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ScienceDirect

Ceramics International 40 (2014) 887–891

CERAMICS INTERNATIONAL

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Single-step wick-debinding and sintering for powder injection molding

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Received 14 May 2013; received in revised form 21 June 2013; accepted 21 June 2013
Available online 29 June 2013

Abstract

We have investigated the possibility of merging the wick-debinding and sintering of injection-molded ceramic parts into a single-step operation. The basic idea is to use an embedment that serves as a wicking agent in the first stage of the procedure, but then burns out completely when the temperature exceeds approximately 500 °C, leaving the samples free of any organic binder or contamination so that they are ready for sintering. Carbon black was used as the wicking agent for two reasons. First, it has great wicking-agent properties, due to its high porosity with a small pore size, while exhibiting good wetting with the molten paraffin binder. Second, it burns in air at high temperature, at which point the wick-debinding has already been completed. The whole process from molded parts to fully sintered parts can be completed in a single furnace. Besides making the process shorter, the tedious and delicate operations of cleaning and transporting the fragile debinded parts after wick-debinding are avoided.

Keywords: A. Sintering; Debinding; Low-pressure injection molding; Carbon black

1. Introduction

Powder injection molding is an important technology for manufacturing complex, net-shape ceramic components. It consists of four processing steps; feedstock preparation, injection molding, debinding and sintering. Although all the steps are crucial, it is generally considered that the debinding represents a particularly delicate and time-consuming operation, during which many defects can be introduced [1,2,3,4]. The binder is generally removed as a gaseous phase by thermal decomposition and vaporization in a process called thermal debinding [1,5,6]. In order to reduce the risk of damaging the parts and also to make the overall process faster, several different techniques were developed to assist in removing some amount of the binder prior to the thermal debinding. For example, in partial solvent debinding process one component of the binder is selectivity leeched from the green body by immersion in a solvent [4,7]; in catalytic debinding one component is decomposed by chemical reaction with strong acid vapors [8,9]; and in wick-debinding (or capillary extraction debinding) part of the binder is melted and extracted into the surrounding embedment by capillary forces [10,11,12,13]. In the case of low-pressure injection-molding (LPIM) the debinding is especially difficult, because in this case the binder is composed solely of wax and does not contain a high-melting-point backbone polymer component that would hold the particles firmly together during the thermal debinding, as is usually the case for high-pressure injection molding (HPIM) [14,15]. When the wax binder in LPIM-shaped parts melts during thermal debinding, only weak attractive forces hold the powder particles together and thus even a small stress can cause an irreversible deformation [2,16]. Solvent debinding or catalytic debinding is difficult to apply for LPIM because the binder contains basically just the paraffin wax. However, wick-debinding is a highly effective way of avoiding the formation of defects for LPIM [5,10,11,14,17–19].

In practice wick-debinding is carried out by embedding the molded parts in a loose granular bed with a fine porosity, where they are heated above the melting point of the binder [10].

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http://dx.doi.org/10.1016/j.ceramint.2013.06.083

The embedment not only takes an active role in the debinding by capillary suction of the molten binder [5,12,13,20], but also serves as a physical support for the softened parts when the binder inside them melts [9,21,22]. During melting a significant amount of the binder exudes from the bulk [14,18], which would form a liquid film on the surface if there was no capillary extraction. Such a film can cause edge rounding or even shape collapse, especially in the case of micro parts [15]. Interestingly, it has been demonstrated, that with a precise control of the thickness of a liquid film on the surface, using a wicking agent with a certain pore size, a defect-healing effect can be achieved, leading to non-deformed parts with improved sintered strength [15]. However, it seems that in order to manufacture high quality LPIM parts, the use of capillary extraction is necessary, unlike in the case of HPIM, where the binder can be removed in a gaseous phase also without any embedment [9,23,24]. In practice, a highly porous oxide ceramic powder or granulate, such as alumina, is used as the wicking embedment. Since it is thermally stable, it can be repeatedly cleaned by burning the binder residuals at high temperature [25]. A significant amount of the binder can be removed with capillary extraction, resulting in parts with open porosity, from which any residual binder can be completely removed in the gaseous phase during the heating up to the sintering temperature. However, after the wick-debinding process, partially debinded parts must first be taken out of the embedment, cleaned and transported to the sintering furnace. This represents one of the main drawbacks of the procedure, because partially debinded parts are generally very fragile and can easily be damaged during handling [25]. The problems are particularly important on an industrial scale, where gentle handling and automation are difficult to apply. In order to make the LPIM process less time consuming and economically more acceptable there is a desire to conduct a debinding together with the sintering in a so-called single-step debinding and sintering. This idea can indeed be applied for HPIM, where the binder is removed in a gaseous phase by thermal debinding without any embedment [9,23,24]. Using vacuum furnace has also been successfully used for the debinding and sintering of metallic compacts [9,26]. Unfortunately, it is more difficult to use the same procedure in the case of LPIM where embedment is also used. The high sintering temperature, usually associated with firing ceramics, could cause an undesirable interaction between the embedment and the ceramic parts. A single-step debinding and sintering could, in principal, be achieved by the use of a sacrificial wicking agent, such as a highly porous form of carbon that would burn out at high temperatures. It was already experimentally confirmed, that activated carbon can be an effective embedment [27] for high pressure injection molding. The authors postulated that the binder leaves green bodies in the gaseous phase and is then adsorbed on the very high specific surface of the activated carbon (above1000 m^2/g). However, they did not mention the possibility of completing the process in a single step, with further heating to the sintering temperature. Additionally, removing the binder in the liquid state (as in capillary extraction), rather than the gaseous phase, could have a different effects on the molded body.

