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Control of the inner stresses in ceramic green bodies formed by gelcasting

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Abstract

The negative effect of inner stresses on the ceramic green body formed by gelcasting is discussed. It is found that a proper amount of hydroxyethyl acrylate (HEA) added into the concentrated suspension can adjust polymer network structure and thus reduce the inner stresses and cracking in the ceramic green body. The debindering time of large ceramic parts can be significantly shortened by reducing the harmful inner stresses in the green body.

Keywords: Gelcasting; Green body; Inner stresses; Debindering process

1. Introduction

Property reliability and product cost are two major considerations in the applications of advanced ceramics and ceramic composites. Both are directly or indirectly related to the micro-structural defects occurring in manufacturing process [1]. The random nature of these defects is often responsible for the poor reliability and performance of ceramic products. It is well known that defects like 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 moulding. These defects can hardly be removed in the subsequent processes and become fracture origins reducing the properties of the product or leading to higher rejection rate. Since 1990s more attention has been paid to colloidal forming processes such as gelcasting, direct coagulation casting and colloidal vibration forming due to their potential to improve the homogeneity of ceramic body and reduce harmful micro-structural defects.

Among these colloidal forming processes, gelcasting, by which complex ceramic parts can be prepared [2], has been widely studied and applied to various ceramic materials [3–5]. Homogeneous green bodies with good strength required for machining can be made through this process. The mechanical properties of the materials after sintering are greatly improved [6–8]. The main steps of gelcasting are as follows [3–5,9]: First, the ceramic powder (e.g., alumina or silicon nitride, etc.) is thoroughly mixed with small quantities of gel initiators, catalysts, monomers, crosslinkers and sintering additives to form a homogeneous suspension with high solid loading and low viscosity. Second, gelation is initiated by casting the suspension into a non-pore mould at elevated temperature. A green body is then formed by in situ polymerisation with a three-dimension gel network holding all the ceramic particles together. The green bodies are then demoulded, dried, debindered and finally sintered at a high temperature.

In this process, the mould temperature is utilized as a method to induce polymerisation in the suspension. However, a temperature gradient exists in the suspension due to the heat transfer from the mould surface to the concentrated suspension. Due to the temperature gradient,

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the solidification of the suspension is not uniform, resulting in inner stresses in the green bodies. The inner stresses are often responsible for the cracking of the green bodies in subsequent drying or debindering process. The larger the parts are, the more harmful the inner stresses are. Therefore, it is of great importance to control the inner stresses in the green bodies in order to prepare large-size ceramic parts by gelcasting.

The inner stresses in the green body originate from differential contraction so that the magnitude of the inner stresses increases with the shrinkage rate and the elastic modulus. There are two sources of shrinkage in gelcasting process: one being the forming shrinkage due to slight contraction in the polymerisation of monomers and the other being the drying shrinkage due to the removing of the moisture. A high solid loading in the suspension is preferred in gelcasting in order to reduce the shrinkage of the green body. However, there is a limit of solid loading in the suspension for desirable viscosity and uniformity [7–8]. In order to control the shrinkage rate, the wet green body is usually dried slowly under controlled temperature and humidity and then debindered at a very low heating rate. This is not favourable in practice because it leads to a prolonged operation time and high production cost. Recently, the authors developed a pressure-assisted gelcasting process using injection moulding of colloidal suspension [10]. The mould temperature and hence the temperature gradient can be reduced owing to the pressure-induced solidification mechanism. The reliability of the products is improved due to more homogeneous solidification but with an extra cost. The authors found that the cracking of the green bodies could be reduced by the addition of a plasticizer or a moderator in the suspension [11–12]. It is thought that the inner stresses are correlated with the elastic modulus of the green body that can be controlled by the modification of the gel network by moderators. This mechanism has been explored in this paper using lab simulations. The strategies to minimize the inner stresses will be reported and the implications on the cracking of green body and the efficiency of debindering process will be discussed.

2. Experimental procedure

2.1. Materials

A commercial Al_2O_3 powder with mean particle size of 3.84 μm, produced by Xin-yuan Al_2O_3 Plant of He-nan in China, was used. Other chemical reagents used were: deionized water with conductivity of 1.02 $\mu S\,cm^{-1}$, acrylamide (AM) as monomer, hydroxyethyl acrylate (HEA) as moderator, methylenebisacrylamide (MBAM) as crosslinker, $(NH_4)_2S_2O_8$ as initiator, ammonium citrate as dispersant and *N*,*N*,*N*′,*N*′-tetraethylmethylenediamine (TEMED) as catalyst.

