GELCASTING OF ALUMINA CERAMICS USING AN EGG WHITE PROTEIN BINDER SYSTEM

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Egg white protein (EW) is a food ingredient commonly used for its gelling properties and has been applied in ceramic fabrication. In this work, EW was used as an environmentally-friendly binder for gelcasting alumina ceramics at elevated temperature (80°C). The gelling behavior was compared with the ambient temperature drying-induced gelation processing. The processing conditions and mechanical properties of the ceramics processed from two different processing variants were compared. The results indicate that the ceramics from heat-induced gelation showed improved mechanical properties and more uniform microstructure after sintering in comparison to the drying-induced ones. Dense and complex-shaped ceramic parts via computer numerical controlled (CNC) green machining have been produced from the EW gelcast ceramics.

INTRODUCTION

Gelcasting is a versatile forming technology that forms green bodies from the slurry containing a cross-linkable binder within a nonporous mould [1]. During the gelcasting process, the binder forms a strong, continuous gel network, which permanently fixes the ceramic particles in their positions, hindering the formation of inhomogeneities during subsequent drying and sintering. Recently, natural polymers [2-5] have been developed as an environmentally-friendly alternative to expensive, toxic organic monomers binder system used in the original gelcasting process. Egg-white protein (EW) is among such natural polymers. When heated at the gelation temperature (80°C), individual EW molecules are denatured and then form a typical thermo-irreversible gel, which is held together by covalent bonds [6]. Below this gelation temperature, the attractive hydrogen bond favors junction-zone formation [7]. Dhara et al [3] and Lyckfeldt et al [5] reported ceramic forming methods using protein as a binder. They investigated rheology and gelation behavior of the protein-based gelcasting systems at the denature temperature of EW. However, no detailed information was given regarding their microstructure, in particular, the mechanical properties of both green and sintered ceramics.

We proposed ceramic green machining as an alternative method for the rapid fabrication of complex-shaped ceramics [8]. The purpose of the current research is to examine the use of a thermal activation mechanism to generate controlled gelation in an aqueous alumina system using the globular EW protein as the gelcasting binder. The ambient temperature drying process has been investigated in this work as a comparative method. The microstructure and mechanical properties of ceramics produced from both heat-induced and drying-induced gelation were then examined as a function of EW concentrations in the green and sintered state. Optimal compositions and processing conditions were identified to produce green ceramics which were suitable for the green machining of complex-shaped alumina components.

EXPERIMENTAL

Materials

Duramax D-3005, an ammonium polyacrylate (MW = 6,000) solution from Rohm and Hass, was used as a dispersant. The alumina powder, Alcoa CT 3000SG, had a surface area of 7 m^2/g and a density of 3.96 g/cm^3.

EW protein, a type of Danish pasteurized spray dried albumin powder from Lactosan-Sanovo (UK) Limited, was used as a binder and gelling agent. 1-Octonal from Sigma-Aldrich was used as defoaming agent.

Slurry preparation

Preparation of initial dispersed slurries was performed by mixing appropriate quantities of deionised water and dispersant Duramax D-3005. Alumina powder was blended into the suspensions to form a homogenous slurry (55 vol.%) after 24 h ball milling, which could break down any soft agglomerates. EW powder was then added in, with a weight percentage of 3-7 % relative to solvent, milled for another hour. No coagulation and flocculation was found at the end of milling. 1-Octanol was added in as 0.1 vol.% of whole volume of the slurry to remove air bubbles generated during ball milling. After separation of milling media (ø10 mm zirconia balls) with the slurry, the media-free slurry continued rolling at a very low speed over night. Finally, a bubble-free slurry was obtained.

Gelation processing

The de-aired slurry was carefully poured into a soft polymer mould. After the mould was filled, the slurry surface was kept covered with a polymer film to reduce subsequent water evaporation during the gelation processing. After casting, the whole mould with slurry was put into a pre-heated oven at 80°C and kept for 1 h to initiate the gelation. This procedure was called heat-induced gelation. After heat treatment, the mould was cooled to the room temperature before the green sample was demoulded. The sample was then air-dried for >24 h. In comparison, drying-induced alumina samples were also produced through a room temperature drying procedure for 48 h after slurry casting. Both dried green bodies were sintered at 1600°C for 2 h in a furnace.