In this paper we show that it is possible to use all the advantages of capillary extraction, while the unfavorable cleaning and transporting operations can be avoided. That can be achieved with the introduction of a single-step debinding and sintering with granular carbon black as the embedment. Carbon black serves as a capillary extraction agent in the first stage, which later on burns out, without any noticeable residual ash, therefore ensuring undisturbed sintering at high temperatures.

2. Experimental

A suspension for low-pressure injection molding was prepared from a powder blend consisting of 96% fine-grained alumina (a mixture of commercial alumina powders MR23 and MR32 from Martinswerk, Germany, with particle-size parameters: $d_{10}=0.7$ μm, $d_{50}=1.9$ μm, and $d_{10}=4.2$ μm) and 4% steatite powder (steatite powder prepared in Hidria AET, Slovenia with particle size parameters: $d_{10}=0.7$ μm, $d_{50}=4.8$ μm, $d_{90}=9.5$ μm). The latter was used as a liquid-phase sintering aid. A paraffin wax (Dunawax DWC from Mol, Hungary) with a melting point of 60 °C was used as a binder. Stearic acid (Stearine D1 from Faci, Italy) in the amount of 0.25%, relative to the mass of the powder, was added as a surfactant to improve the rheological properties of the suspension. The suspension with 88% solids content was homogenized in a ball mill at 80 °C for 5 h. The trapped air in the suspension was removed by stirring in a low vacuum for 15 min. The samples were then shaped in a steel die by low-pressure injection molding, using an industrial molding machine designed and built in the Hidria AET company (Slovenia). The temperature of the suspension before injecting was 65 °C. During the molding cycle the pressure linearly increased to a maximum pressure of 0.5 MPa in 2 s, followed by a 10 s holding time at maximum pressure and finally a release of pressure in approximately 0.1 s. The samples were removed from the die approximately 5 s after the pressure release. The temperature of the steel die was held at 25 °C. The shrinkage of the suspension during cooling and solidifying in the die was 1%. The samples were shaped as rods with dimensions of 60 mm × 4.8 mm × 3.5 mm (in molded state), which corresponds to dimensions of 52 mm × 4.1 mm × 3.0 mm in the sintered state (considering a typical 14% shrinkage). Such dimensions are suitable for the standard bending strength test [28].

The molded samples were debinded and sintered with the following single-step procedure. First, 15 samples were put in alumina crucibles (12 cm × 12 cm) on top of an approximately 1 mm-thick layer of carbon black (Elftex TP, Cabot Corporation, USA), supplied in the form of spherical granules with a specific surface of 130 m^2/g, a tap density of 0.4 g/cm^3, and an ash content below 0.1%. Then, an additional amount of the carbon black (0.25 g per 1 g of sample weight) was used to completely cover the samples. The crucibles were then placed in the furnace, where debinding and sintering took place. The temperature regime for the process was 0.7 K/min to 200 °C, 4 h dwelling at 200 °C, 2.5 K/min to 1600 °C, 3 h sintering at 1600 °C and then cooling (the complete process takes 25 h). The dwell at 200 °C is necessary for the exothermic reaction (oxidation of the binder) to go to completion (19). The exothermic effect was measured with a thermocouple placed in the carbon bed between the samples.

For comparison, a two-step debinding and sintering was also carried out. In this case the molded samples were buried in a highly porous alumina embedment (Nabalox N201, Nabaltec, Germany) and exposed to the same temperature regime as in the case of the single-step procedure described previously.

