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A new partially isostatic method for fast debinding of low-pressure injection molded ceramic parts

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Abstract

Injection molding has many important advantages over other methods for the production of advanced ceramic bodies with complex shapes. However, the particle size has been a limiting factor both in conventional injection molding as well as in low-pressure injection molding (LPIM). Besides that, both low- and high-pressure processes are very often limited to the production of thin ceramic bodies, due to common problems arising in the debinding stage. In this paper, we present a new method for fast debinding of relatively large cross-section ceramic parts (~ 10 mm) with particle size less than $0.5 \mu\text{m}$ that we call partially isostatic debinding. The green body is embedded in a ceramic powder bed subjected to external pressure. A substantial extraction of the organic additives was achieved in just a few hours. Sintered alumina bodies with large cross section can be obtained free of defects, with little distortion and densities higher than 98% of the theoretical value.

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1. Introduction

Low-pressure injection molding (LPIM) has many advantages for complex shape ceramic parts production. Compared with other methods, including traditional high-pressure injection molding, LPIM is characterized by lower costs, especially for the injection

equipment and molds, and by simplicity in operation [1–3]. This technique is interesting for near-net-shape forming of complex ceramic parts in the range of 100 to 10000 units [1]. The binders for LPIM are usually constituted by various organic ingredients that have different melting points, and behave differently during thermal decomposition [2]. LPIM uses a relatively large content of low viscosity binders, mainly based on waxes, which render the mixture very fluid thus enabling the use of rather low pressure for injection. But, on the other hand, this

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high fluidity also makes debinding more complicated because of the increased risk of large deformations of the part at the temperatures used to remove the organic additives, due to the low viscosity of the binder under these conditions. Accordingly, the debinding is the most critical step in ceramic production mainly for LPIM, being an expensive and difficult operation, which can take weeks for the production of high density, defect-free ceramic parts [4].

For many reasons, the production of ceramic bodies with large cross section represents a technological challenge, especially when these ceramics are made with submicrometer-sized powder [2–5]. However, for many applications it requires the production of parts with both large cross sections and fine grain size, which present very important difficulties for the debinding process. In the case of LPIM, these difficulties arise mainly due to the high binder content in the green bodies, and also to the high impedance for fluid transport which is very much hampered by the small dimensions of the channels formed in the early stages of debinding.

This work presents a new method for binder removal, which permits a fast debinding from thick parts (~ 10 mm) made with very fine ceramic powders (with particle size less than $0.5 \mu\text{m}$), using an especially designed differential pressure cell. An almost complete extraction of the organic additives was achieved in just a few hours, with no appreciable distortion of the green bodies.

2. Principle of the method

The basic principle of the method developed in this work consists in involving the major part of the green ceramic body in a ceramic powder bed, over which it is applied an external pressure that compacts the powder, producing a rigid mold and forming a quasi-isostatic pressure environment. At the same time, however, the channels formed by the interconnected voids between particles remain at a lower pressure, preferentially under vacuum.

The application of an external pressure over a granular system forces the particles one against the other, and due to the friction forces acting between them, powder bed will become more rigid as the compacting pressure increases. The shear strength (τ) for a granular system can be expressed as [6]

$$\tau = \mu P \quad (1)$$

where μ is the inner friction coefficient between the powder bed particles and P is the pressure applied over the system. Owing to the increased shear strength for the granular system, one obtains a rigid mold that avoids the collapse of the part when the binder melts. The external pressure also prevents the production of bubbles and cracks, as would occur otherwise by the fast evaporation of the organic additives.

Since the voids between ceramics particles in the mold are under a lower pressure (or vacuum), as the

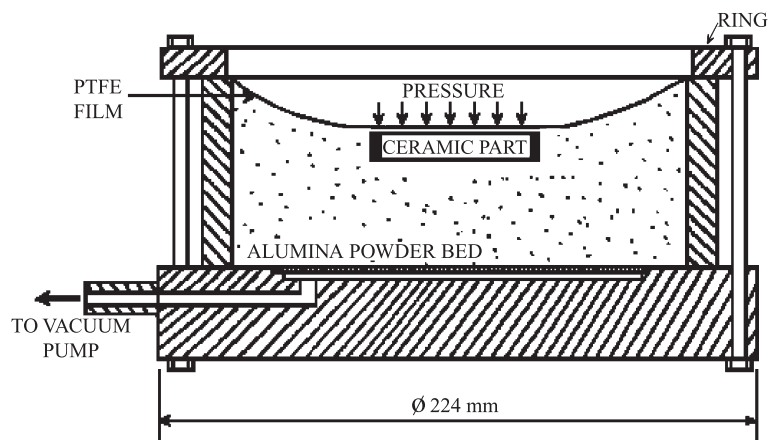


Fig. 1. Cell for partially isostatic debinding.

