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Transient effects during catalytic binder removal in ceramic injection moulding

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Abstract

This work is part of a comprehensive study of the incidence and cause of defects in large section ceramic injection mouldings. In previous related work, the defects associated with mould-filling and with solidification and packing in the cavity were identified. Such defects sometimes manifest themselves only after binder removal or after sintering and so may be causally connected with those stages by mistake. In the present work, defects which do indeed arise from the binder removal stage itself as a result of minor process interruptions are isolated. These are identifiable by a pattern of defects which are distinct from those due to solidification and are independent of solidification conditions. This work reports on the systematic study of perturbations to conditions in the binder removal oven in order to track the origin of these defects and hence distinguish them from shrinkage-related defects. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Binder removal; Defects; Injection moulding

1. Introduction

Ceramic injection moulding is a versatile mass production method for complex shaped ceramic components.[1,2] Its wider industrial implementation however requires high quality standards and low rejection rates. It tends to be limited to thin components because defects appear more frequently in thicker moulded sections. In many cases these defects present themselves for attention after binder removal or sintering, nevertheless their origin is often in the injection moulding stage.[3–5]

However, there are certain types of defect which can be unambiguously related to the binder removal stage. The mouldings may slump or deform as the binder reaches its softening point during thermal binder removal. The decomposition and boiling of the binder may cause cracks in the mouldings or lead to bloating.[1,2,6–8] These experiences have limited the use of conventional pyrolysis of wax or low molecular weight polymeric binder systems to small sections only.[9] The emergence of a polyoxymethylene-based binder system for powder injection moulding[10–12] has made it possible to remove the polymer vehicle from up to 35 mm thick sections.[3] The binder decomposes predominantly to formaldehyde in the presence of an acid vapour well below its softening point, that is, in the solid state. The speed of the inward moving binder interface is initially limited by chemical reaction rates and reaches 3.56×10^{-4} mm s^{-1} (1.3 mm h^{-1} at a metered nitric acid rate of 43 ml/h) for an alumina suspension.[13] However, gas diffusion through the growing porous layer subsequently reduces the rate during the progressive shrinking-core reaction.[13]

The wide variety of defects found in ceramic injection mouldings are not easily attributed to their correct origins. A comprehensive study of defects in large section ceramic mouldings[3,4,14–18] distinguished mould filling defects and solidification-induced defects. Identifiable patterns of cracks which appear during binder removal or sintering are, in many cases related to the solidification stage in injection moulding. In contrast, it is the intention of this study to isolate defects which originate from the catalytic binder removal process and thereby to distinguish them from moulding-induced defects. The

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intention is to understand their origin and to determine the critical furnace control conditions that allow them to be ameliorated. In this work all mouldings were made by the insulated sprue method, previously described, that allows pressure to be transmitted to the moulding for prolonged periods.

2. Experimental details

The injection moulding material was a polyoxymethylene-alumina suspension which is commercially available under the designation Catamold AO-F (BASF, Ludwigshafen, Germany). The alumina powder was grade CT3000SG (Alcoa Chemie GmbH, Ludwigshafen, Germany). The powder was blended by high shear mixing at 56 vol.% into a thermally stabilised polyoxymethylene (POM) together with processing additives at 3 vol.% level of addition.

A Negri Bossi NB90 injection moulding machine was used. The suspension was injected into a 25×45×60 mm mould tool using the processing conditions shown in Table 1. The cavity was direct-gated through a sprue made out of polyetheretherketone (12 mm diameter, 10 mm long) which reduced radial heat loss and allowed a significant contribution from axial heat flow from the nozzle and hence prolonged the sprue solidification time.[3,4,16]

Samples were cut from various mouldings and 0.5 mm thick PVC sheathed k-Type thermocouples were welded by thermolamination between two samples according to Fig. 1 providing samples 30×38×45 mm and 8×12×20 mm thick. The data logger used to read the temperatures in the samples and in the oven environment was a PicoLog TC-8 (Pico Technology Limited, Hardwick, UK).

Table 1
Injection moulding conditions

Parameter	Settings
Barrel temperature profile	170–170–173–175°C (nozzle)
Mould temperature	135°C
Injection speed	8×10^{-5} m^3 s^{-1}
Maximum injection pressure	95 MPa
Hold pressure	6–120 MPa for 400 s

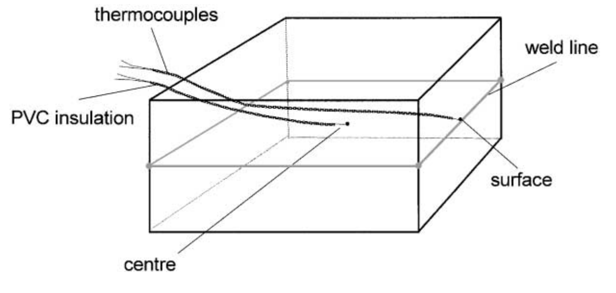

Fig. 1. Schematic diagram showing the position of thermocouples to measure temperature changes during binder removal.

