some excellent properties.¹⁶ The most attractive is that gelatine can be dissolved quickly at a rather low temperature (about 40°C). This work investigated the gelling property of gelatine and the influence of gelatine on an alumina ceramic suspension. Rigid alumina green bodies were also prepared by in-situ coagulation of slurries containing gelatine.

2 Experimental Procedures

2.1 Materials

The gelatine powder with molecular weights ranging from 15 000 to 90 000 was provided by Shanghai Chemical Reagent Works. The analysis

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of the gelatine is shown in Table 1. A 1 wt% gelatine solution changes into strong and stable gel over a wide pH range of 4–10 when cooled.

The alumina powder used here was a commercial grade An-05, which was produced by Henan Xinyuan Aluminum, Industry Co. Ltd in China. The average size of the powder was 2.0 μm . The chemical composition of the powder is shown in Table 2.

2.2 Procedure

The forming process is described in Fig. 1. First, the alumina powder and dispersant were added to deionized water, ball-milled for more than 12 h, and then mixed with gelatine solution prepared by dissolving gelatine powder in deionized water at 40–50°C. After degassing by vibrating or stirring under a vacuum (10 mm Hg), the warm slurry was cast into a nonporous mould made of steel, glass or polyester plastics. Cooling down to the gel point of the gelatine, the slurry coagulated to form a green body. After demoulding and drying under 80°C for 24 h, the green parts could be sintered without special binder removal processing.

2.3 Properties measurement

The rheological properties of the gelatine solution and mixed ceramic slurry were measured by a rotary rheometer (NXS-11, Chengdu, China). The gel strength was examined by a simple device usually used in the gums industry²⁰ (shown in Fig. 2) Supposing the total weight recorded on the load cell was W when the push pin broke the surface of gel sample, and the cross-sectional area of the push pin was A , then the gel strength could be calculated using the formula $G = W/A$, where the unit of G is gram per square centimeter (g cm^{-2}).

A dried green body was cut into sample bars of $6 \times 5 \times 36 \text{ mm}^3$. A sintered plate was cut into samples of $3 \times 4 \times 36 \text{ mm}^3$ and then polished. Their room temperature mechanical strength were determined by three-point flexure test with space of 30 mm (crosshead speed of 0.5 mm min^{-1}). The microscopic morphology was observed by SEM (OPTON.CSM950).

3 Results and Discussion

3.1 The gelation process of the gelatine solution

The apparent viscosity change of a 6 wt% gelatine solution with temperature is shown in Fig. 3. Above

Table 2. Chemical composition of alumina powder (wt%)

Al_2O_3	$\alpha\text{-Al}_2\text{O}_3$	SiO_2	Fe_2O_3	Na_2O	B_2O	Loss on ignition
>99.7	>95	0.05	0.03	0.05	0.04	0.1

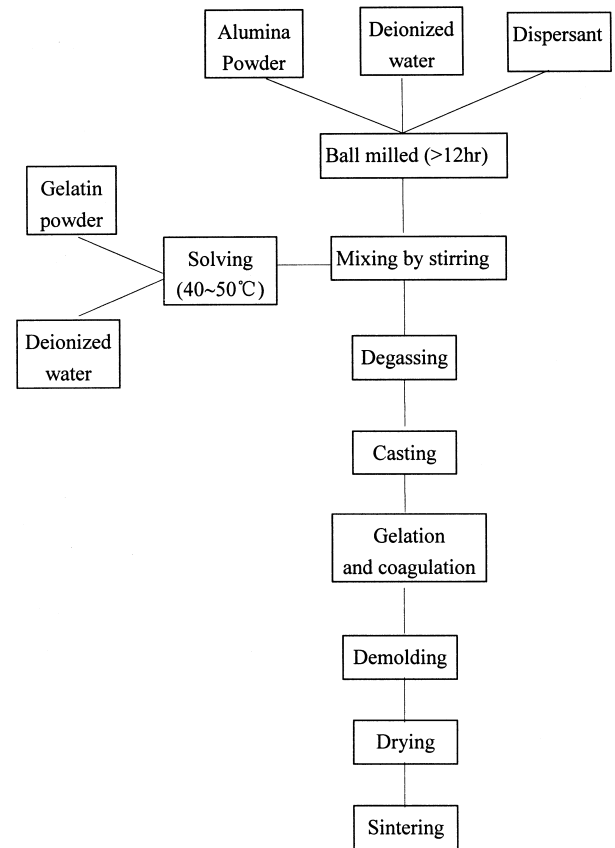


Fig. 1. Flow chart of forming process.