Characterisation

The samples were characterised in terms of green and sintered density, shrinkage, mechanical properties and microstructure. Green density was calculated by measuring the dimension and mass of the original casting block. Density of sintered samples was measured using a traditional Archimedes method. Shrinkage was calculated by measuring thickness of the samples before and after sintering. Mechanical testing involved measuring the 3-point flexural strength of green/sintered specimens (36 mm × 4 mm × 3 mm) produced from both processing variants as a function of EW concentration. Each mechanical experiment was repeated three times. For the Weibull modulus measurement, at least 8 green samples have been used for maximum probability estimation. Because of limited number of samples available for this study, the Weibull data listed in this report was obtained only to relatively compare sample behavior and was not intended to represent true material parameters. The microstructure of samples was observed under a field emission scanning electron microscope (JEOL JSM 6330F). Samples were polished and thermally etched (10 min at 1450°C) to reveal the pores and grain boundaries. Finally, the alumina ceramics were green machined using a Roland MDX-650 CNC milling machine to demonstrate the suitability of EW gelcasting for the fabrication of complex-shaped ceramics.

RESULTS AND DISCUSSION

Comparison of heat-induced and drying-induced gelcasting

Figure 1 showed the density of green alumina from both heat- and drying-induced gelcasting, and revealed that the green density decreased with the increase of EW concentration in both processing variants. However, the bulk density of the green body made from drying-induced processing was slightly lower than the one from heat-induced processing, probably due to the gel network formed in the heat-induced gelation processing. During the heat-induced processing, natural EW molecules became unfolded and formed a gel network. This network prevented alumina particles from packing together, but on the other hand it also reduced particle sedimentation through gravity during the subsequent drying process. This sedimentation could cause density gradients [9], non-uniform shrinkage and inhomogeneous microstructure in the sintered ceramics. In addition, aggregates of denatured EW molecules expanded from their natural globular size and inevitably occupied more space [10]. In the drying-induced processing, severe warpage was observed in the green and sintered ceramics

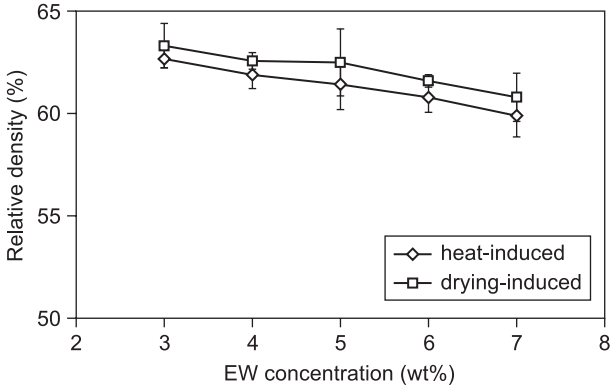

Figure 1. Green density as a function of egg white concentration for both heat- and drying-induced alumina ceramics.

apart from the higher green density. This was because that there was no such gel network formed in the drying-induced processing to prevent alumina particles from packing and sedimentation since the EW remained in the natural globular state in the junction-zone [11]. In the long drying process, the particles also underwent slow sedimentation and binder migration, which resulted in inhomogeneous microstructure and distortion upon sintering.

After sintering, the density was still decreased with the increase of EW concentration in both processing variants (Figure 2), because more EW in the green body would occupy more space between alumina particles and leave more space to be filled during sintering. However, the heat-induced samples appeared denser than the drying-induced ones; this was in agreement with the shrinkage results as shown in Figure 3. The heat-induced samples showed higher sintered shrinkage than the drying-induced ones. Apparently, the denatured EW gel network facilitated the shrinkage of embedded ceramic particles during the binder burn-out and sintering processes.