The polyoxymethylene was removed from these samples by catalytic decomposition in the solid state at 110°C in an oven (Model VT6060-MU-2 Heraeus Instruments, Hanau, Germany) fitted with safety interlocks and an afterburner. The furnace was supplied with oxygen-free nitrogen at 500 l/h and liquid fuming nitric acid (99.5% assay, ex BDH-Merck, Lutterworth, Leicestershire, UK) at rates up to 68 ml/h from a metered pump (Constrakron 3, Kron-lab Sinsheim, Germany). The 25-mm thick samples were catalytically degraded at 30 ml/h nitric acid for 550 ks. All samples were sintered at 1600°C for 2 h. The temperature ramp was 2°C/min to 400°C with a hold for 1 h at 270°C followed by 5°C/min to 1600°C, a 2 h hold and cooling at 2°C/min to 400°C.

The thermal expansion of the ceramic injection moulding suspension and of the ceramic powder assembly after binder removal was measured with a thermomechanical analyser (model TMS-1, Perkin Elmer, Buckinghamshire, UK) calibrated with an aluminium standard.

3. Results and discussion

3.1. Defects in mouldings

This section of our comprehensive study of defects in large ceramic sections came about because one batch of 20 mouldings, each measuring 25×45×60 mm and each made with different injection moulding conditions, emerged from the binder removal and sintering stages with a concentric crack pattern superimposed on defects known to have originated at the solidification stage. In previous work[3] it was very clear that the arrangement of cracks in large mouldings was dependent on the solidification conditions in the cavity. Both the presence or absence of defects and their configuration could be related to the injection moulding stage. In this batch, an identical pattern of superimposed defects was found in each moulding.

Fig. 2(a) shows a 25-mm thick alumina moulding made with 60 MPa hold pressure after binder removal and sintering. The fracture surface revealed this characteristic defect pattern. Cracks run parallel to the moulding surface and become concentric towards the moulding centre. Fig. 2(b) shows a moulding processed at quite a different holding pressure (6 MPa) which was mechanically fractured after binder removal but before sintering. The defect patterns in the mouldings before and after sintering clearly correspond in terms of shape and location. The individual shells are at the same distance from the surface for mouldings from this binder removal batch. It quickly became clear that there had been a processing discontinuity in that batch.

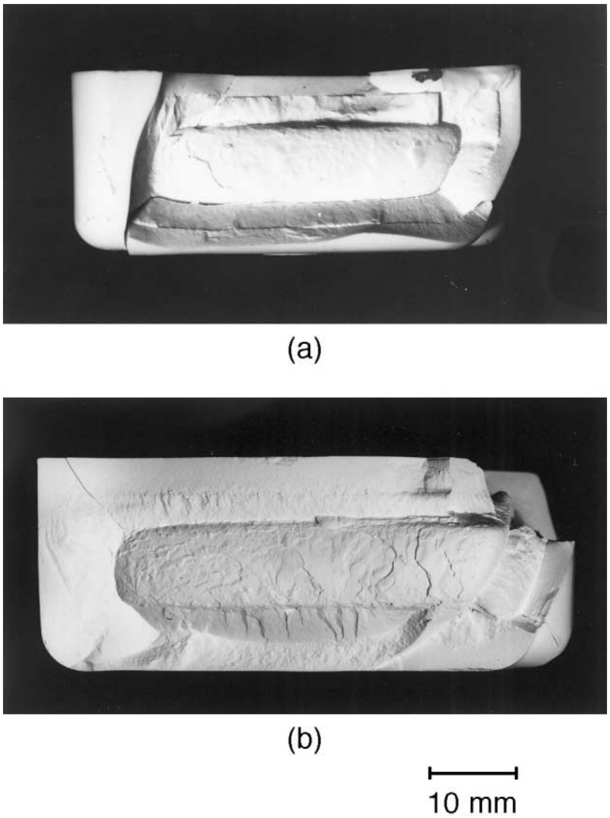

Fig. 2. Insulated sprue mouldings (25 mm thick): (a) fractured after sintering; (b) fractured after binder removal.

Fig. 3 shows X-ray radiographs from mouldings which were produced over a wide hold pressure range from 20 to 120 MPa but were processed in the same binder removal furnace charge. The location of the concentric crack pattern is identical in each moulding. It has already been established[3] that the pattern of cracking which results from different hold pressures applied during solidification in the mould cavity gives rise to distinct and distinguishable arrays of defects in X-ray radiographs and in some cases, mouldings without any of these cracks are produced if binder removal is correctly executed.

3.2. Binder removal experiments

To investigate these concentric defects and their presumed relation to the binder removal process, the follow parameters where deliberately interrupted or changed during binder removal: (a) acid concentration; (b) chamber gas circulation; and (c) oven temperature. These simulated disruptions are of great practical relevance and may easily be inadvertently introduced. The long lasting binder removal (up to 550 ks) for thick moulding sections (25 mm) may require the exchange of the nitric acid bottle (1 litre), the nitrogen or the burner gas bottles. As a result, the constant rate of acid input to the oven may be interrupted and the acid concentration in the chamber environment may change. If, for example, the acid runs out, the concentration decays and the process temporarily stops. The acid transport into the oven is also stopped by the safety system of the oven if either the nitrogen, which acts as an inert carrier gas, or the gas supply for the after-burner run out.