25°C, the apparent viscosity changes little, ranging from 2 to 8 mPa·s. Over this temperature range, the shape of polymer molecule changed from random clew ball to single-helix chain. When the temperature drops below 25°C, single-helices entangled with each other, resulting in an obvious rise of apparent viscosity. With the apparent viscosity rising sharply to more than 20 Pa·s, a three-dimensional network was formed by the attraction between molecular chains. At the joints of the gel network, the molecular chains are ordered into microcrystal zones.^{13,15,16}

3.2 Gel strength

The gel strength increased with the increment of the gelatine content (Fig. 4) As more microcrystal zones were formed by gelatine polymer chains, the

Table 1. Impurities in gelatine powder

Composition	Chloride (Cl^-)	Heavy metal ash (Pb)	Ash	Sulfur dioxide (SiO_2)	Arsenide (As)	Iron (Fe)
Content (< wt%)	0.2	0.008	2	0.015	0.0003	0.007

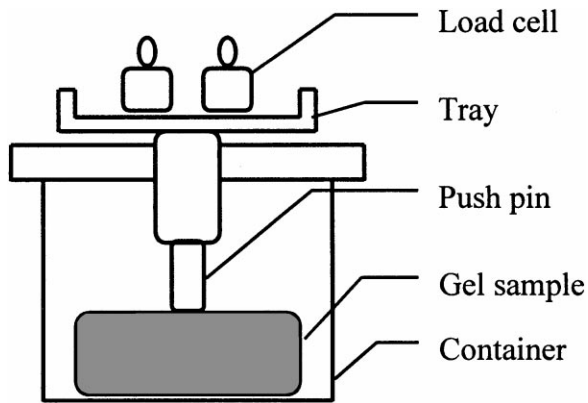


Fig. 2. Device for gel strength measuring.

structure of the gel network became tighter and the gel strength higher. Compared with agarose, the strength of the gelatine gel is relatively low.^{17–19} With the content of 3 wt%, the strength of agarose gel is greater than 1000 g cm^{-2} , while the strength of gelatine gel is only 100 g cm^{-2} . Because the strength of the gel, along with the solids loading, ultimately determines the strength of the wet and dry green body, it proved more effective to add more gelatine into the slurry to increase the strength of the green body. However, in order to realize the forming process of gelcasting, the slurry should have an appropriate viscosity and fluidity. Therefore, the content of gelatine must also be determined from the rheology of the slurry besides the strength of green body.

3.3 Rheology of the slurry

Figure 5 shows the flow curve of the Al_2O_3 suspensions with different gelatine concentration at 30°C . The pure alumina slurry with a volume fraction of 53 vol% had an average viscosity of $50 \text{ mPa}\cdot\text{s}$. Adding gelatine, the viscosity increased greatly. When the content of gelatine was less than 4.5 wt% (based on water), the apparent viscosity was lower than $1 \text{ Pa}\cdot\text{s}$, which allowed the casting process to take place. Slurries with gelatine contents

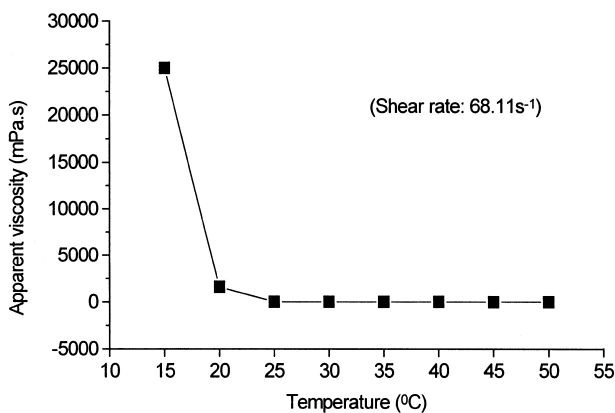


Fig. 3. Apparent viscosity change for gelatine solution (6 wt%).

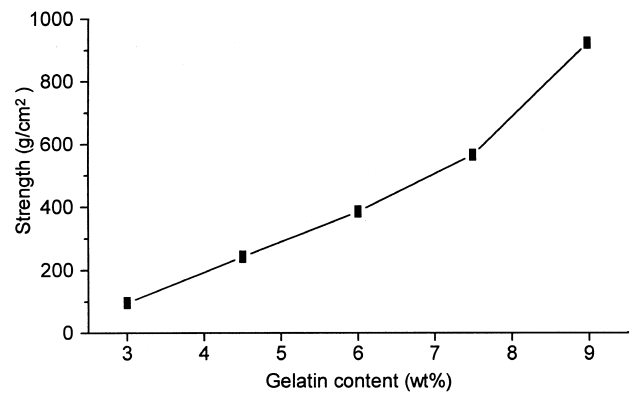


Fig. 4. Gel strength variation with gelatine concentration.

greater than 6 wt% were thick and did not flow into the mould easily due to their apparent viscosity being higher than $3 \text{ Pa}\cdot\text{s}$. Under those conditions, agglomerates or flocculation may occur and the homogeneous microstructure of ceramic body will be destroyed.

