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Cracking defect and porosity evolution during thermal debinding in ceramic injection moldings

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Abstract

Formation of cracking defect during thermal debinding of a wax-based zirconia–binder system has been investigated at varying binder formulations (volumetric ratio of low-melting vs high-melting binder constitutes ranging from 1.7 to 2.8), heating rates (5–30°C h^{-1}) and the use of wicking powders in ceramic injection moldings. Increase of the low-melting binder ingredients to a critical ratio of 2.8 resulted in an apparent cracking at a relatively low pyrolysis temperature of 250°C as the heating rate was increased to 30°C h^{-1}. The cracking was avoided by use of wicking powders during thermolysis. The most frequent pore diameter of samples debound without the packing powders rapidly increased by nearly 3-fold over a temperature range from 200 to 250°C; contrarily, a gradual increase in the pore size was resulted when moldings were debound under the identical condition but with the packing powders. This finding is correlated with the incidence of cracking and its possible causes are discussed. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved.

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1. Introduction

Binder burnout is often the most time-consuming process in fabrication of ceramic components by injection molding. The removal process restrains the overall manufacturing throughput and the molded part becomes inherently vulnerable to defects in the pyrolysis stage. Various flaws may be introduced if an intricate balance between the generation and removal rate of degradation products cannot be maintained [1–6]. When an excessive pressure is built up within moldings from the degradation species during burnout, a propensity to form bubbles, distortions or even cracks may become inevitable.

Optimization of the debinding schedule with the aim of avoiding defects has long been an interesting subject attracting many theoretical and experimental investigations [1–6]. Calvert and Cima [2] have estimated the time required for binder removal through binder-filled pores at various molding thicknesses. The polymeric additives were assumed to decompose directly into volatile species and transported through diffusion from core to surface at an equilibrium rate sufficiently slow for not inducing defects such as bubbles. They concluded that, in order to successfully burnout ceramic–binder moldings with a thickness of several millimeters, a long heating schedule typically in a matter of days is necessary. A formation of porosity in the molded compact at an early stage of binder pyrolysis, however, was suggested to effectively enhance the removal kinetics, which would shorten the cycle time as confirmed experimentally by other researchers [7–10]. It is believed that the interconnected pores facilitate mass transport of the evaporation products by serving as a rapid conduit for outward diffusion of the degraded species.

Binder vehicles used for powder injection molding normally contain constitutes of varying attributes; therefore, different constitutes can be removed progressively as the temperature gradually increased. Polymeric binders presenting a higher melting temperature act as a backbone for shape retention during burnout while wax and surfactants/plasticizers are often removed at lower temperatures. Recent interests in modification of interfacial properties between powder and binder phases give a particular emphasis on proper selection of various

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surfactants [11–14]. These surface-active dispersants normally present a low melting characteristic and an affinity to preferentially adsorbed onto powder surfaces, forming a densely thin outer layer on a particle surface which leads to a more homogeneous packing structure [13,14]. However, bubbles and cracks were reported to occur as the amount of the surfactants increases [12,14], presumably owning to the reduced vaporization temperature since the surfactants are composed of mostly short molecules. Additionally, cracks may also be induced from the non-uniform shrinkage during injection molding [15], and from particle flocculations during low-temperature reheating of the unstablized powder–binder mixtures [16] as well. Understanding of the origin of defects with the varying surfactants is not extensive. In this study, a zirconia–binder mixture containing varying amounts of stearic acid as a surfactant (or critically speaking, various low-melting binder fractions including wax and stearic acid) was injection-molded and thermally debound at progressively elevated temperatures with a wide range of heating rates (5–30°C h^{-1}). Some moldings were immersed in packing powders under the identical pyrolysis schedule for comparison reasons. The onset of cracking of the debound moldings was correlated to their porosity evolution during heating.