Samples measuring $30\times38\times45$ mm and $8\times12\times20$ mm were equipped with thermocouples according to the scheme in Fig. 1 and placed in the oven during binder removal. Fig. 4 shows the temperature record as a function of time in the oven environment both at the moulding centre and at the surface of the samples. The oven was constantly flooded with 500 l/h nitrogen. As the oven and the samples reached the processing temperature of 110°C the liquid nitric acid was pumped into the oven environment at a constant rate of 68 ml/h. The graph shows a rapid response of the temperature in the samples caused by the exothermic decomposition of the polyacetal binder. The minimum at the centre of the 8 mm thick sample occurs after 360 s. The enthalpy of polymerisation for the polyacetal binder is 63 kJ mol^{-1} being both high and negative.[19] After an initial

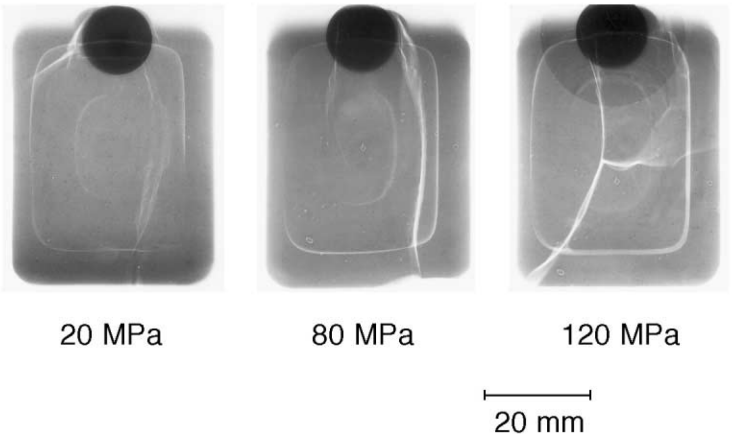

Fig. 3. X-ray radiographs from 25-mm thick sintered alumina mouldings manufactured with various hold pressures.

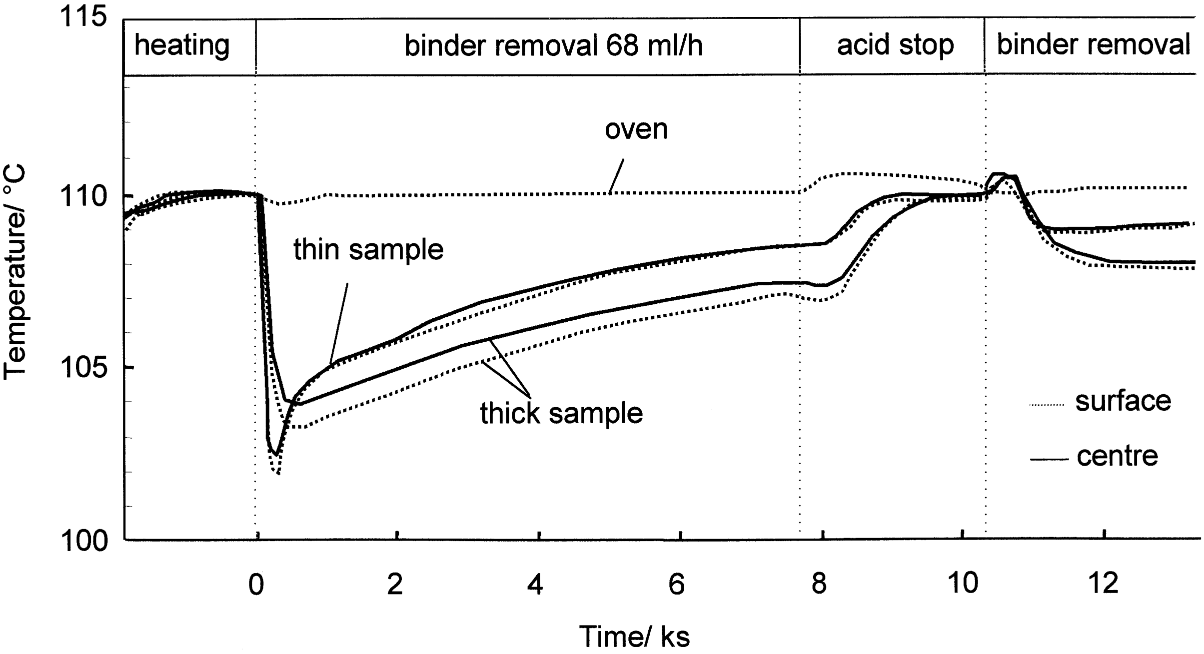

Fig. 4. Temperature traces in the oven environment and in a 30×38×45 mm and a 8×12×20 mm thick sample at the moulding surface and at the moulding centre during a binder removal run in which the nitric acid supply (68 ml/h) was interrupted.

temperature minimum, the temperature of the samples gradually approached the oven set temperature.

