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Solidification of large section ceramic injection mouldings under low hold pressures

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Many of the problems of making large ceramic injection mouldings have been identified with solidification in the cavity, particularly with the level of hold pressure applied during cooling. In this work, a wide range of hold pressures (0.1–120 MPa) was used to compensate for thermal contraction of large mouldings. A new pneumatic technique for applying pressure was designed. An insulated sprue was used to prolong solidification of the gate. These techniques provide a combination of high injection pressure during mould filling (95 MPa) with hold pressure control in a range from 0.1–1 MPa during solidification. Large (25 × 45 × 60 mm) mouldings made at these low hold pressures did not have shrinkage-related cracking and the organic vehicle could be safely removed.

1. Introduction

Ceramic injection moulding is widely used for complicated shaped ceramic components [1, 2] but is restricted to thin sections because a range of defects frequently appears in thicker mouldings. Often, defects which occur after injection moulding or during the subsequent binder removal and sintering stages can be attributed to the solidification stage of the ceramic-polymer suspension in the mould cavity [3, 4].

Shrinkage voids tend to appear in thick ceramic mouldings [3, 5, 6] and can often be extinguished by the use of higher hold pressures. Unfortunately the use of higher pressures during solidification tends to generate a stress distribution which creates cracks. The hold pressure is applied to compensate for shrinkage of the solidifying moulding but when the gate solidifies, the pressure in the isolated liquid core decays with time. Mills [7] has stated that "The level of residual stresses can be reduced by any method that minimises the variation in the cavity pressure during solidification".

Various injection moulding techniques namely; modulated pressure moulding [8], heated sprue [9] and insulated sprue moulding [3], have been applied to prolong the gate solidification and hence successfully prevent void formation during packing and solidification at lower hold pressures.

The use of a polypropylene-based binder in earlier related work identified [10] and modelled [11] the problem of void formation but the resulting mouldings were not suitable for binder removal and so inspection of the moulding after the binder removal stage was not possible.

The emergence of a polyacetal-based binder system for powder injection moulding [12–14] has made it possible to remove the polymer binder from sections up to 35 mm thick [3]. It has therefore become possible to investigate the influence of various solidification conditions on the integrity of such large mouldings at the binder removal and sintering stages.

Residual stresses developed during solidification are believed to be one of the main causes of the cracking that presents itself during binder removal [15]. The stress distribution is influenced by the hold pressure. In conventional mouldings in which the pressure decayed before the moulding centre solidified, the stress distribution was centre-tensile and surface-compressive. In contrast, it was found that high and constant hold pressures applied during insulated sprue moulding led to tensile stresses at the moulding surface balanced by compression in the centre of 25 mm thick mouldings. The use of low and constant applied hold pressures reduced residual stresses in thick section mouldings made by the insulated sprue method yet did not result in voids [15]. Thus the implication of prior work was that prolonged low hold pressure should be applied for thick section mouldings.

It is important to distinguish the use of low hold pressures in this work from so-called "low pressure ceramic injection moulding" [16–19]. In low pressure ceramic injection moulding, a low solids volume fraction, low viscosity, wax based suspension is transferred from a molten reservior to a mould cavity by pneumatic pressure (typically <0.6 MPa). The high pressures (∼140 MPa) available for the complete mould

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TABLE I Injection moulding conditions

Parameter	Settings
Barrel temperature profile	175-175-176-178°C (measured at nozzle 178 ± 3°C)
Mould temperature	135°C
Injection speed	$8 \times 10^{-5}\ \mathrm{m^3\,s^{-1}}$
Max. injection pressure	95 MPa
Holding time	Up to 400 s
Hold pressure	12–120 MPa (conventional injection moulder) 5–12 MPa (pressure reducing valve) 0.1–1 MPa (gas injection unit)

filling of complex cavities in modern injection moulding machines are not generated in pneumatic moulders.

In this work, a new technique of controlling hold pressures below the conventional pressure range for ceramic injection moulding is introduced in order that high injection pressures can be combined with very low hold pressures. Further, the influence of the hold pressure on the development of cracks during binder removal is illustrated and the effect of moulding thickness is discussed.

2. Experimental details

The injection moulding material was a polyoxymethylene-alumina suspension which is commercially available under the designation Catamold AO-F (BASF, Ludwigshafen, Ger.). The alumina powder was grade CT3000SG (Alcoa Chemie GmbH, Ludwigshafen, Ger.). 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 using the processing conditions shown in Table I into a 45 × 60 mm mould tool which could be adjusted in thickness (15 mm, 20 mm and 25 mm) by the addition of matching face plates (Fig. 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 from 26 s using a conventional steel sprue up to 300 s [20, 21].