Microstructure and mechanical properties of the gelcast alumina in both green and sintered states

The effect of EW concentration on the alumina green strength derived from 55 vol.% alumina slurries is shown in Figure 4. The green strength of ceramics from both processing methods increased with EW concentration. Higher EW binder contents resulted in stronger green ceramic bodies.

The covalent bonding of the denatured EW gel network provided a stronger bond between alumina particles than the hydrogen bonding of natural EW aggregates, which did not form an interconnected gel network [12]. Therefore, the heat-induced green samples exhibited better mechanical properties. Because of the three-dimensional interconnected EW gel network, the heat-induced samples maintained better homogeneity in the green body. The Weibull distribution of fracture strengths of ceramics from both processing variants is shown in Figure 5. The Weibull modulus was 13.4 for the heat-induced samples, comparing to a much smaller

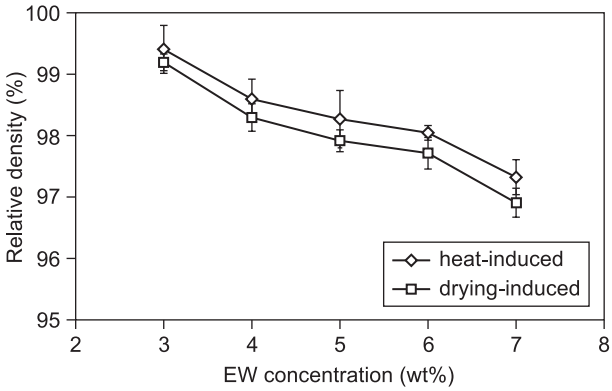

Figure 2. Sintered density as a function of egg white protein concentration for both heat- and drying-induced alumina ceramics.

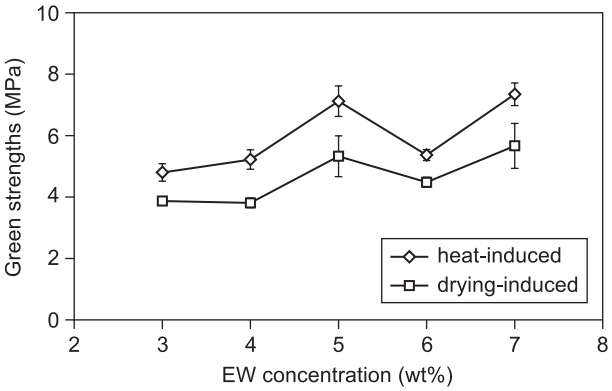

Figure 4. Green body's bending strength as a function of egg white protein concentration for both heat- and drying-induced alumina ceramics.

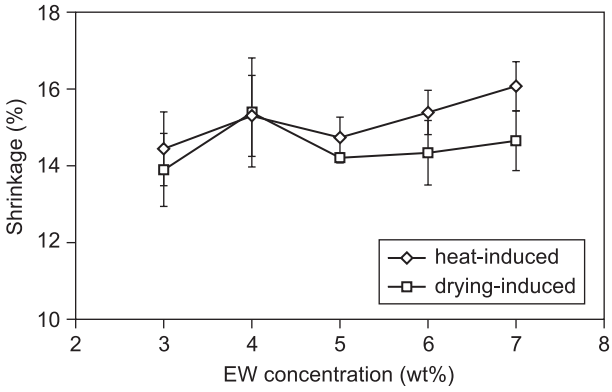

Figure 3. Sintering shrinkage as a function of egg white protein concentration for both heat- and drying-induced alumina ceramics.