The wetting angle of the molten binder on the surface of the carbon is difficult to measure directly, so it was qualitatively assessed by using simple experiments. A disc with a diameter and height of 5 mm, made from pure paraffin binder, was put either on a flat graphite paper or on a thin layer of Elftex TP carbon black and put into an oven heated at 70 °C for 20 min. After the paraffin melted a spreading over the surface was observed. In the case of the graphite paper substrate it was cooled to room temperature and cut. While observing the cross-section, the wetting angle was quantified.

The four point bending strength was measured on sintered samples, according to the standard test method [28] at 25 °C and 50–55% relative humidity. The experiments were carried out with a load-driven rate of 8 N/s. The Weibull parameters were calculated with the maximum-likelihood method based on 50 measurements for each group—the single-step and the two-step.

The pore size distributions of the carbon black embedment and that of the sample (measured in a state with a completely removed binder, achieved by heating the sample for 3 h at 600 °C in air) were determined with a mercury porosimeter (AvtoPore IV 9500, Micromeritics Instrument Corporation).

3. Results and discussion

The large scale morphology of the carbon black, used as an embedment, can be seen in the optical micrograph (Fig. 1a) and the detailed structure of the individual spherical granule is presented in SEM micrograph in Fig. 1b. It is clear, that the granule is composed of fine, nano sized particles, forming interconnected pores. The samples after complete binder removal are shown in Fig. 2a, together with an SEM micrograph of their fracture surface (Fig. 2b), revealing the finer inner structure of the packed particles.

The pore size distribution inside the carbon black is presented in Fig. 3, together with the pore size distribution of the molded sample with completely a removed binder. The large pores of carbon black in the range from 10 μm to 100 μm are actually voids between the more-or-less spherical granules. These pores are too large to take an active role in the wick-debinding process, since the molded sample has significantly smaller pores, between 0.05 μm and 0.4 μm, as can also be seen from Fig. 3. However, the fine pores of the carbon black are even smaller (0.02–0.04 μm). The difference in the size of the pores in the sample and those in the embedment is one of the necessary conditions for the capillary action to take place.

Good wetting or spreading of the molten binder over the surface of the pores of the carbon black is another important and necessary condition for effective capillary extraction. Based on simple experiments, described in the experimental section, we estimated that the molten binder wets carbon surface quite well and that the wetting angle is less than 5°.

The wetting, together with the pore size distribution, determines the kinetics of the debinding, which can be easily and accurately measured by weighing the samples at different times in the process

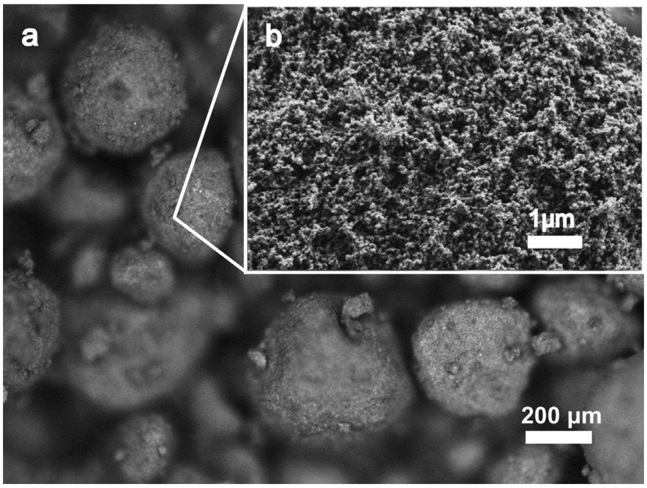

Fig. 1. Morphology of the granular carbon black. The image (**a**) showing the carbon black granule, is taken with an optical microscope and image (**b**), showing their fine structure, with a scanning electron microscope.

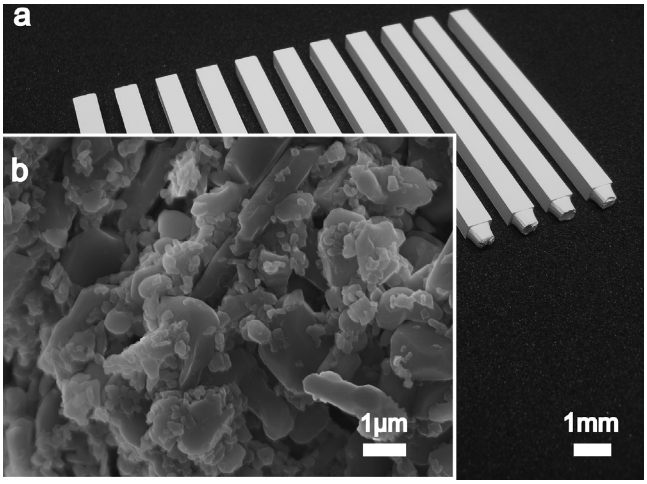

Fig. 2. Photograph of injection-molded samples after complete binder removal with heating at 600 °C for 3 h (a) and SEM micrograph of fractured surface of such sample (b).