The behaviours of the thin and the thick samples were different. Having a lower ratio of volume to surface area, the thinner samples showed a quicker response and cooled down to about 102°C. The thicker mouldings showed a slightly less pronounced temperature drop. Except for the initial temperature drop there was almost no difference in temperature between the centre and the moulding surface measured in the thinner samples. In the thicker samples, the temperature was only about 1°C higher at the surface. This indicates a very shallow temperature distribution in these mouldings during binder removal. This part of the experiment demonstrates that temperature differences of up to 8 K can prevail in this process. The fact that this occurs at the start of decomposition where the moulding consists of strong ceramic-polymer composite means that it is not harmful. Temperature changes which result in differential expansion at a later stage where part of the sample is a polymer-depleted ceramic skeleton may not be so forgiving.

After 7.68 ks (128 min) the nitric acid delivery was interrupted for 2.64ks (44 min). As a response, the sample temperature rose slowly to reach the oven temperature as the endothermic reaction slowed. The oven temperature was also influenced by these changes; both the initial endotherm and the reheating, to the extent of about 0.5 K within the control band. The slow rise to 110°C after the nitric acid was stopped is associated with the gradual exhaustion of nitric acid from the pores of the sample; the nitric acid in the furnace atmosphere having been quickly swept by the nitrogen flow. Renewed starting of the process led to an initial temperature rise followed by a temperature reduction in the samples. The low but clearly distinguished temperature increase in the mouldings after restarting the acid transport into the oven environment indicates an exothermic reaction caused by the oxidation of formaldehyde by the nitric acid.[20,21] In the initial binder removal process however, this exothermic reaction is not detected because it is overwhelmed by the initial and pronounced temperature drop caused by the endothermic decomposition of the polyacetal binder. In contrast, on restarting the binder removal process when the interface is already well advanced into the moulding, the short temperature rise corresponds to the exothermic oxidation of formaldehyde already present in the alumina powder layer.

The consequences of acid interruption during binder removal for the development of defects are displayed in Fig. 5(a) and (b). They show 20×20×10 mm thick samples sectioned from a 25-mm thick moulding processed at 60 MPa hold pressure. During their binder removal at constant nitric acid rate of 65 ml/h^{-1}, the acid supply was intentionally interrupted for 0.6, 2.7 and 61.2 ks after steady flow for 4.68, 7.8 and 14.4 ks, respectively. The sample in Fig. 5(a) was mechanically fractured after binder removal. A concentric crack pattern is visible in the fracture face. Fig. 5(b) shows a polished section of a sample having the same size which was a companion in the same batch and which displays exactly the same crack pattern in the sintered ceramic. Although processed in a different batch from samples

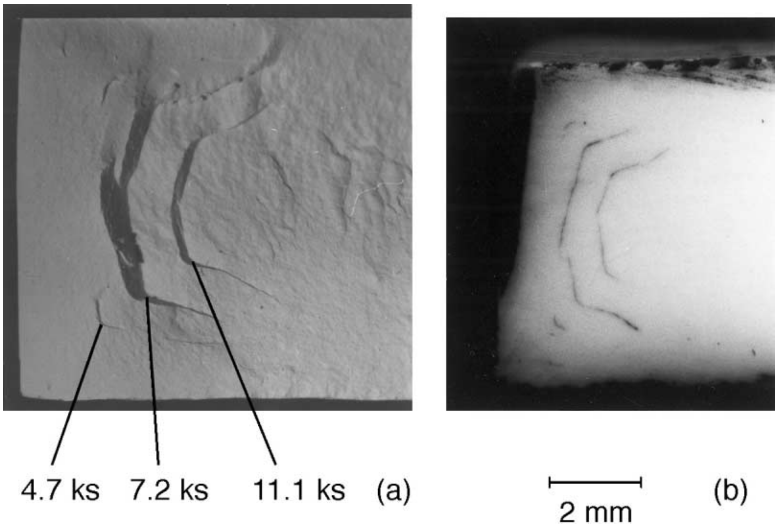

Fig. 5. Defects in 10×20×20 mm thick samples cut from insulated sprue mouldings: (a) fractured after binder removal; (b) sintered and polished surface.

shown in Fig. 2(a) and (b). This pattern is consistent with the moulding defects they show where a fracture surface perpendicular to the one in Fig. 5(a) and (b) is displayed.

Fig. 6 shows a polished section of a sample from which the binder was partly removed. The unreacted core is clearly visible and is surrounded by the ceramic powder layer from which polyacetal has been expelled. The interface is definable by scanning electron microscopy to within about 3 μm or 6 particle diameters.[13] By using a technique for interrupting the binder removal process instantaneously (vide infra) it was shown that the concentric crack pattern found in the samples displayed in Fig. 5 appeared along this interface during binder removal.

Plotting the distance from the moulding surface to the cracks and hence the depth of the binder interface at the time of interruption as a function of time reveals how the binder interface gradually moves into the moulding and is displayed in Fig. 7. The graph, which is obtained from samples processed at a nitric acid rate of 65 ml/h is consistent with the reaction depth measured in related work.[13] The lower pump settings used in previous work led to a reduction of the removal rate and the corresponding reaction depths are plotted in Fig. 7 as a function of time.