temperature increases the organic binder melts and is capillary transported along the powder mold. The pressure applied over the powder mold can be the atmospheric pressure itself. In this case, the powder bed and the ceramic body are isolated from the furnace atmosphere by a flexible film resistant to high temperatures and a vacuum is made in the interparticle voids, according to the device depicted in Fig. 1.

3. Experimental procedure

In order to demonstrate the method and study its performance, we have carried out some experiments, whose representative results are described below.

3.1. Materials

The ceramic powder used in this work was submicrometer-sized alumina, Al₂O₃ (A-1000SG—Alcoa), with specific surface area of 9 m²/g, 99.9% purity and particle size of about 0.4 μm. In some experiments, alumina with a bigger particle size (APC-2011SG—Alcoa) was also employed for comparison of results. The alumina powder was dried for 3 h at 150 °C before use. The major binder component was paraffin wax (120/125-3 Petrobras-BR) with melting point between 49 and 52 °C. Other minor components were polyethylene wax (Ipiranga Petroquímica-BR), carnauba wax (type III), and stearic and oleic acids [2].

3.2. Injection of parts

The mixture was prepared directly in the LPIM machine (Peltsman MIGL-33), with 86 wt.% of alumina and 14 wt.% of binders [2]. The major binder component was paraffin wax, which constitutes 75 wt.% of the binder. In order to guarantee good homogeneity, the binder and ceramic powder were mixed for 20 h at 90 °C before injection. This mixture was injected into the mold at 90 °C and 400 kPa of pressure, keeping the pressure applied during 12 s. The ceramic parts molded were bricks with dimensions of 10 × 34 × 63 mm.

3.3. Partially isostatic debinding

The debinding cell was manufactured according to the drawing presented in Fig. 1. The system consists of a steel cylinder, filled with the same alumina powder employed to make the ceramic parts. The powder bed prevents major distortions during debinding and provides a physical support to the ceramic bodies [2,3]. The upper opening of the cell is sealed with a flexible film (e.g. PTFE) resistant to high temperatures. The film is fixed with a steel ring (see Fig. 1). A vacuum pump is connected to the inner part of the cell through the bottom opening that is coated by a filter paper, which does not permit the fine powder draw into the vacuum pump. A trap is placed before the vacuum pump to collect the organic additives removed from the ceramic body.

The green ceramic bodies are embedded in the ceramic powder inside the cell, below the flexible film, as shown in Fig. 1. After that, the chamber is sealed and is transferred to the furnace, and the pressure in the interparticle spaces is reduced to about 10 Pa.

For the debinding of large cross-section ceramic parts, several furnace temperature programs were tested in order to find the better conditions under which one could obtain pre-sintered ceramic bodies free of defects. The debinding inside the cell was carried out up to a temperature of 250 °C. After cooling, the ceramic part was removed from the system and fired in air at 1000 °C during 8 h, to extract the residual binder. Finally, the ceramic parts were sintered at 1600 °C for 2 h, with a heating rate of 1 °C/min.

4. Experimental results and discussion

Fig. 2 illustrates some of the furnace temperature programs for this work. The (a) and (b) programs in Fig. 2 are representative of the tests performed with the partially isostatic debinding cell. After fast debinding, the sintered ceramic parts made with the coarse alumina APC-2011SG (grain size < 1 μm) did not present cracks and bubbles. However, the ceramic parts injected with fine particle size alumina A-1000SG exhibited cracks after sintering.