Table 1
The weight percent of HEA in the monomers in different premix solutions

Pemix solution	HEA/(HEA + AM)
M_1	1
a	1/3
b	1/5
c	1/9
d	1/11
e	0

2.2. Procedure

Premix solutions were prepared by dissolving MBAM, AM and HEA in deionized water. Since the moderator (HEA) was in fact a kind of monomer, the total concentration of HEA and AM was kept constant at 14 wt.% while the ratio of HEA to AM varied. The concentration of the crosslinker, MBAM was kept at 0.6 wt.%. The concentrations of initiator and catalyst are referred to reference [10]. Six premix solutions with decreasing HEA concentration, M_1, a, b, c, d, e, were prepared, as summarized in Table 1. Al_2O_3 powder was dispersed into the premix solutions at a solid loading of 50 vol.%. In order to obtain a low viscosity, 1 wt.% of ammonium citrate of the ceramic powder was added into the suspensions as dispersant. The suspensions were subjected to ball milling for 24 h and then poured into a mould to form ceramic green bodies. The moulds are listed in Table 2. The green bodies were dried for 48 h at the room temperature and then put into an oven at 80 °C until constant weight was obtained. The dried green bodies were debindered for 40–50 h by heating slowly from the room temperature to 600 °C and then sintered in a furnace at 1560 °C for 2 h.

2.3. Testing methods

Viscosity of suspensions was measured using a viscometer (MCR-300 mode, Physica Corporation, Germany). The images of the cracks in the ceramic green bodies were taken at a short focal distance ratio with a digit camera. Test bars with dimensions of 6.5 mm × 5.5 mm × 42 mm were prepared for evaluation of the flexural strength and elastic modulus of the dry green bodies using three-point bending tests on a testing machine (Dujin 2000A, Japan).

In order to simulate the asynchronous solidification of ceramic suspensions, an organic glass mould was made.

Table 2
The moulds used to form green bodies

Number	Name	Dimensions
1	Simulation mould	Shown in Fig. 1
2	A glass beaker of 150 ml	Φ5.6 cm
3	A plastics beaker of 1000 ml	Φ11.3 cm
4	An annular stainless steel mould	External: Φ12.0 cm Inner: Φ5.3 cm
5	A spherical nylon mould	Φ7.0 cm

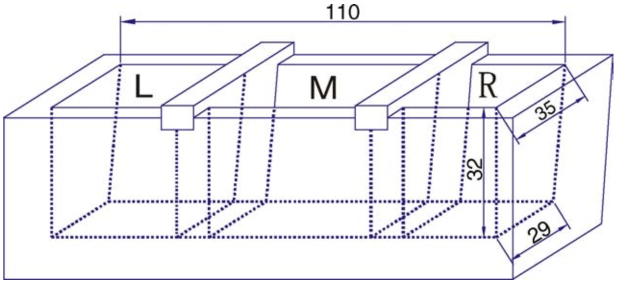

Fig. 1. The mould to simulate non-uniform solidification of ceramic suspension.

The mould was divided into three slots (L, M and R) using two dummy plates, as shown in Fig. 1. The suspensions with different solidification rates were cast into different slots, respectively, and then merged by withdrawing the two dummy plates immediately after casting. In order to facilitate demoulding, a trapezoidal section of the mould was used.

3. Results and discussion

3.1. Initiation of inner stresses

The solidification rate of a ceramic suspension increases with the temperature and the concentrations of the solidification agents including initiator and catalyst [10]. Using the equipment shown in Fig. 1, a series of experiments were designed, as summarized in Table 3, to examine the effect of non-uniform solidification rate on the cracking of ceramic green bodies. In experiment #1, the dose of the catalyst in the middle slot was less than that in the left one and the right one. In experiment #3, the dose of the catalyst decreased in turn from the left to right. To investigate the influence of the temperature gradient on solidification, experiment #2 was performed with the initial temperature in the middle slot being lower than that in the other two. The dose of initiator is the same in all suspensions as shown in Table 3.