To record the exact location of the interface during binder removal, samples were positioned in the oven in such a way that they could be dropped into a silicone oil bath at the same time as the interruptions were initiated. For these samples, the binder removal reactions stopped immediately. The location and shape of the unreacted core could then be compared with the defect pattern found in the samples processed at the same time as their companions in the oven. The result was unambiguous. The defect patterns clearly map onto the remaining unreacted core. Thus the defects are created along the polyacetal-gas interface during the discontinuities imposed on the binder removal process. Attention to Fig. 5(a) and (b) indicates three concentric crack lines. These cracks correspond to the position of the binder interface at the times when the acid supply was interrupted. Since the reaction interface is almost static between interruption and reconnection of the acid supply, it is not possible to distinguish the temperature increase or decrease as the source of defects. As discussed below, both involve differential displacement at the interface. The cracks are more pronounced at the curved regions near corners. They either travel along the interface, in extreme cases separating a complete core, or as shown in Fig. 5, start from the curved interface but then deviate from the interface and move in a straight line into the brittle ceramic layer.

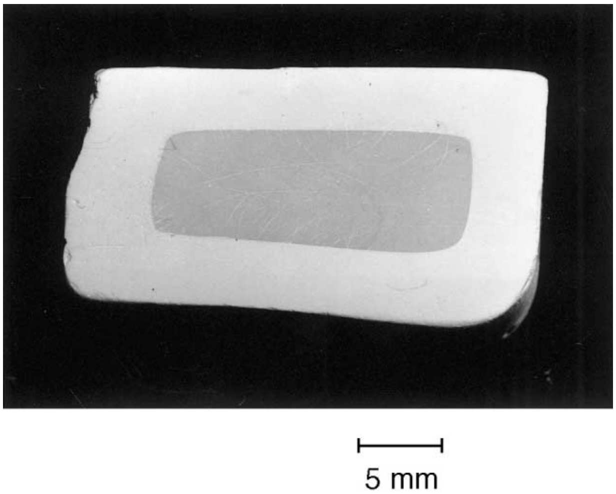

Fig. 6. Polished section of a 15-mm thick sample displaying the reaction interface during binder removal.

In the following experiment the gas circulation in the furnace was also shown to have an effect on reaction rate and temperature uniformity. Fig. 8 shows the temperature recorded by an embedded thermocouple in an 8×12×20 mm alumina sample during binder removal. The nitric acid rate was constant at 40 ml/h and during binder removal, the fan in the oven chamber was switched off for 0.9 ks (15 min). This interruption led to a rapid temperature drop in the oven and, as a result, the temperature in the moulding centre dropped by about

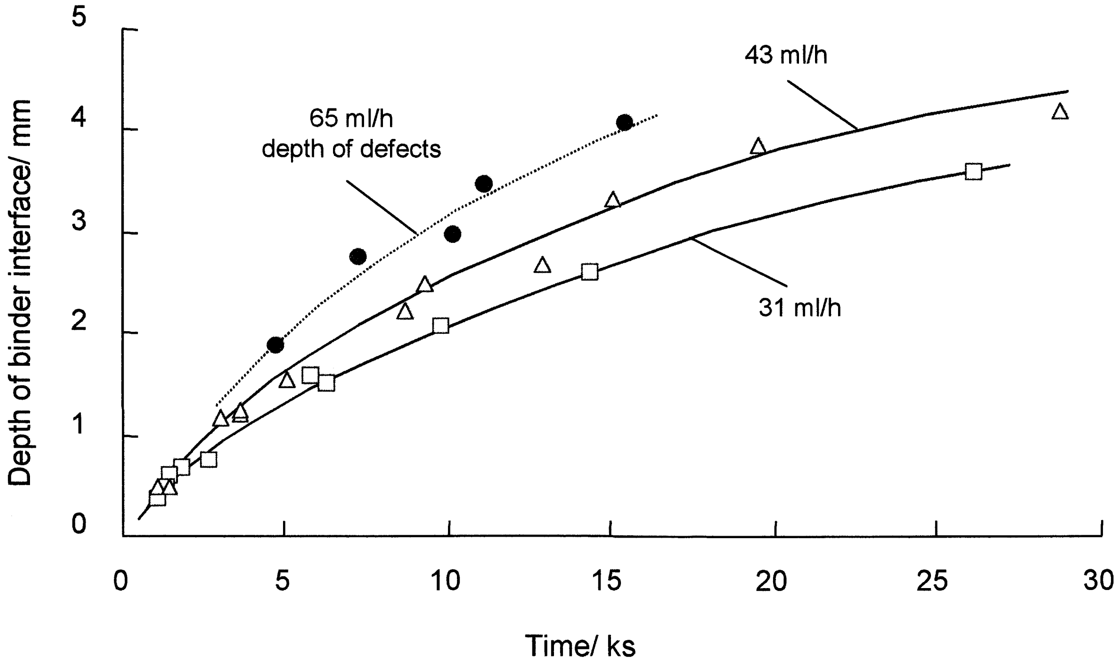

Fig. 7. Distance between the moulding surface and the defect as a function of time compared with the measured reaction depth from related work.[14]