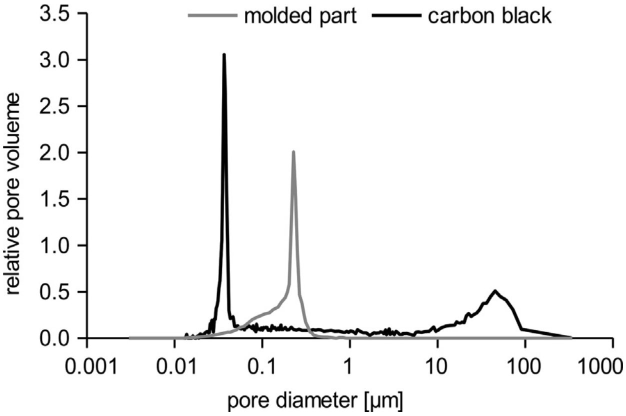

Fig. 3. Comparison of pore size distributions by volume of carbon black and that of the molded part without any binder.

(samples were removed from wick embedment, cleaned and then weighed). The debinding kinetics, which takes place during the first stage of the single-step process (heating to 200 °C and then dwelling for 4 h at this temperature), is presented in Fig. 4. It is clear, that the carbon black is indeed an effective wicking agent, since the binder is extracted fast and in large quantities when the temperature is raised above the melting point of the binder. It is important to note that when the temperature inside the embedment reaches approximately 180 °C, the debinding process changes and the dominant mechanism of binder removal becomes the decomposition of the paraffin due to a reaction with the oxygen in air. This effect has already been described in detail in Ref. [19]. The oxidation reaction is causing an exothermic effect, which can be seen from Fig. 4—note that the temperature inside the embedment (full line) is higher than that of the surrounding (dashed line) in the certain time interval. During the exothermic reaction, which lasts for about 2 h, the binder content drops to approximately 1.5%. Most of the binder decomposes into gaseous products; however a small amount of the binder remains in the sample and supposedly transforms into a cross-linked structure under these conditions [19,29]. Samples, having a only small amount of residual binder can be quite fragile at this stage. However, this is not important in this case, since they will not be handled until the end of the sintering, when they will reach full strength. This is an important benefit of the single-step processing.

The results of the thermogravimetric analysis (TG), shown in Fig. 5, indicate that the paraffin binder in the molded part and the carbon black embedment decompose in completely different temperature intervals and do not interfere with each other. The first decomposes between 200 °C and 400 °C, while the later starts to decompose after 500 °C. This means that in practice we can control the decomposition of the binder and that of the carbon black separately. It can be also seen, that in the case of the molded parts in carbon black there is a slower degradation of the binder into the volatile species than in the case of the molded parts alone. This is probably because oxygen diffusion is hindered by the layer of carbon black and so oxidation of the binder is slower. However, it must be mentioned, that samples for the TG analysis are significantly smaller than the size of typical molded products.

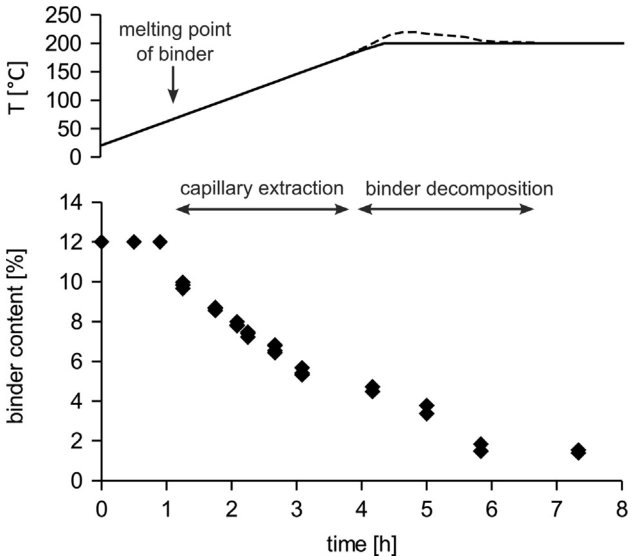

Fig. 4. Temperature inside the oven (full line) and temperature in the embedment (dashed line) are presented in the upper graph. Binder content as a function of the debinding time in the carbon embedment is presented in the lower graph. For the experiment, 15 samples were put on top of 1 mm layer of carbon black in alumina crucible (12 cm × 12 cm) and covered with an additional layer of the carbon black (0.25 g per 1 g of sample weight).