Table 3
Experiments to simulate non-uniform solidification in ceramic suspension[a]

Test number	Temperature (°C)	Catalyst (μl)	Initiator (μl)
#1			
L	18	150	150
M	18	**50**	150
R	18	150	150
#2			
L	18	150	150
M	**4**	150	150
R	18	150	150
#3			
L	18	150	150
M	18	**100**	150
R	18	**50**	150

[a] Room temperature is 18 °C each slot with 50 ml of 50 vol.% Al_2O_3 suspension which was made from premix solution "e".

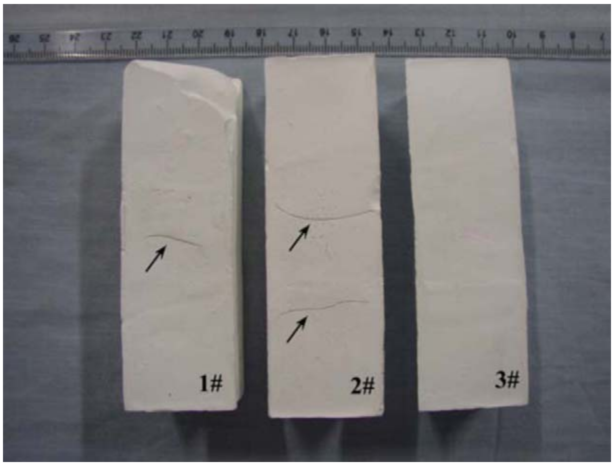

Fig. 2. Samples to simulate the non-uniform solidification of ceramic suspensions.

Under the conditions in experiments #1 and #2, the suspension in the right and the left slots solidified faster than that in the middle slot. In contrast in experiment #3, the suspension in the left slot solidified first, then the middle one and finally the right one. No cracks were observed in all three samples after drying and debindering. However, samples #1 and #2 cracked after sintering, as shown in Fig. 2. The cracking of samples #1 and #2 is due to the development of inner stresses in the green bodies. Since the suspensions in the left and right slot solidified earlier, the contraction of the green body in the middle slot was restricted. Therefore, a tensile stress developed in vertical direction in the middle layer. The maximum tensile stress occurred in half depth where the cracking was observed in sample #1. The temperature distribution in experiment #2 is complicated by the heat transfer from the suspensions on both sides and the atmosphere to the suspension in the middle. The solidification rate is not uniform in each layer leading to a complex distribution of the inner stresses and thus sample #2 cracked at the one-third regions in the length direction. Sample #3 did not crack because the inner stresses is significantly reduced by a gradual transition in the solidification rate from the left to the right. These simulations confirm that the inner stresses can be traced back to the forming stage due to the gradient of initial temperature or the concentrations of solidification agents. In the subsequent drying stage, the inner stresses is inherited and magnified due to further contraction. The control of the inner stresses developed in forming process is critical to the success of the subsequent drying and debinering processes after gelcasting.

3.2. Control of inner stresses

Fig. 3 shows the effect of the amount of the moderator on the strength of ceramic green goodies. It is found that the strength of the green bodies decreases almost linearly with

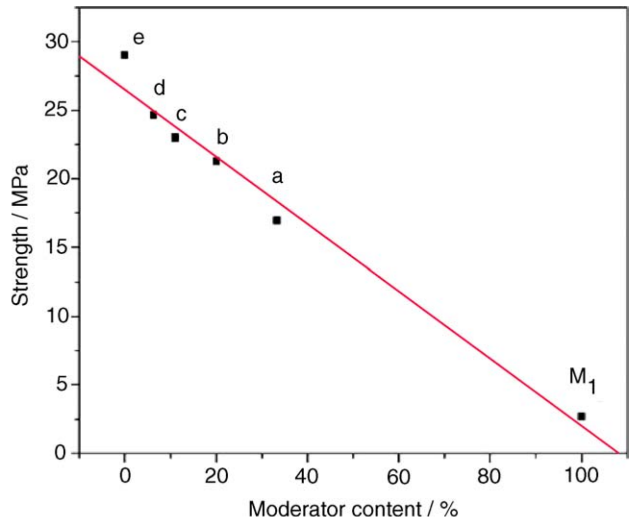

Fig. 3. Strength of ceramic green bodies versus the amount of HEA.