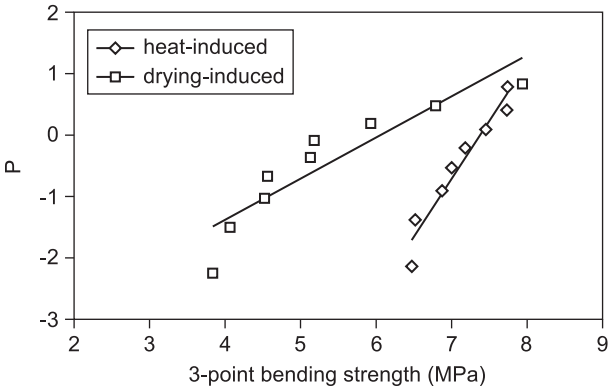

Figure 5. Weibull modulus of green samples with 6 wt.% egg white protein concentration from both heat- and drying-induced processing.

value of 3.9 for the drying-induced ones. The main reason of the smaller Weibull modulus was the inhomogeneity which occurred in the drying-induced processing, where water evaporation was slow at as-room temperature. Since the cast slurry had to be held in an open top mould during drying process, the EW binder would migrate to the top surface during water evaporation. This resulted in a binder-rich layer at the top part. For the heat-induced samples, the rapidly formed EW gel network between alumina particles could substantially maintain the homogeneity of the structure, which resulted from the well-dispersed colloidal slurry [13]. The more uniformly distributed gel network within the heat-induced green body provided stronger green ceramics with a more homogeneous microstructure.

Figure 6 shows the variation of strength of the sintered alumina samples produced from both processing variants as a function of EW concentration. When the EW concentration was less than 6wt%, the strengths exhibit a very slight increase for the drying-induced samples and almost no changes for the heat-induced samples with increasing EW concentration. However, both samples exhibited a decrease when the EW concentration reached 7 wt.%. In comparison, all samples produced from the heat-induced method were stronger than those from the drying-induced method at the similar EW concentrations. From this result it was evident that the EW gel network formed through different processing variants and its quantity were important factors determining the mechanical property of alumina ceramics. This, in turn, was correspondingly reflected in their final sintered microstructure.

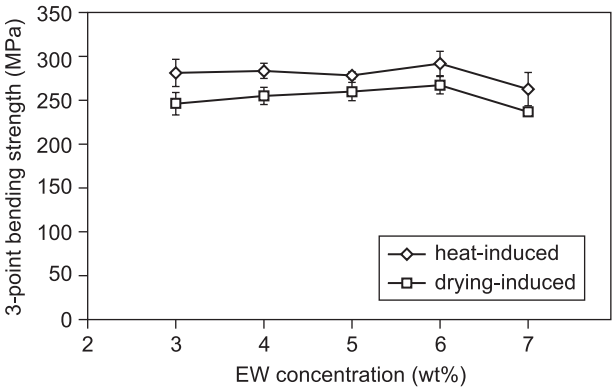

Figure 6. Sintered body's bending strength as a function of egg white protein concentration for both heat- and drying-induced alumina ceramics.