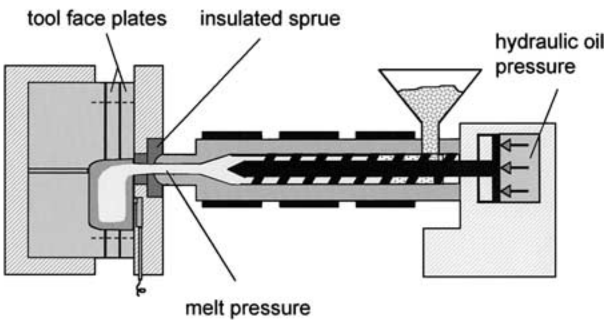

Figure 1 Schematic drawing of the injection moulding machine, showing the mould tool with the tool face plates, the insulated sprue insert and the positions at which melt pressure and hydraulic oil pressure are controlled.

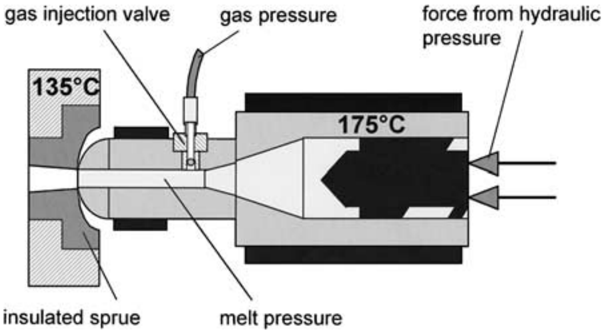

Figure 2 Schematic drawing of the gas injection valve in the nozzle.

The hold pressure range of the injection moulder (12–120 MPa) was reduced by using either a pressure reducing valve or a gas injection unit. In the former case a variable pressure reducing valve was placed before the injection cylinder. After mould filling at a maximum injection pressure of 95 MPa, the hydraulic oil flow was by-passed through a pressure reducing valve. The hydraulic oil pressure (Fig. 1) could then be controlled down to a pressure of 0.4 MPa. The hold pressure calculated from the screw diameter was therefore reduced to 5 MPa. Alternatively, the hold pressure was controlled by compressed gas injected into the melt channel (Fig. 2). After the high injection pressure of 95 MPa during mould filling, compressed nitrogen was injected into the melt channel to control hold pressure. The applied gas pressure was taken from a nitrogen bottle and was controlled by a pressure reduction gauge. A "one way" non-return ball valve prevented the high injection pressure pushing melt into the gas channel. This simple prototype mechanism required the replacing of the ball after each cycle. The resulting hold pressure window was 0.1–1 MPa. In this pressure regime, cavity pressure transducers embedded in the mould that record the pressure transmitted through the solidified wall do not adequately represent the pressure in the melt. Cavity pressure traces are not therefore reported.

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, Ger.) 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, Leics., UK) at 30 ml/h from a metered pump (Telab Dosiertechnik GmbH, Duisburg, Germany, Model BF 408 CAT/250). Samples up to 25 mm in thickness were catalytically degraded for 550 ks. All samples were sintered at 1600°C for 2 hours. The temperature ramp was 2°C/min to 1600°C with a hold for 1 h at 270°C, a 2 h hold. Cooling was at 2°C/min to 400°C. Two mouldings were heated stepwise at 1°C/min to 600°C, after that at 2°C/min in 100°C steps up to 1200°C, and after each step cooled for visual inspection.

3. Results and discussion

3.1. Low hold pressure injection moulding

The hold pressure used in previous work [3, 4] on large ceramic injection mouldings (12–120 MPa) was limited by the pressure range of the injection moulder. In order to achieve lower hold pressures, the injection unit was equipped with a variable pressure reducing valve [4, 15, 21] and a switched by-pass circuit. In this way high injection pressure could be maintained to fill complex cavities but during the holding pressure stage, pressure could be reduced to about 5 MPa.

During the experimental application of low hydraulic hold pressures, a slip-stick effect appeared between barrel and screw (Fig. 1). This was sensitive to the barrel temperature which of course influenced the melt viscosity and hence the overall friction between barrel and screw. The slip-stick behaviour is encountered when the static friction coefficient is higher than the dynamic. This impedes screw movement and pressure transmission so that the pressure applied to the melt during the packing stage was irregular.

However previous work [15] in which this pressure-reducing unit was used indicated a possible window for large section ceramic moulding in the low hold pressure regime. Thus a new technique for achieving fine control of low hold pressures was designed (Fig. 2). This method had several advantages. It allows a simple change-over in an experimental rig that involves minimum machine changes and direct pressure control of the melt in the nozzle without the slip-stick effect produced by the hydraulic control of screw travel. The close location to the moulding reduced the pressure loss in the melt and the sprue. Thus low pressures in a range from 0.1–1 MPa could be controlled. The high pressure end (1 MPa) was limited by the pressure range of the gauge and by safety aspects.