2. Experimental procedure

A commercially available zirconia powder containing 3 mol% yttria (HSY3.0, Daiichi Kigenso Kagaku, Japan) with an average particle size of 0.25 μm and a specific surface area of 6.9 m^2 g^{-1} was used. The powder was first treated by surface adsorption of differing amounts of stearic acid (Showa Chemicals Inc., Japan, density = 0.942 g cm^{-3} and melting point about 72°C) in a procedure detailed elsewhere [17]. The surface-modified powders were then mixed with paraffin wax (Gin-Ming Chemicals, Taiwan, molecular weight about 320 and melting point about 55°C) and vinyl acetate polymer (Gin-Ming Chemicals, Taiwan, softening point about 150°C) in a ball mill for 24 h at various binder proportions listed in Table 1. The solid loading was held constant at 50 vol% for comparison reasons. In addition, the volumetric ratio of wax:polymer was fixed at 60:40 whilst the ratio between low-melting and high-melting binder constitutes varied from 1.7 to 2.8. Thermal gravimetric analysis (Seiko Instruments Inc., Japan) was used to guide weight-loss behaviors of the ceramic–binder mixtures.Fig. 1 shows a typical weight change of the samples in size of 5 × 5 × 5 mm when heated up to 500°C at a rate of 300°C h^{-1} in air. Incipient temperature for the binder removal reduced substantially as the low-melting constitutes increased. Similarly, temperature at which the maximum weight loss occurs also decreased proportionally to the amount of stearic acid (and, to the low-melting binder fractions as well).

The ceramic feedstocks were then fed into an injection molding machine (Battenfeld BA 250/50 CDC, Austria) to form parallelepiped moldings of dimensions 4 × 5 × 60 mm. Molding temperature from feed to nozzle was 90–140–150–150°C and a maximum pressure of 100 MPa was employed. The molded bars were thermally debound in air with heating rates ranging from 5–30°C h^{-1} over temperatures up to 600°C. Some moldings were embedded in zirconia packing powders (HSY-3.0) during the heating. The loss of organic vehicles was calculated from weight comparison (accuracy within ±0.1 mg) before and after the heating. The occurrence of defects was determined by both optical and scanning electron microscopy (Cambridge Instrument, S360) on "green" and partially debound, fractured samples. Pore-size distribution (PSD) of debound samples was measured using mercury porosimetry (Autopore 9220, USA). Samples in duplicate, sometimes triplicate, were measured to ensure the reproducibility.

3. Results and discussion

3.1. Incidence of cracking defect

Apparent voiding, blistering or cracking were not found in green moldings which contain the different binder formulations. Raising the temperature to 600°C with heating rates below 30°C h^{-1} did not result in any

Table 1
Composition of zirconiaa–binder mixtures

Stearic acid fraction		Binder composition (wt%)			
		Low melting		High melting	
(wt%, with respect to powder loading)	Zirconia	Stearic acid	Paraffin wax	Vinyl acetate polymer	Volumetric ration of low/high-melting binders
1	86.7 (50.0)	0.9 (3.3)	7.0 (28.0)	5.4 (18.7)	1.7
2	86.7 (50.0)	1.7 (6.7)	6.5 (26.0)	5.1 (17.3)	1.9
3	86.7 (50.0)	2.6 (10.0)	6.0 (24.0)	4.7 (16.0)	2.1
5	86.7 (50.0)	4.3 (16.7)	5.0 (20.0)	3.9 (13.3)	2.8

Volume percent in parentheses.

detectable defect. However, as heating rate was increased to 30°C h^{-1}, cracking defects shown representatively in Fig. 2 were found in moldings containing the maximum concentration of the low-melting binders.

Onset temperature for the cracking occurred at about 250°C. This relatively low temperature indicates that the cracks were formed at an early stage of binder thermolysis at which binders became soft. These cracks all extended in the longitudinal direction of the bar-shaped moldings. In addition, the cracks were all located at about the central position of the moldings (i.e. dividing the moldings into two halves along the thickness direction) and often spanned across the moldings. Two possible mechanisms may be responsible for this to occur. Firstly, the feedstock melt entered into the die cavity and solidified from the surface near the cavity wall to core of the moldings progressively, it is hence suspected that center of the moldings is the last solidified region (except for maybe the gate region) and may become the weakest "interface" of the compacts. This presumes that the channel (e.g. sprue, gate, etc.) which feeds the melt into the cavity to compensate for the volume shrinkage was closed prematurely before a full solidification of the moldings was reached. Secondly, a residual stress would exist within samples after injection molding, and this stress is expected to reach a maximum tensile stress at the center of the bar-shaped moldings [18,19]. As temperature was raised, binders near surface of the moldings would experience both thermal and oxidation degradations, and be removed preferentially from that in the core (which only subject to the thermal degradation). This leads to formation of a surface layer which has a deficiency of binders relative to the core, and hence is less flexible for the residual stress at the core to relax. It has been found that a complete removal of the residual stress may not be attainable even with a prolonged annealing before any binder has been lost by pyrolysis [18,20]. The difference in stiffness between surface and center of the moldings during debinding may then lead to crackings to occur if a heating rate exceeding a certain critical level was applied. The electron microscopy failed to observe any void or hair-line crack in the green molding, indicating the latter hypothesis may be responsible. However, the weak "interface" might still operable, according to Thomas and Evans [15] who used an X-ray radiography to detect initially minor cracks (which are hard to be identified) which later evolved into catastrophic cracks after heating.