The rheological properties of a slurry with 53 vol% Al_2O_3 and 3 wt% gelatine at temperatures is shown in Fig. 6. Before gelation, the slurry is a pseudo plasticity fluid, because gelatine polymer chains could turn and transform to decrease the resistance of shearing. Since the process of slurry degassing and casting are usually performed under dynamic conditions rather than static, pseudo plasticity is helpful.

3.4 Forming of a wet green body

On casting the warm slurry of alumina and gelatine into a nonporous mould, it would coagulate at the gel-point of gelatine. The change in apparent viscosity of the slurry (Fig. 7) is similar to that of a pure gelatine solution (Fig. 3). Above the gel-point, the slurry had a relatively low viscosity (less than $200 \text{ mPa}\cdot\text{s}$). At the temperature between $15\text{--}20^\circ\text{C}$, the viscosity rose abruptly to higher than $30 \text{ Pa}\cdot\text{s}$.

It has been reported that the network of gelatine gel contains many microcrystal zones, which act as the joints of gel. After gelation, the polymer chains

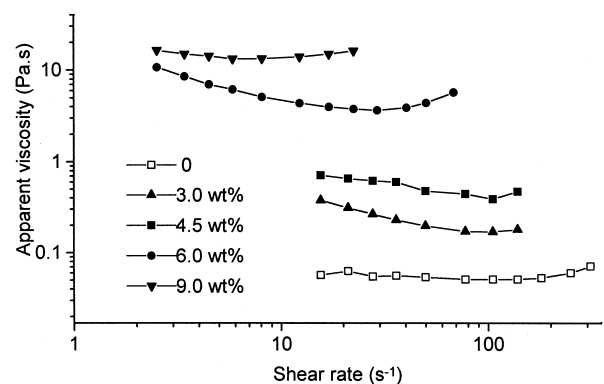


Fig. 5. Effect of gelatine concentration on viscosity of the suspension containing 53 vol% solids loading.

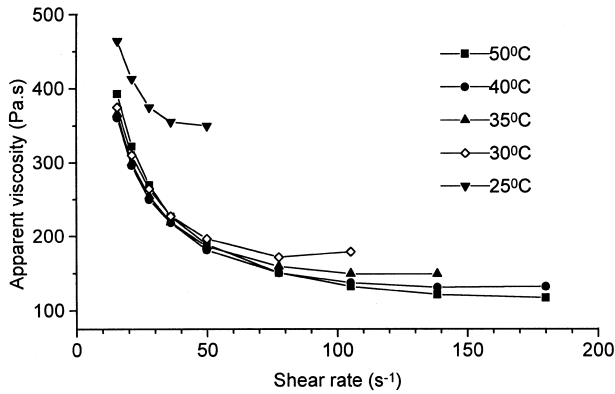


Fig. 6. Rheologic behaviour of the slurry with 53 vol% alumina and 3 wt% gelatine.

continue to rearrange in the network to form more microcrystal zones, and thus increase the rigidity of the gel.

The wet green body was very weak and had poor strength when just formed. It could not be demoulded until the structure of gelatine gel developed through the arrangement of polymer chains. A simple ceramic part, such as a disc with 150 mm in diameter and 20 mm in thickness could be demoulded 6–8 h after slurry casting. While for a complex compact, such as a turbine blade, nearly 24 h was required in order to avoid deferring or cracking of the wet body when demoulding. In general, the demoulded bodies had precise size reproduction and very smooth surface if the surface of the moulds are smooth.

3.5 Properties of the dry bodies and sintered bodies

The green body has a shrinkage of 2–3% (linear) during drying. Figure 8 shows an SEM photocopy of a dry body. It can be seen that powders are connected by slender polymer chains, which are responsible for the strength of the green body. The influence of the gelatine content on the strength of the dry body is shown in Fig. 9. The strength is greater than 8 MPa when the gelatine content is more than 4.5 wt%. Although the body is stronger

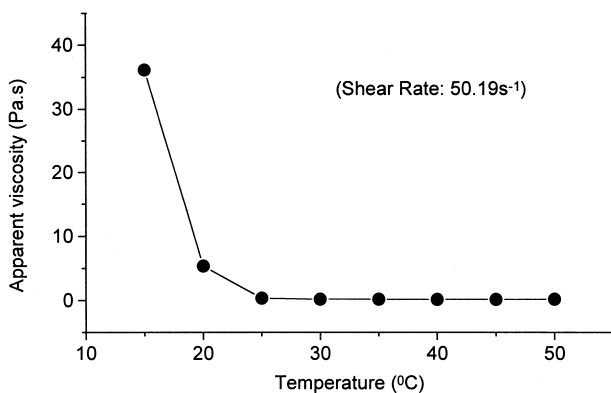


Fig. 7. Apparent viscosity change for the slurry with 53 vol% alumina and 3 wt% gelatine.