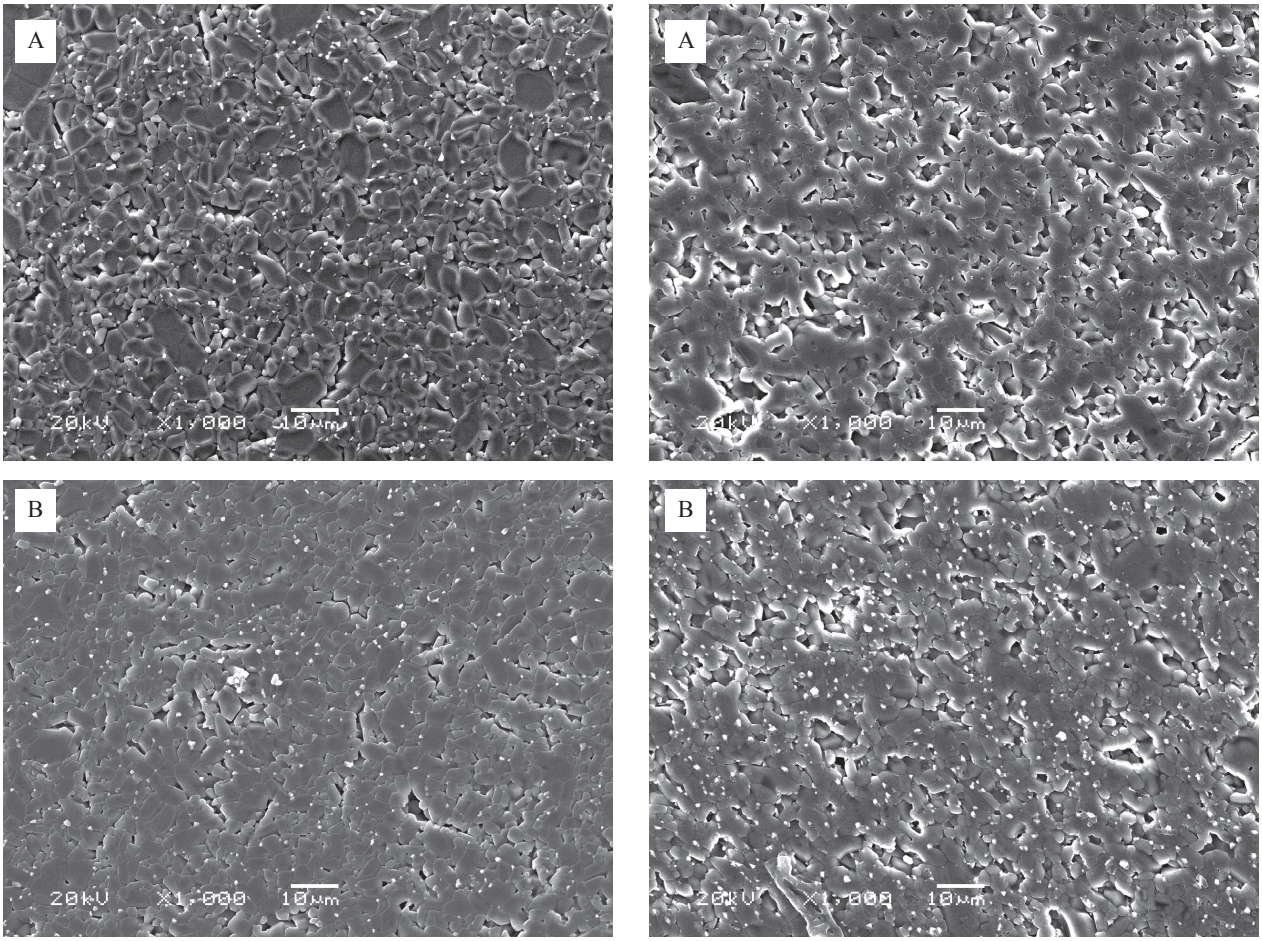

Figure 7. SEM micrographs of sintered and polished alumina ceramics from the heat-induced (left) and the drying-induced (right) samples. The egg white protein concentration from A to E is 3, 4, 5, 6 and 7 wt.%, respectively. *(continue on next page)*