3.2. Moulding defects

Insulated sprue mouldings 15 mm, 20 mm and 25 mm thick were produced over a wide hold pressure range from 100 MPa down to 0.1 MPa. In the pressure range from 100 MPa to 12 MPa the conventional valve arrangement on the injection moulding machine was used. From 12 MPa to about 5 MPa the electrically switched by-pass pressure reducing valve was used and from 1 MPa to 0.1 MPa the gas injection method (Fig. 2) was used.

It is remarkable that all these large, low hold pressure mouldings solidified without the creation of voids and without pronounced sinking marks or deformation. Such defects are commonly found in conventional mouldings which experience early pressure decay during solidification [5, 21].

Observation of these mouldings after binder removal revealed a potential process parameter window at low hold pressures. Insulated sprue mouldings 15 mm, 20 mm and 25 mm thick that were subjected to a constant applied hold pressure in the range from 0.1 MPa to 1 MPa developed no externally visible cracks during binder removal. In contrast, mouldings of the same sizes, produced at higher hold pressures and subjected to the same binder removal run, did develop cracks during binder removal and they became visible at the moulding surface. All these mouldings were produced at the same injection moulding settings (Table I) with the exception of the applied hold pressure.

The sectioning of some mouldings from each hold pressure setting in the as-moulded stage as well as fractography of surfaces from mouldings broken after binder removal or sintering revealed no macroscopic voids even if a hold pressure as low as 0.1 MPa (gauge) was used. Mouldings 20 mm and 25 mm in thickness made with zero hold pressure (gauge) did, however, show such defects. Only three out of 26 mouldings produced by the pneumatic hold pressure method in the 0.1–1 MPa window developed externally visible cracks during binder removal while none of the mouldings made by using a higher hold pressure (5–100 MPa) survived binder removal without defects.

In earlier work [4, 15] some 25 mm thickness insulated sprue mouldings made at 5 MPa also did not develop cracks visible on the moulding surface during binder removal. However they were subjected to uncertain pressure in the melt caused by the slip-stick effect described above. It may well be that friction between barrel and screw caused a reduction of the applied pressure for these mouldings. Thus the effective melt pressure was reduced to a value close to the pressure window of the pneumatic hold pressure mouldings. Since these results show the importance of fine control in the low hold pressure regime, this uncertainty emphasises the limited value of indirect hydraulic pressure control (Fig. 1) below 12 MPa.

3.3. Overall shrinkage and moulding stresses

For the practical application of powder injection moulding, these results offer some guidance for the preparation of large section mouldings. However powder injection moulding is already widely used for thinner moulding sections [1, 2] where higher hold pressures are used successfully. The relationships between applied hold pressure, moulding size and crack formation during binder removal need to be established. Analytical models for the development of stress in mouldings need to consider (a) thermally induced stress (b) the contribution to stress from pressure changes during solidification and (c) the effect of restrictions on shrinkage caused by the pressure in the molten core and by mould geometry.

The effective hold pressure and hence the melt pressure in mouldings during packing and solidification has a significant influence on moulding dimensions. Fig. 3 shows the room temperature (20°C) dimensions of nominally 25 × 45 × 60 mm thick mouldings in two perpendicular directions as a function of the applied hold pressure. In the hold pressure range from about 12–100 MPa the moulding dimensions showed only a slight dependence on pressure and had much less shrinkage than conventional mouldings. In the lower pressure range between 5–8 MPa, achieved by using a pressure reducing valve, contraction of the mouldings is seen and this appears at almost constant moulding density [21]. At even lower hold pressures, controlled by the gas injection method (0.1–1 MPa) further shrinkage of the mouldings is evident.

During low pressure solidification, there is insufficient pressure in the molten core to oppose the thermal contraction of the solid shell. The solid layer grows and the projected area of the molten core decreases until the