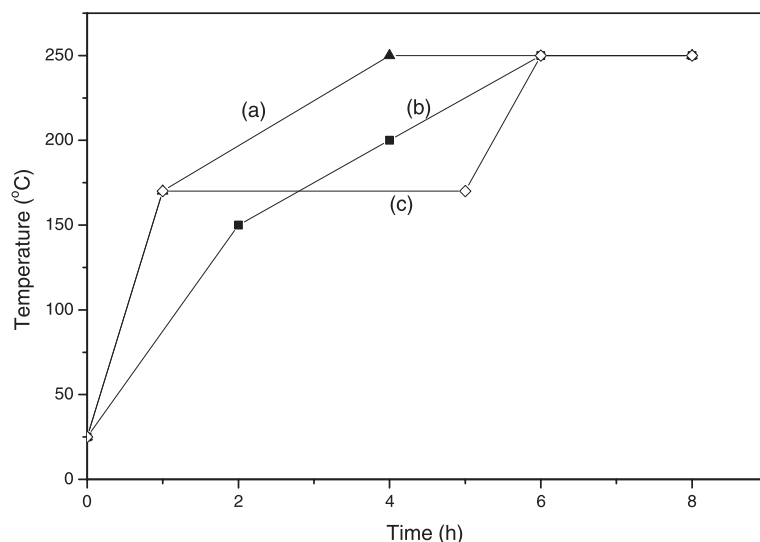


Fig. 2. Furnace temperature programs for binder removal from large ceramic parts. See text for discussion.

This probably happened because of differential contraction resulting from binder/powder segregation. This segregation can promote cracks in sintering stage for stress relief. The same behavior was observed earlier in conventional wick debinding, even for very long debinding times [5]. Crack formation was eliminated with the use of the partially isostatic debinding cell, when a dwell at 170 °C was used, keeping the ceramic part at this temperature for 4 h, followed by an increase of temperature to 250 °C (ramp (c) in Fig. 2). Fig. 3 shows one sample molded with A-1000SG that was submitted to the same furnace temperature program outside of the partially isostatic debinding cell. Under these conditions, ceramic parts whose debinding was conducted in conventional wicking presented a high production of defects, with many cracks and bubbles. It must be remarked that the conventional debinding of large cross-section ceramic bodies made from very fine particle alumina powder can take over 70 h in wicking [7]. In the partially isostatic debinding cell, the binding of large cross-section ceramic parts can be carried out in a fraction of that time.

The debinding method described in this work, together with the development of adequate furnace temperature program for the debinding (represented in Fig. 2c), enabled the production of large ceramic

parts of submicrometer-sized alumina free of defects, as showed in Fig 4. Some experiments were done with larger cross-section samples, which required a larger time for a successful debinding.



Fig. 3. Ceramic part fired under the same time/temperature conditions outside of the partially isostatic debinding system.

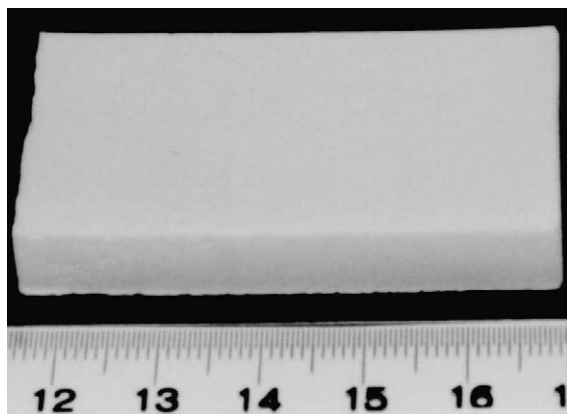


Fig. 4. Ceramic part fired in the partially isostatic debinding system and sintered at 1600 °C for 2 h.

The ceramic parts sintered at 1600 °C/2 h presented a density which varies from 96% to 98% of the alumina theoretical density.

5. Conclusion

The development of a new method for partially isostatic debinding made it possible to reduce drastically the time necessary for binder extraction of submicrometer-sized, large cross-section ceramic parts, molded by LPIM. The parts are obtained free of defects after sintering. The partially isostatic cell can reduce by one order of magnitude the time needed to extract the binder from large cross-section ceramic parts. The external pressure applied over the powder bed promotes a physical support, which prevents large distortion and avoids bubble development in the ceramic parts, resulting in a faster binder extraction. The vacuum in the interparticle voids also accelerates the binder extraction in the bed. In spite of the method

be somewhat more complex than traditional wicking, the partially isostatic debinding accelerates the extraction of the organic additives, thus reducing the costs for the production of ceramic parts.

Further improvements of this method include the use of greater external pressures, which could accelerate even more the process of binder removal. It is also necessary to fully optimize the time and temperature furnace program for this new method of debinding. Furthermore, there is also room to improve this method aiming to reduce the small distortions yet seen in the parts after debinding. The suitability and general application of the partially isostatic debinding method will be addressed by testing it for the binder removal of submicrometer-sized ceramic parts with more complex shapes.

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