The decomposition of the embedment was complete, since there was no visible residual material or ash on any of the samples or crucibles after the sintering. This indicates that the carbon black is pure enough and burns without causing any discoloration of the ceramic surface. The surface of the sintered samples was also not distorted. The measured bending strengths of the samples sintered in the single-step process are shown in Fig. 6. For comparison, the strength values of the samples made from the same material and shaped similarly, but thermally processed with separate operations of wick-debinding and sintering (the two-step process), are also shown. Highly porous

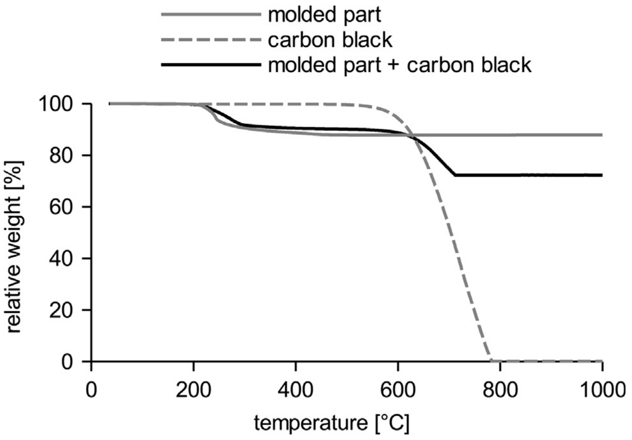

Fig. 5. TG curves for the molded part, for the pure carbon black and the molded part inside the carbon black embedment. Heating rate was 5 K/min (in an air atmosphere).

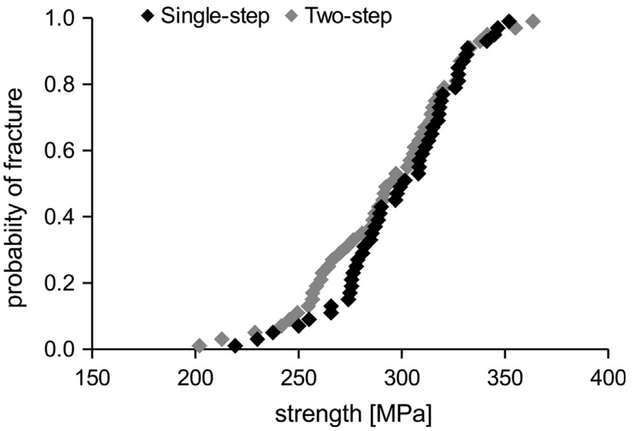

Fig. 6. Bending strength of sintered alumina bars prepared with the single-step procedure using carbon black as the embedment compared with the strength of bars with the same composition, but prepared by the two-step procedure. Each dot presents one measurement. Fitting the data with the Weibull function gives parameters $\sigma_0=307$ MPa, and $m=9.4$ for the two-step samples and $\sigma_0=313$ MPa, and $m=9.7$ for single-step samples (σ_0 is the characteristic strength parameter and m is the Weibull modulus).

alumina was used as an embedment during the wick-debinding in that case. Fitting the data with the Weibull function gives parameters $\sigma_0 = 307$ MPa and $m = 9.4$ for the two-step samples and $\sigma_0 = 313$ MPa and $m = 9.7$ for single-step samples (σ_0 is the characteristic strength parameter and m is the Weibull modulus). There seems to be a difference in the strength distribution in the region 250–300 MPa. The reason for this could be improved surface quality of the sintered specimen in the case of single-step debinding. However, further research would be needed to confirm if the effect is significant. The results indicate that the carbon black is effective as a capillary extraction agent and that it burns out without decreasing the strength of samples.

4. Conclusion

A single-step process for the low-pressure injection molding of alumina, going from molded to sintered parts in only 25 h, was demonstrated in which the benefits of wick-debinding are used, while its main drawbacks, i.e., additional cleaning and handling operations, are avoided. This was achieved by using a high-purity carbon black as a wicking embedment, which burns out after its role as the wicking agent is completed. The bending strengths of the sintered samples indicate that the burn out of the carbon black does not influence the final properties. The presented procedure has great potential for the practice of low-pressure injection molding. On an industrial scale it would eliminate the labor-intensive and delicate operations of cleaning and transporting the parts between the debinding and the sintering process. Also, the overall processing time and energy consumption would be reduced. Similar debinding and sintering process could be applied also for the high-pressure injection molding.

Acknowledgments

We would like to thank the Cabot Corporation for supplying as with the samples of carbon black. We would also like to thank European social fund for co-financing the research.

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