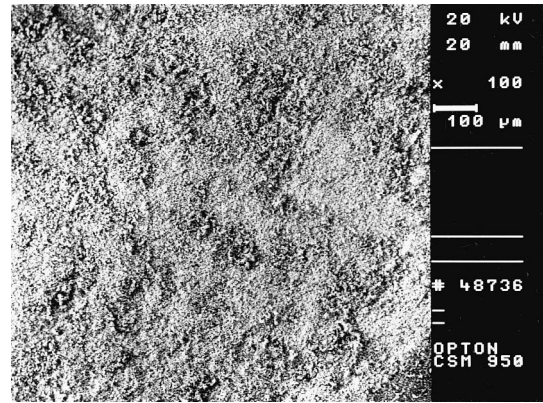


Fig. 8. SEM micrograph of a dry green body.

with more gelatine (with gelatine content higher than 4.5 wt%, strength is greater than 8 MPa), the error bar is also enlarged, indicating that homogeneity is reduced. This may be accounted for by the incomplete degassing, inhomogeneous slurry mixing, or the presence of agglomerates resulting from the higher viscosity.

Regarding the fluidity of the slurry and the strength of the green body, 4–5 wt% gelatine (based on water) is suitable for the suspension containing 50–55 vol% alumina powder used in this research. Various ceramic green bodies were prepared by this forming process (shown in Fig. 10)

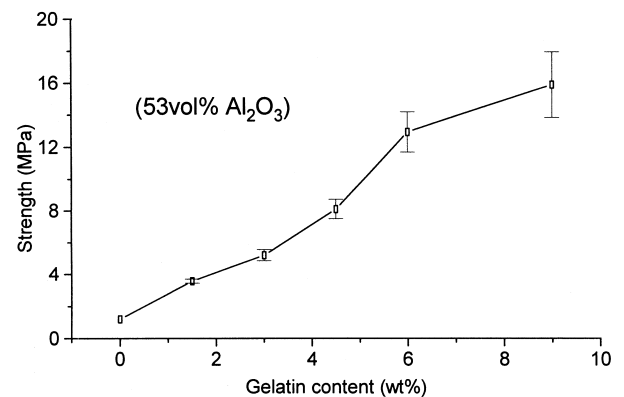


Fig. 9. Influence of gelatine content on the strength of a dry green body.

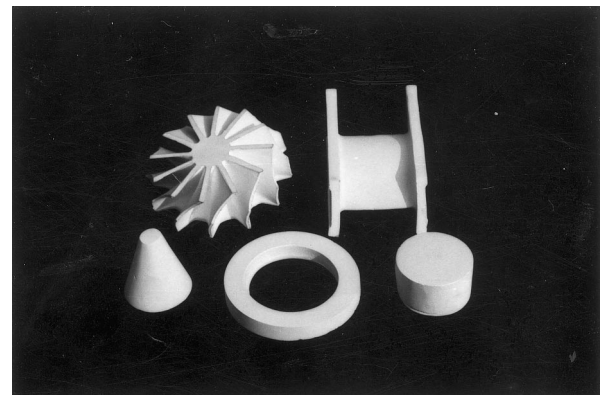


Fig. 10. Examples of ceramic green parts made by the forming method.

Green parts can be sintered directly without special binder removal procedures because the organic binder content is 1 wt% based on the powder weight. Ceramics with the formation of 95 wt% alumina and 5 wt% clay made by this method have linear shrinkage of 15–16% during firing. Theoretical density of final product is 96.5% and bending strength reaches 304.6 MPa.

4 Conclusion

1. Gelatine can be dissolved in water above 40°C, and the solutions gel at 15–20°C. Higher content gelatine solution produce greater gel rigidity and green body strength. On the other hand, higher viscosity and poor uniformity of the slurry and green body were observed at such concentration as higher than 6 wt% (based on water).
2. A suitable gelatine content for suspensions of 50–53 vol% alumina powder is 4–5 wt% (based on water). Such slurries have apparent viscosities lower than 1 Pa and are pseudo plastic in nature, which is helpful for casting.
3. Wet green compacts can be formed from the alumina slurry by gelatine gelation. The strength of a coagulated body increases with the development of the gelatine gel structure. Therefore, a gelation time of several hours or more is needed from starting the process to demoulding.
4. The resultant green bodies have precise size and relative smooth surface with linear drying shrinkages of 2–3%. The strength of the dry body is higher than 8 MPa with about 1 wt% gelatine (based on the powder weight). Sintered samples have shrinkage of 15–16% and bending strength of 304.5 MPa.

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