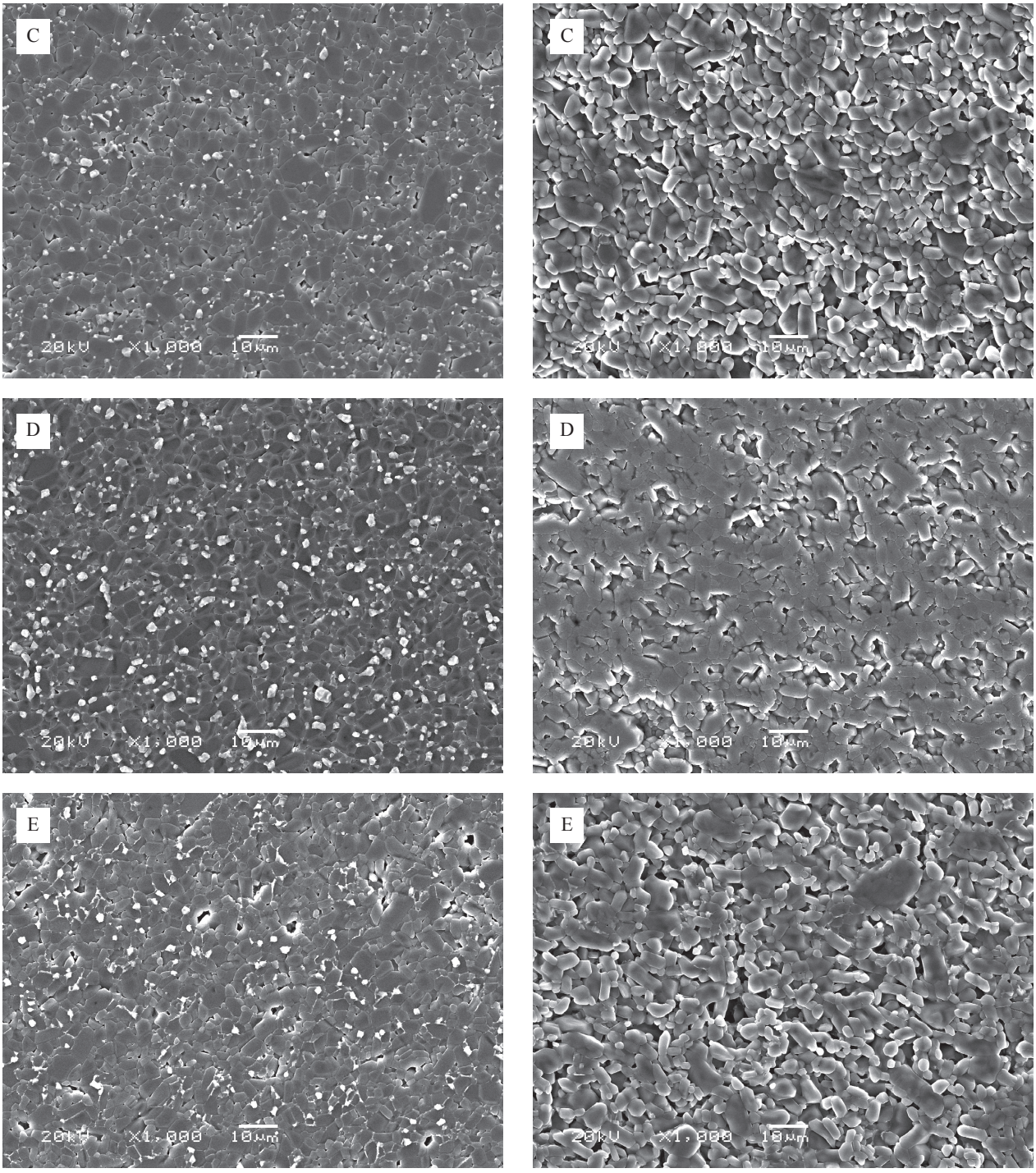

Figure 7. SEM micrographs of sintered and polished alumina ceramics from the heat-induced (left) and the drying-induced (right) samples. The egg white protein concentration from A to E is 3, 4, 5, 6 and 7 wt.%, respectively.

Figure 7 showed the microstructure of samples from both processing variants with different EW concentrations. On the left and right, polished and thermally etched alumina samples are presented for different EW concentrations produced by the heat-induced and drying-induced method, respectively. For the heat-induced samples (left), their microstructure became more uniform with finer grain size as the EW concentration was increased from 3 to 6 wt.%. At the EW concentration of 6 wt%, the microstructure is highly dense and uniform. However as the EW concentration was increased further to 7 wt.%, a less dense and uniform microstructure was observed. The results indicate that the EW molecules could facilitate the formation of uniform packing of alumina particles by forming a continuous network structure during the heat-induced