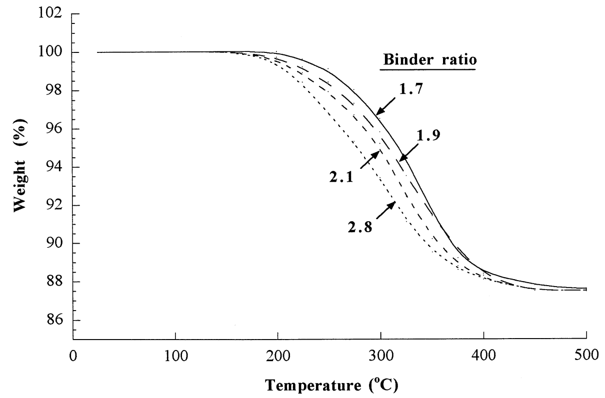

Fig. 1. Weight-loss behavior of zirconia–binder mixtures pyrolysed at a heating rate of 300°C h^{-1} in air.

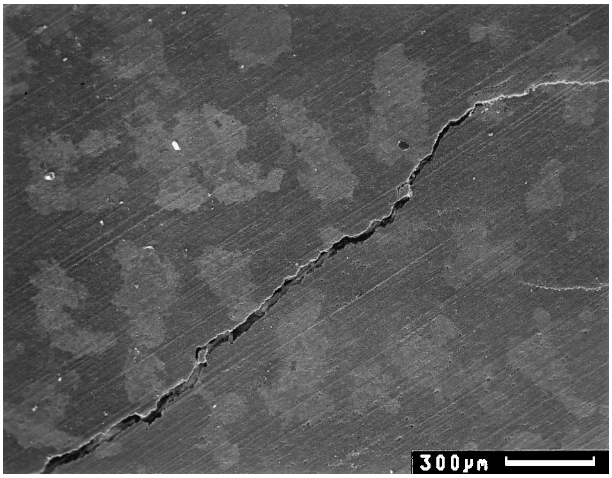

Fig. 2. Typical crackings observed in moldings containing the binder ratio of 2.8 after thermal pyrolysis.

At elevated temperatures, mechanical integrity of molding compacts is reduced, and this reduction is expected to become more pronounced as the low-melting binder fraction increases [12]. Accordingly, even if the weak "interface" exists in moldings with all the differing binder ratios, the moldings which contain the amount of the low-melting binders the most are expected to be the most susceptible to the cracking defects as temperature was raised above the melting temperatures of the binders at given heating rates. The critical volumetric ratio of the low:high melting binders is experimentally determined to be 2.8 in our model system and the critical heating rate was 30°C h^{-1}. Cracking, however, was not found when moldings of the same composition (i.e. the binder ratio of 2.8) were immersed in the powder bed and subjected to the identical heating schedule. Porosity development during thermolysis was examined to elucidate the underlying mechanisms and will be described in the following section.

