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Short Communication

A simple and effective method for gel casting of zirconia green bodies using phenolic resin as a binder

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Abstract

A simple, effective method for fabricating zirconia green bodies is described that utilizes phenolic resin as a binder in the gel casting process. Both the zeta potential of zirconia particles and the rheological behavior of the slurries were measured. To prepare stable, homogeneous, fluidic zirconia slurry with high solid loading, the zeta potential was adjusted by varying the phenolic resin content of the premixed solution. This represented a departure from normally adjusting the slurry pH by using an acids, alkali or dispersants. To promote gelation of the slurry, a curing agent was added. Gel casting a mixture of a 42 vol.% zirconia slurry containing 13 wt.% phenolic resin yielded an easily sintered, very homogeneous green body with the desired strength. The gelation time of the slurries and the mechanical strength of the green bodies were controlled by adjusting the quantity of the curing agent in the slurries.

Keywords: Gel casting; Green body; Phenolic resin; Zirconia; Strength

1. Introduction

Advanced structural ceramics are preferred in many industries, because of their hardness, high-temperature strength, corrosion resistance, wear resistance and low thermal expansion. However, the materials requirements of high-quality complex shaped ceramic products have become increasingly stringent. It is widely recognized that fabrication of ceramic products using traditional forming techniques is labor-intensive and time-consuming.[1] In the past few decades, several colloidal processing techniques have been proposed for fabricating ceramic green bodies employing stable, fluidic ceramic slurries.[2,3] These techniques have proven to be superior for forming complex shapes and producing green bodies with a homogeneous microstructure. In the family of these new techniques, gel casting was developed by Oak Ridge National Laboratory as a means of circumventing the inherent drawbacks of machining, injection molding and slip casting ceramics.[1,2]

In this gel casting process, ceramic powder is dispersed into a premixed solution containing monomers, a cross-linker and a dispersant. After adjusting the pH and dispersant content, subsequent ball-milling of this mixture yields a homogeneous, stable and fluidic slurry with high solid loading. Following the addition of a catalyst and an initiator, the slurry is then poured directly into the cavity of a mold to form a green body. Thermal polymerization of the monomers yields a rigid three-dimensional polymer network structure that retains the ceramic particles in the desired shape. The green body is then removed from the mold and sintered to form the complex ceramic structure. Therefore, gel casting shows great potential for fabricating complex high-quality ceramic structures.[4,5]

The early gel casting systems were found to be hazardous to health primarily because of the use of neurotoxic acrylate monomer binders. This drawback limited wide application of this system. Recently, gel casting systems that employ binders with little or no toxicity have been developed.[6] These include the use of binders such as boehmite,[7] alginates,[8] polysaccharides,[9,10] proteins,[11,12] and silica sol.[13–15] Even so, preparation of homogeneous ceramic slurries with high solid loading still relies on the addition of dispersants, acids and alkalis to optimize the zeta potential of ceramic particles. Consequently, development of a practical and commercially viable method for gel casting of ceramic green bodies will require the development of a new simple, effective procedure.

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Table 1
Chemical composition of zirconia powder (wt.%).

Y_2O_3	Fe_2O_3	Na_2O	SiO_2	TiO_2	Al_2O_3	Cl^-
5.2 ± 0.2	0.0026	≤0.001	0.0064	≤0.001	≤0.25	≤0.01

In this paper, we describe a novel gel casting system for preparing ceramic green bodies which employs a low toxicity resole phenolic resin as a binder. Resole phenolic resin (PR, neat liquid or in solution) is commonly used in the coatings, adhesives and foundry industries.[16] This material is prepared by the reacting phenol with formaldehyde under alkaline conditions. Resole phenolic resin can be used as a binder and as zeta potential regulator, because it contains phenoxide and hydroxyl ions. Therefore, the zeta potential of ceramic particles in the aqueous solution of PR can be adjusted by changing the concentration of the PR instead of using acid–base or other dispersants for this purpose. This greatly simplifies the preparation of homogeneous, stable, fluidic ceramic slurries.