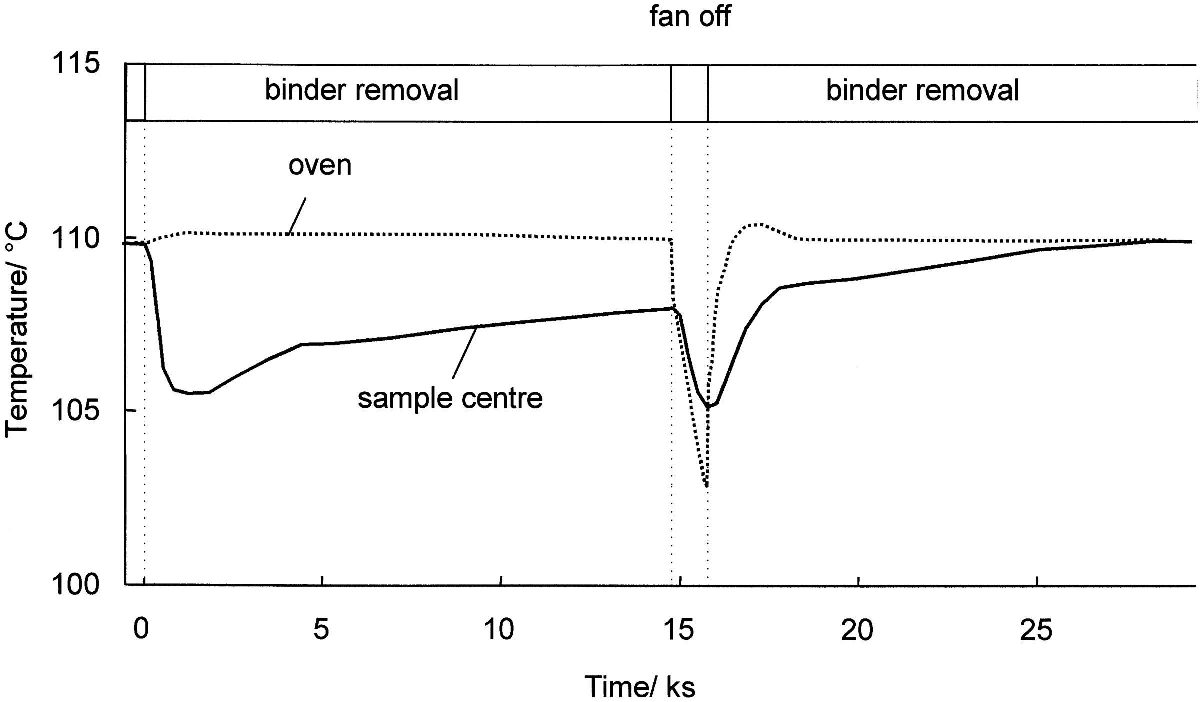

Fig. 8. Temperature trace in the oven environment and in the moulding centre during a binder removal run in which the oven gas forced circulation was interrupted.

3°C. As the fan was switched on again, the oven and sample temperatures re-established themselves. This temperature variation in the mouldings again led to a concentric crack pattern. After 28 ks the sample and furnace temperatures converged implying the reaction had ceased.

A similar temperature drop in the moulding centre appeared if the acid rate was increased during binder removal. Fig. 9 shows the temperature trace in the centre of an $8\times12\times20$ mm sample during binder removal as the initial nitric acid rate of 20 ml/h was doubled to 40 ml/h for 0.6 ks and afterwards reduced to 20 ml/h. The temperature drop measured in the moulding centre is again explained by an increase in the endothermic decomposition of the polyacetal binder and hence to a temperature reduction at the reaction interface.

Unlike the nitric acid interruption which led to a temperature rise in the samples (Fig. 4), an increase in the nitric acid flow rate or the failure of the oven circulation led to a sudden temperature decrease. The samples processed according to the schedule in Fig. 9 did not present a defect. However an increase in acid flow rate from 20 to 60 ml/h which is likely to be associated with a more pronounced temperature drop did cause a concentric crack defect. Thus the effects of increased nitric acid flow rate on defects were similar to those of nitric acid starvation.

The magnitude of the temperature change in the mouldings seems to influence the incidence of defects. Samples processed with the temperature drop of 3 K shown in Fig. 8 which was caused by the interruption of the oven circulation for 1 ks produced a defect but a shorter interruption of 0.6 ks (for which the moulding temperature was not recorded but which was expected to lead to a less pronounced temperature drop) did not produce a defect. Similar results were obtained on changing the acid concentration as described above. Thus it appears to be the severity of the sudden temperature change that matters.

This could be confirmed by changing the oven temperature whilst leaving the other parameters constant. A gradual temperature drop of 7×10^{-3} °C/s down to 105°C in the oven did not initiate a defect, whilst a drop in oven temperature down to 100°C did. Although the temperature changes in the mouldings themselves where not measured during this experiment, the result confirms that temperature changes during binder removal are responsible for defects.

Thus it can be seen that temperature changes during binder removal that are caused by processing discontinuities are responsible for the characteristic concentric crack pattern found in the 25 mm thick mouldings and shown in Figs. 2, 3 and 5. It would augment this thesis to show that the binder can be removed from such large mouldings without the creation of such defects if processing discontinuities are avoided.