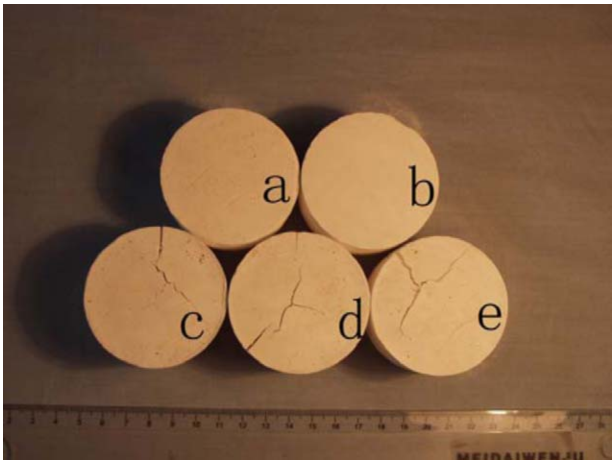

Fig. 4. Surface patterns of the Al_2O_3 green bodies after debindering.

increasing concentration of the moderator. The strength of the green bodies (M_1) is less than 2 MPa in which the moderator replaces the original acrylamide (AM) monomer entirely. While the strength of green bodies with a concentration of moderator of 20 wt.% to 33 wt.% (samples "b" and "a") is about 20 MPa, which is slightly less than the strength of green bodies produced without any moderator (sample "e"). The elastic modulus of green body versus different concentration of the moderator was listed in Table 4 showing that the elastic modulus of the green bodies also decreases with the concentration of moderator. The elastic modulus of green body "e" (prepared from original AM premix solution) is 8.63 GPa while the green body "M_1" has an elastic modulus of 0.84 GPa in which the modulator replaces the original acrylamide (AM) monomer entirely. It is known that the elastic modulus of a green body is determined by the strength of the gel network structure. The results indicate that the structure of the polymer network can be adjusted by the co-polymerisation of the acrymide (AM) and moderator (HEA) monomers.

Five Al_2O_3 green bodies "a–e" were produced by casting 100 ml of the suspensions into a 150 ml beaker respectively. The amount of moderator was varied from 33 wt.% to 0 in the total weight of monomers as summarized in Table 1. The surfaces of these Al_2O_3 green bodies after debindering are shown in Fig. 4. The green bodies (c–e) cracked when the amount of the moderator is not sufficient to soften the polymer network. However, the inner stresses was effectively reduced and cracking was suppressed at a concentration of moderator >20 wt.%. By choosing a proper amount of the moderator, cracking of green body can be avoided while sufficient strength of the green bodies retained.

Table 4
Elastic modulus of green bodies versus the concentration of moderator[a]

Test sample	M_1	a	c	e
Content of the modulator (%)	100	33.3	11	0
Elastic modulus (GPa)	0.84	3.57	5.00	8.63

[a] The concentration of the moderator was referred to Table 1.

Fig. 5 indicates the influence of HEA on the viscosity of ceramic suspension with 50 vol.% solid loading. It is found that the viscosity increased slightly with the amount of HEA. Nevertheless, the viscosity is less than 1 Pa·s, even if the amount of HEA was one-third of the total weight of HEA and AM (sample "a"). Therefore the suspension was still suitable for gelcasting.

3.3. Effect on cracking of large ceramic green bodies

Two annular Al_2O_3 green bodies with diameter as large as 12 cm were obtained by casting suspensions, one containing 33 wt.% moderator, the other with no moderator, into hot moulds (the annular type in Table 2) respectively. It is shown in Fig. 6 that the green body without HEA cracked annularly, while the other containing HEA did not crack at all. Discs

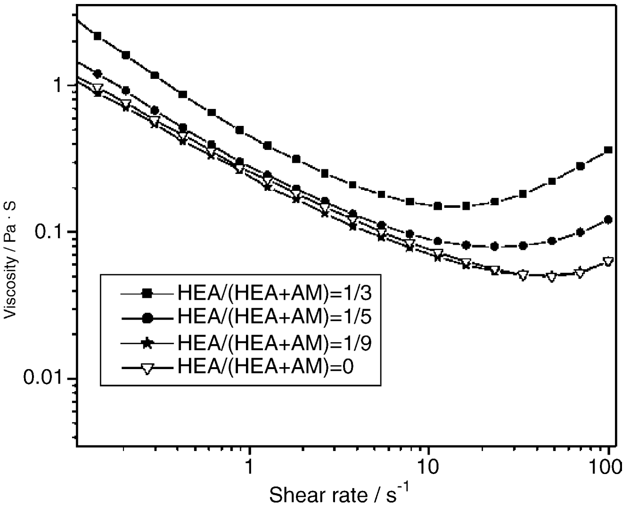

Fig. 5. Effect of HEA on the viscosity of ceramic suspension.