3.2. Porosity development

Porosity formed during binder thermolysis increased as the temperature was raised, as shown in Fig. 3 for samples containing the binder ratio of 2.8 and were heated at a heating rate of 30°C h^{-1}. A substantially higher porosity was found when the wicking powders were used, especially at the "initial" stage of the binder removal (although vaguely defined, the organic binders

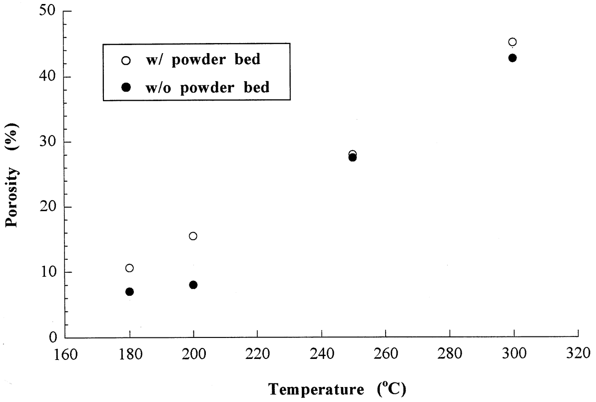

Fig. 3. The measured porosity of moldings at varying temperatures.

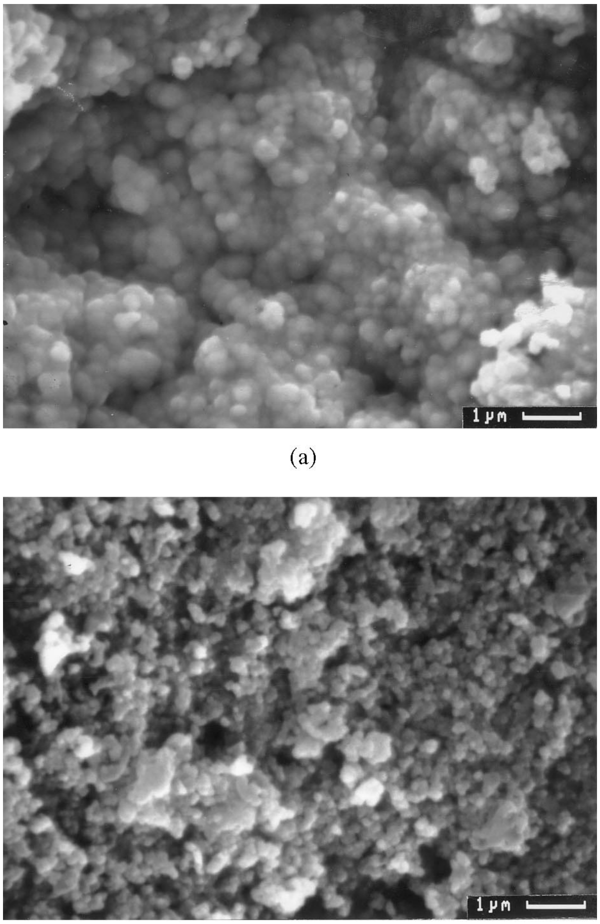

Fig. 4. Near-surface microstructure of partially debound moldings heated to 200°C (a) without and (b) with the powder bed.

less than 20% of their original amount was lost at temperatures prior to 200°C). The porosity discrepancy between the samples debound with and without the packing powder increases as the temperature approached to 200°C at which even the high-melting binder ingredient was presumably softened. This indicates that the capillary force imposed by the surrounding powder effectively removed the near-surface binders during heating, creating perforated channels in the compacts. Nevertheless, the porosity discrepancy might also have been exaggerated because of the method used for determining the porosity. Since the samples were cooled down to ambient temperature for the mercury porosimetry, deposition (and/or solidification) of the degradation species on existing pore channels might have taken place and blocked the surface pores to a certain extent so that the overall porosity was reduced.