Fig. 10 shows the temperature traces measured in the oven and in the centre of a $25\times45\times55$ mm thick sample for the first 30 ks of a 600 ks binder removal run. The sample was prepared with an embeded thermocouple

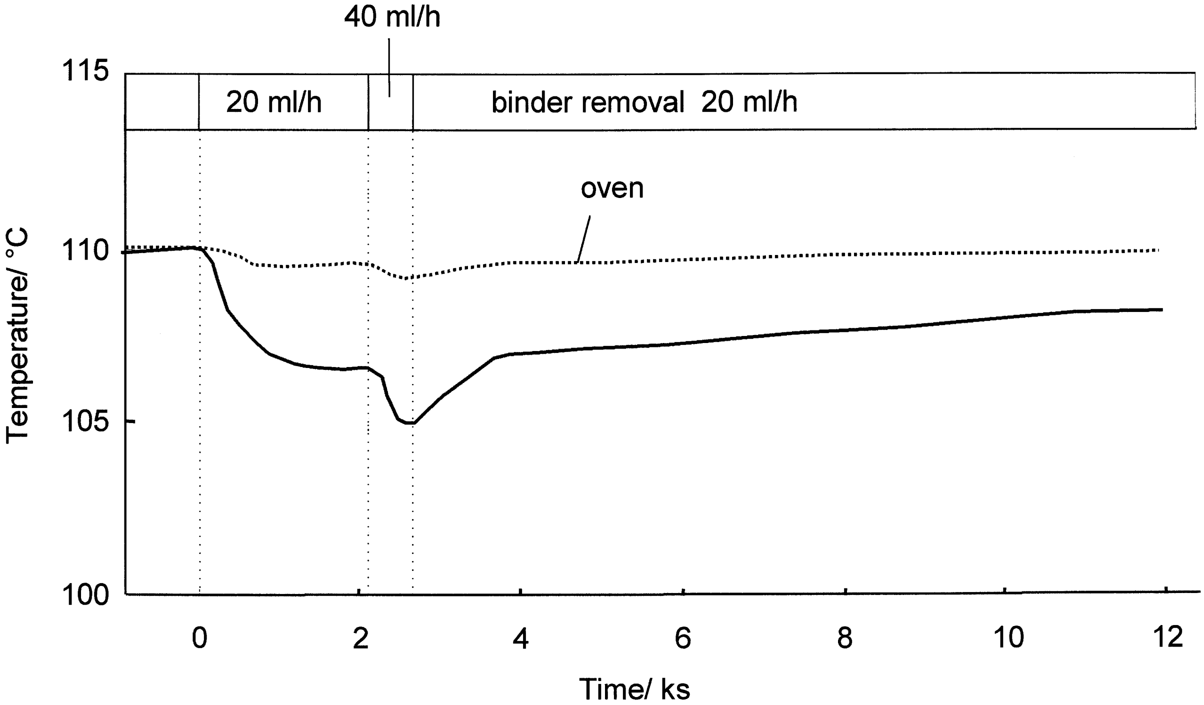

Fig. 9. Temperature trace in the oven environment and in the moulding centre during a binder removal run in which the acid concentration was increased.

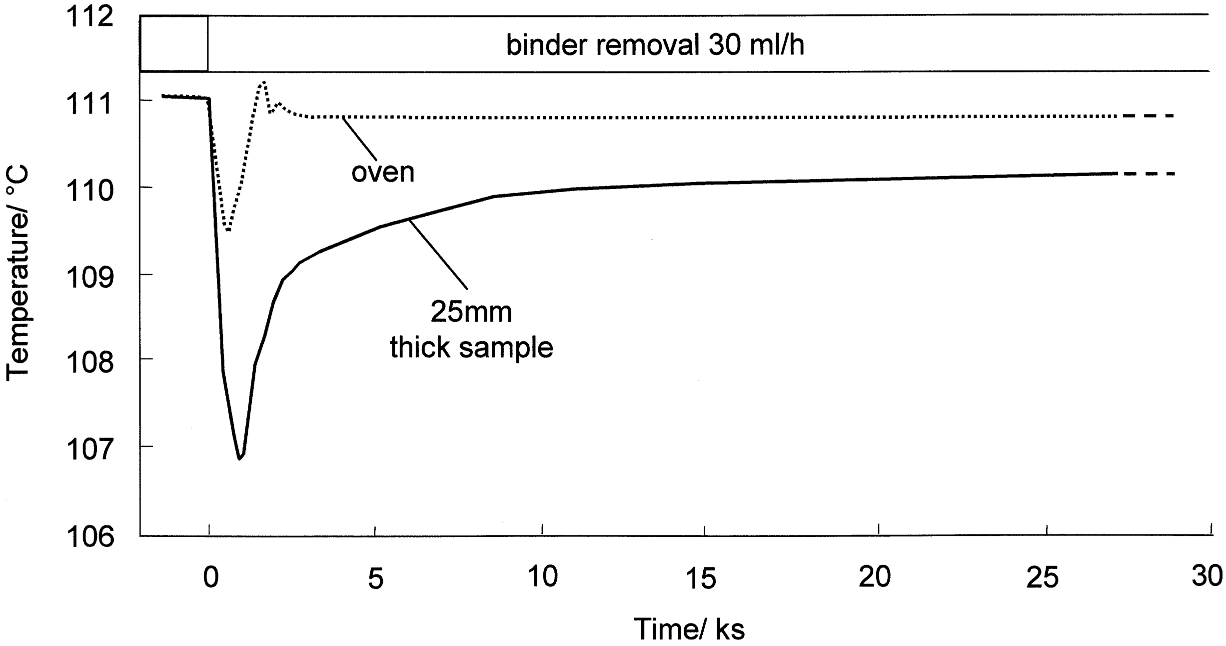

Fig. 10. Temperature trace in the oven environment and in the moulding centre during a commercial binder removal run at full oven loading.