Table 5
Results of large-size ceramic ball

Number	1	2	3	4
Gel system	Without HEA	Without HEA	Adding HEA	Adding HEA
Casting method	Hot mould	Microwave	Hot mould	Microwave
Result	Cracked after debindering	Cracked after debindering	Not cracked after debindering Cracked after sintering	Good

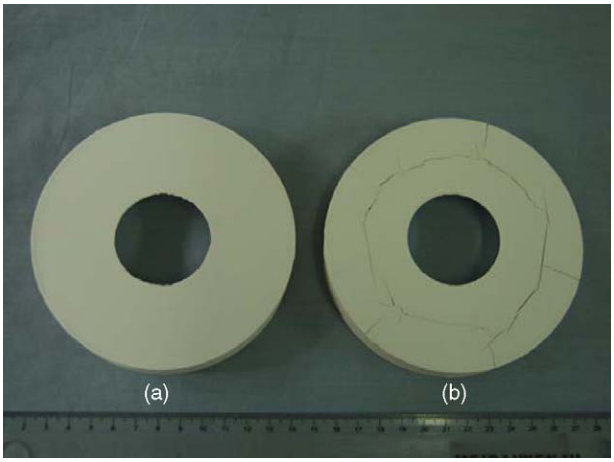

Fig. 6. Annular alumina green bodies: (a) with 33 wt.% moderator and (b) no moderator.

Fig. 8. Sintered alumina balls (the linear shrinkage rate was 16.4% after sintering and the final diameter was 5.6 cm).

were also prepared from these suspensions using a plastic beaker with a diameter of 11.3 cm. Similarly, the disc with moderator was free of cracks as shown in Fig. 7. The results confirm that relatively large ceramic green bodies can be made successfully by gelcasting with the addition of a proper moderator.

3.4. Improvement on the efficiency of debindering

As shown in Table 5, a series of large-size ceramic balls were prepared using a spherical nylon mould under various conditions. The green bodies were dried, debindered and sintered following the procedure described in Section 2.2. It is found that both samples without HEA (sample #1 and #2) cracked after debindering even if the solidification was induced by microwave heating to minimise the gradient of temperature. It is inferred that the gel network with no moderator is very stiff and significant inner stresses develop in the green body. The inner stresses are significantly reduced with the addition of HEA so that sample #3 survived the debindering process. However, the sample cracked during the sintering process indicating that certain level of inner stresses existed in the green body due to the temperature gradient and went up with further shrinkage during sintering. In experiment #4, both strategies were exploited: the gradient of temperature was minimised by using microwave and the gel was softened with the addition of HEA. Ceramic balls were successfully debindered and sintered without cracking, as shown in Fig. 8 (the linear shrinkage rate was 16.4% after sintering and the final diameter was 5.6 cm). Further experiments showed that the debindering time could be reduced to 9 h (from room temperature to 600 °C) without cracking, compared to 40–50 h using conventional heating process [9]. This will significantly increase productivity and reduce production cost.

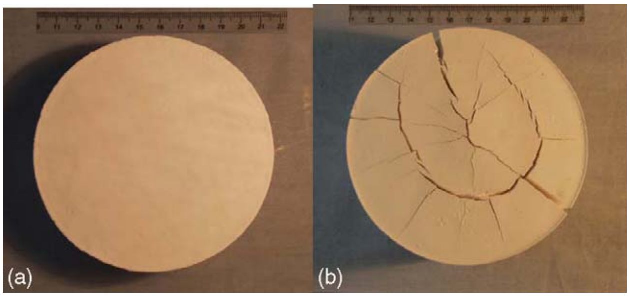

Fig. 7. Green bodies of alumina discs: (a) with 33 wt.% moderator and (b) no moderator.

4. Conclusions

The initiation and evolution of inner stresses in the green body formed by gelcasting were discussed. The important factors responsible for the inner stresses were the temperature gradient and the distribution of the solidification agents. Adding proper amount of HEA into the concentrated suspension improves the flexibility of the polymer network and thus reduces the inner stresses in the green body. By reducing the inner stresses in the green body at the forming stage, the debindering time of large ceramic parts can be significantly shortened.

Acknowledgments

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