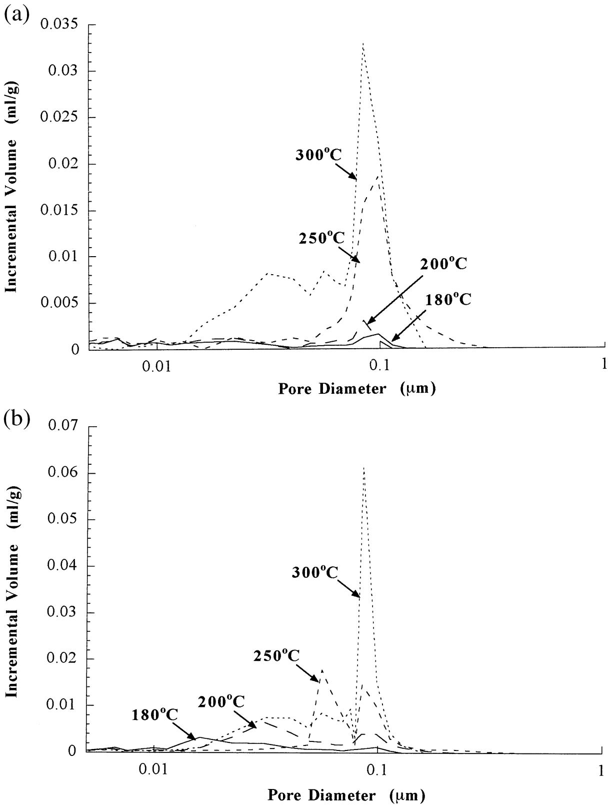

Fig. 5. The pore-size distribution of partially debound samples at varying temperatures (a) without and (b) with the powder bed.

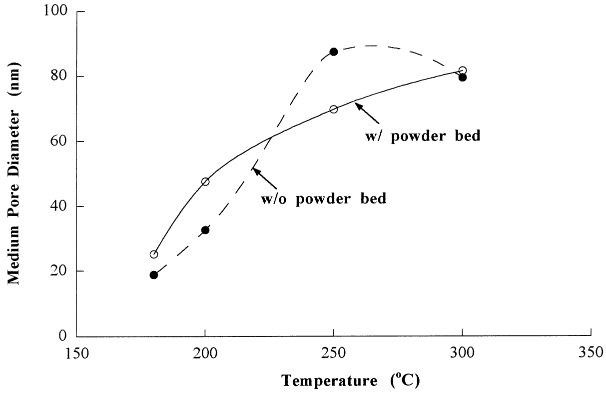

Fig. 6. The medium pore diameter of moldings at varying debinding temperatures.

Microstructural examination on the partially debound samples pyrolysed at 200°C revealed that a significant contrast on near-surface microstructure was resulted (Fig. 4). A substantially rich fraction of the binders remained near surface of the moldings when the powder bed was not used. This finding further indicates that the surface porosity is the rate-determining factor during the early stage of binder thermolysis. Lack of the surface area hinders the overall outward transportation of the degradation ingredients.

In Fig. 3, difference in the porosity of samples with and without the powder bed diminishes as the temperature was further increased toward 250°C, the temperature at which the crackings occurred. It suggests that the degradation products stored within the moldings might have reached a critical point at this temperature and, for the samples debound without the packing powder, these degradation products were eventually liberated through formation of crackings at the weak site. This hypothesis is further substantiated by observations in the pore-size development of the debound moldings. The PSD of the moldings debound without the packing powders showed a unimodal distribution [Fig. 5(a)] over a temperature range from 180–300°C. A bimodal pore distribution was apparently observed at temperatures below 250°C, and was most pronounced at 250°C, for the moldings debound in the powder bed under the identical heating rate of 30°C h^{-1} [Fig. 5(b)]. Corresponding evolution in the medium pore diameters is shown in Fig. 6. A gradual increase in the pore size over temperatures of 180–300°C was found for the powder-bed case; on the contrarily, a steep increase in size by as large as 3-fold was found over a temperature range of 200 to 250°C for the moldings debound without the wicking powders. This notable increase in the pore size is believed to result from the massive production of the degrading binders, especially the vaporization of the low-melting ingredients at the given temperature, in couple with the inhibited liberation of these degradation species because of the lack of surface porosity.

4. Conclusions

Cracks were found during pyrolysis of ceramic injection moldings when the volumetric binder ratio of given ceramic–binder mixtures and the heating rate increased to a critical level. The moldings are most susceptible to defects when binders soften and, from which, the molding integrity becomes insufficient to withstand the internal pressure built up within the sample from the degradation of binder species. Interconnected pores produced from the capillarity of packing powders at the early stage of pyrolysis favorably reduce the cracking incidence. A gradual increase on the pore size was seen for the powder-bed debinding case while a rapid increase in pore size by nearly 3-fold was found over a narrow temperature range when no powder bed was used. These findings suggest that the debinding defect and the minimum debinding time are both influenced by the chosen binder formulations.

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