The successful fabrication of high-quality ceramic parts is dependent on the zeta potential of the ceramic particles, the rheological behaviors and gelling of slurries, and the mechanical strength of green bodies. Consequently, in this study we conducted systematic experiments to better understand the effects of these operational parameters in the preparation of zirconia green bodies with a homogeneous microstructure.

2. Experimental

2.1. Materials

Zirconia powder (YSZ-F-DM-5.0, Jiangxi Farmeiya Materials Co., Ltd., China) was used as received directly from the supplier without further purification. This powder has a mean diameter of 1.15 μm (MS2000, Malvern Instruments, UK), and a BET surface area of 7.49 m^2/g (SSA-3600, Builder, China). Its chemical composition is shown in Table 1. Resole phenolic resin (JF103D, Jinan Shengquan Group Co., Ltd., China) was used as a binder in the slurry compositions. The technical indices of JF103D are provided in Table 2. Glyceryl triacetate (GT) (Sinopharm Chemical Reagent Co., Ltd., China) with a water solubility of about 64 g/L was used as the curing agent and cross-linker in the compositions.

2.2. Slurry preparation and gel casting

Premixed solutions containing 1–20 wt.% binder were prepared by dissolving PR in deionized water. The pH values of the solutions were determined after the addition of PR. The zirconia powder was added to the solutions using mechanical stirring to form 30–42 vol.% slurries. In order to promote the breakdown of the agglomerate and facilitate mixing, the slurries were ball-milled in a planetary mill with zirconia balls and a polyethylene container for 8–46 h at 160 rpm. Following this, 14–26 g of glyceryl triacetate per 100 g of PR was stirred added into the slurries. The slurries were degassed in a vacuum chamber to release the trapped air bubbles, and then poured into individual silicone molds and allowed to gel at room temperature. The stirring and pouring operations were carried out slowly to avoid entrapment of air. The wet green bodies were removed from the mold, and dried at 25 °C for 25 h and at 110 °C for 2 h. Subsequently, the organics in the dried bodies were burned out at 800 °C for 3 h and sintered at 1450 °C for 3 h.

Table 2
Technical indices of JF103D.

pH	Viscosity (25 °C, mPa s)	Density (25 °C, g/cm^3)	Free phenol (wt.%)	Free formaldehyde (wt.%)
12.9	103	1.23	≤0.5	≤0.1

2.3. Characterization

The pH values of the premixed solutions were measured using a pH meter. The zeta potential of the zirconia particles was measured using a ZetaProbe instrument (Agilent Technology Corp., USA) and aliquots of 0.01 wt.% zirconia suspension. The viscosity of zirconia slurries was measured using a high shear CAP 2000+ viscometer (Brookfield Engineering Laboratories, USA). The gelation time (the gel point) was determined by observing the time for the prepared slurries to cease flowing in a gently inverted test tube at 25 °C. The density and shrinkage of zirconia bodies were calculated according to dimensional measurement and Archimedes' principle. The microstructure of the green and sintered bodies studies were performed using a scanning electron microscopy (SEM, Sirion 200, FEI). The three-point bending strength was determined using a MTS810 universal testing machine with a span of 30 mm and a punch displacement speed of 0.05 mm/min. The dimensions of the test specimens were 6 mm × 8 mm × 60 mm, and six specimens were tested to obtain the average strength values.

3. Results and discussion

3.1. Stability of zirconia particles in premixed solutions

The critical step in the successful production of ceramics by gel casting is the production of a stable, homogeneous slurry. The dispersion and stability of ceramic particles in the premixed solution depends on the zeta potential. A highly negative or positive zeta potential will produce a more stable slurry.[5,17]

The stability of zirconia particles in premixed solutions was studied by zeta potential measurements at different PR contents. Results are shown in Fig. 1. The zeta potential is strongly affected by the PR content. The negative zeta potential decreases rapidly with an increase of the PR content from −44 mV at 1 wt.% to −97 mV at 11 wt.%. A further increase to15 wt.%, causes the zeta potential to remain almost constant. However, when the PR content of the solution is increased, above 15 wt.% the zeta potential once again increases. This variation of zeta potential is due to the change in the ionic strength of the premixed solution.[18] Consequently, the adjustment of PR content in the slurry is significant in this gel casting system. It appears that