according to the scheme in Fig. 1 and placed together with thirty 25×45×60 mm, 17 20×45×60 mm and 10 15×45×60 mm thick alumina mouldings in the oven. The oven temperature was set at 110°C within ± 1°C and after 1 h preheating, the nitric acid was constantly metered at 30 ml/h into the oven. The oven was fully loaded; the settings used and the procedure followed represent the commercial application of this process. As in the experiments described above, the initial endothermic decomposition at the moulding surface led to a reduction of the temperature in the mouldings. Unlike the temperature traces shown above where only a few small samples were placed in the oven, the oven temperature here reveals a pronounced temperature drop at the initiation of the process.

Two factors may give rise to this effect; the endothermic evaporation of the nitric acid metered in to the oven or the endothermic decomposition of the polymer binder may both contribute to cooling. Since the oven loading and hence the sample surface area has a pronounced influence on the magnitude of the temperature drop, the later is held responsible.

Fig. 11 shows a fracture surface broken after binder removal of a 20-mm thick moulding which was representative of the 57 samples in the batch. It reveals a smooth fracture surface without any sign of the concentric crack pattern. This result indicates that temperature control in the oven environment once the reaction is underway and a constant delivery of nitric acid prevents sudden temperature variations in the mouldings and does not lead to defect initiation during the binder removal process.

3.3. Crack formation

The main mechanism leading to cracking is differential thermal expansion. The thermal expansion coefficients of the ceramic suspension and the ceramic powder assembly after binder removal were measured as 7.4×10^{-5} $°C^{-1}$ and 3.2×10^{-6} $°C^{-1}$, respectively. The value for the powder assembly is lower than the theoretical coefficient for alumina (5.5×10^{-6} K^{-1})[22] because of the scope for particle rearrangement under light push-rod loading.

A temperature rise in the sample, for example in the case of a nitric acid interruption according to Fig. 4, leads to a significant relative expansion of the unreacted core compared with the surrounding powder assembly. A temperature drop in the sample that is caused by an increasing acid concentration or by an arrest in the oven circulation in the chamber (Figs. 8 and 9) causes a relative contraction of the unreacted core with respect to the powder layer.

The relative displacement between the unreacted core and the powder shell is proportional to the temperature change and the length of the interface. This implies an influence of the moulding length as a critical factor. A 3°C temperature change during binder removal would cause a 2.1 μm relative shift at both ends of a 20 mm long binder interface corresponding to about 3 particle diameters. In a smaller moulding, for example with a 5 mm long binder interface, the maximum relative displacement between the core and the powder layer is only 0.53 μm or about 1 particle diameter. This explains the preferred appearance of this defect pattern in thicker

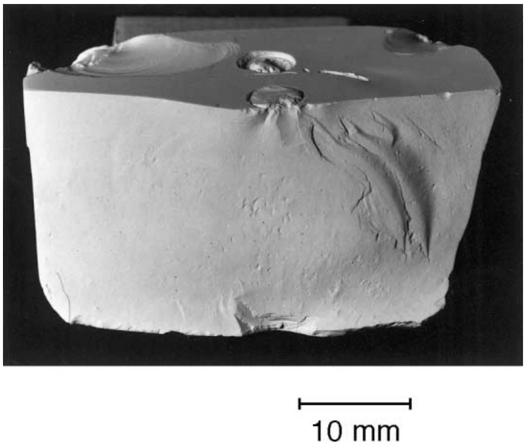

Fig. 11. Fracture surface of a 20-mm thick moulding broken after binder removal free of the concentric crack pattern.

mouldings. It also offers an explanation for the preferred appearance of the cracks at the curved edge (Fig. 5). This is because the displacement between core and shell along the binder interface increases proportionally from the middle towards the edges.

4. Conclusions

The concentric defects which appear in mouldings after binder removal are attributed to discontinuities during the binder removal process. These might include: (a) changes or interruptions in the nitric acid supply rate; (b) interruptions to the furnace gas circulation; or (c) temperature changes in the furnace environment.

In each case, these disruptions lead to temperature variations in the mouldings. The different thermal expansion of the solid polymer-ceramic core and the surrounding powder layer led to a relative movement and hence to disorganisation of the assembly of particles at the binder interface. This causes a concentric defect pattern in the mouldings at or adjacent to the moving boundary that can be distinguished clearly from the pattern of defects resulting from the injection moulding stage.

In binder removal carried out within a close temperature control band and with a steady nitric acid supply rate this type of defect does not appear. The binder could be removed from 25 mm thick mouldings without the creation of the characteristic defect pattern.

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