gelation processing. 6 wt.% of EW seems to be an optimal concentration to form such a structure. When the EW content is too high (>6 wt.%), excessive EW would occupy too much space and thus prevent the densification process during the sintering stage. This result is also in agreement with the mechanical strength change observed in Figure 6, where the strength decreased at 7 wt.% of EW. The general trend for the drying-induced samples (right) appears similar when compared to the above heat-induced samples. The major difference is that their overall density is not as high as that of the heat-induced ones at the sintered state. This might be owing to the fact that EW molecules did not undergo the denaturing process as opposed to the heat-induced processing, but only coagulated together with hydrogen bonding at the junction area. Even though this agglomeration behaved in a similar way as in the denatured EW gel network, due to the weak bonding between the hydrogen bonding, this agglomeration is not so strong as to form a continuous network as the covalent disulfide bond formed in the denatured gel network. The ceramic particles might be prone to segregate and sediment during the slow drying process, as discussed previously. The formation of non-uniform agglomeration of ceramic particles could hinder the densification of final ceramics at the sintering stage [14].

Green machinability of heat-induced gelcast alumina ceramics

The heat-induced green sample was employed to demonstrate the machinability of gelcast ceramics using EW. Ceramic green machining has many advantages over direct machining of sintered ceramics, because direct machining of brittle ceramics could cause chipping [15] and sub-surface microcracks [16]. With the advances in CNC machining technology, ceramic green machining can produce the desired shapes and structures for one-off products. Ceramic green machining could therefore represent a top-down approach for the rapid fabrication of complex shaped ceramics. All heat-induced samples produced in this work were strong enough to be machinable. In Figure 8, a sample of 55 vol.% alumina slurry with 6 wt.% of EW concentration was CNC green machined and the machined sample was shown in both the green and sintered states. The sintering shrinkage in the x, y, and z direction was 15.3 ± 2.1%, 14.0 ± 1.7 % and 14.1 ± 1.5 %, respectively. There were no obvious warpage and bending after sintering.

CONCLUSIONS

The following conclusions can be drawn from the present work:

1. Heat-induced gelcasting using EW as a binder produced dense alumina ceramics. The green and sintered densities and mechanical properties were dependent on the EW concentration. 6 wt.% appeared to be the optimal EW concentration in this work.
2. Alumina ceramics produced by heat-induced processing exhibited improved uniformity and higher strength in both green and sintered states compared to the drying-induced ones. The green and sintered strength were 7.3 MPa and 314 MPa, respectively for the alumina with 6 wt.% of EW concentration.
3. All heat-induced samples were green machinable and appeared to have no obvious warpage and bending after sintering.

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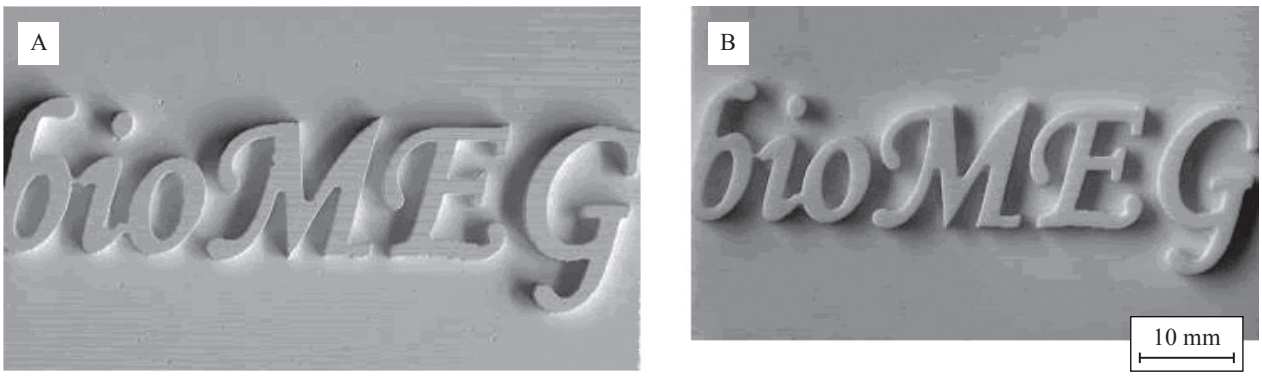

Figure 8. The green machined alumina ceramic from the heat-induced gelcasting with 6 wt.% egg white protein in both green (A) and sintered (B) state.

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