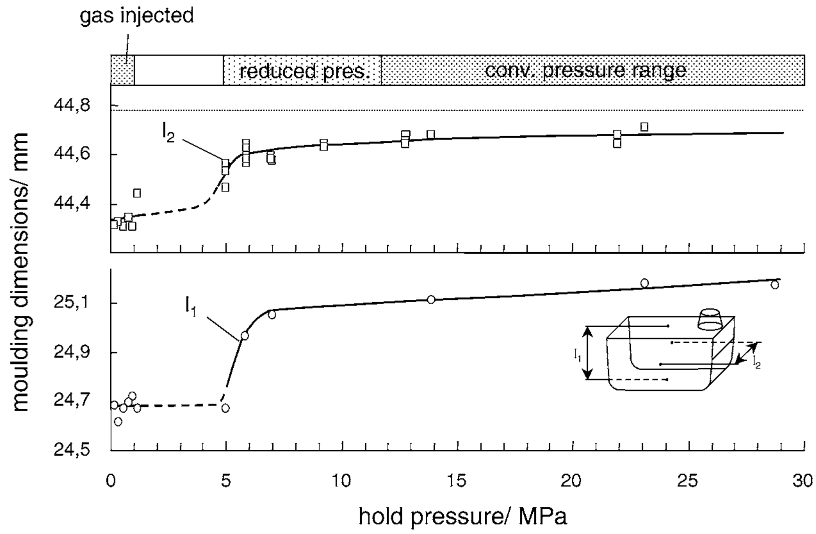

Figure 3 Moulding dimensions for 25 mm thick mouldings as a function of the applied hold pressure. (The reference line indicates the moulding dimension at 20°C).

imbalance of forces allows the moulding to shrink and to separate from the die wall. The final moulding dimensions are related to this restricted shrinkage [15]. In larger moulded sections the projected area of the molten core is greater and separation from the moulding wall appears either at a lower hold pressure or at a later stage during solidification.

The reference value of cavity dimension L2 at 20°C was 44.79 mm (Fig. 3) and at a mould temperature of 135°C this becomes 44.85 mm. The coefficient of thermal expansion of the solid polymer-ceramic suspension was measured as $7.43 \times 10^{-5}\,\mathrm{K}^{-1}$ (the value deduced from the PVT diagram at normal pressure was $7.48 \times 10^{-5}\,\mathrm{K}^{-1}$). Assuming unrestrained thermal contraction from the mould cavity dimension at 135°C, the value of L2 at 20°C would be 44.46 mm. At very low hold pressures (<2 MPa), where the solidifying material is unrestrained, the final moulding dimensions are close to this value. In fact they are slightly lower because they are measured near the centre where some sinking deformation occurs. The corresponding measurements for L1 are made slightly less reliable by the variability in clamp position but present the same trend.

In the case of higher hold pressures, the pressure in the melt acts on the projected areas of the surrounding solid layer causing it to stay in contact with the mould wall. The overall shrinkage is restricted and the final moulding dimension L2 is close to that of the mould tool namely 44.8 mm which is represented by the reference line in Fig. 3.

Cooling-related stresses in quenched [22–24] or injection moulded plastics [7, 25–27, 28–35] are widely reported but the effect of moulding size on residual stresses is not. Investigations [24] on thin (3–7 mm) quenched polymer sheets report compressive stresses at the surface and tension in the moulding centre. The sheet thickness is reported to influence the tensile stresses in the centre region and leads to an increase of the compressive stresses with increasing thickness. The melt and mould temperatures also influence the stress distribution in mouldings but these parameters were held constant in this study.

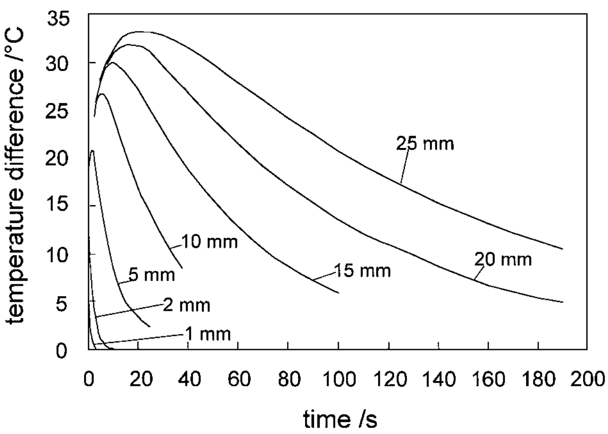

Figure 4 Temperature differences in a 45 mm thick infinitely long bar calculated for moulding thickness from 1–25 mm as a function of time (tool temperature 135°C, melt temperature 180°C).

It was shown in previous work [15] that restricted shrinkage in thick mouldings influences the development of residual stresses. Bending of samples that were cut from the surface of 25 mm thick mouldings and subjected to layer removal clearly indicated tensile stresses at the surface of insulated sprue mouldings. With decreasing hold pressures, the stress distribution changed and at about 8 MPa the samples showed no bending, indicating that low residual stresses prevailed in the mouldings. At 5 MPa the bending was reversed indicating compressive stresses in the surface layers. These results are in good agreement with theoretical work of Jansen and Titomanlio [25–27]. It could further be shown that the sudden appearance of moulding shrinkage at low hold pressures corresponds with the reversal of the sign of surface stresses. At low holding pressure (<8 MPa), the surrounding solid layer is able to contract during cooling and low tensile stresses are created. At higher holding pressures, the shrinkage of the surface layers is restricted and tensile stresses develop.

It is not always appreciated how large and also how persistent are the temperature differences within large mouldings even when, as in this case, the moulding temperature has been set as close to the solidification

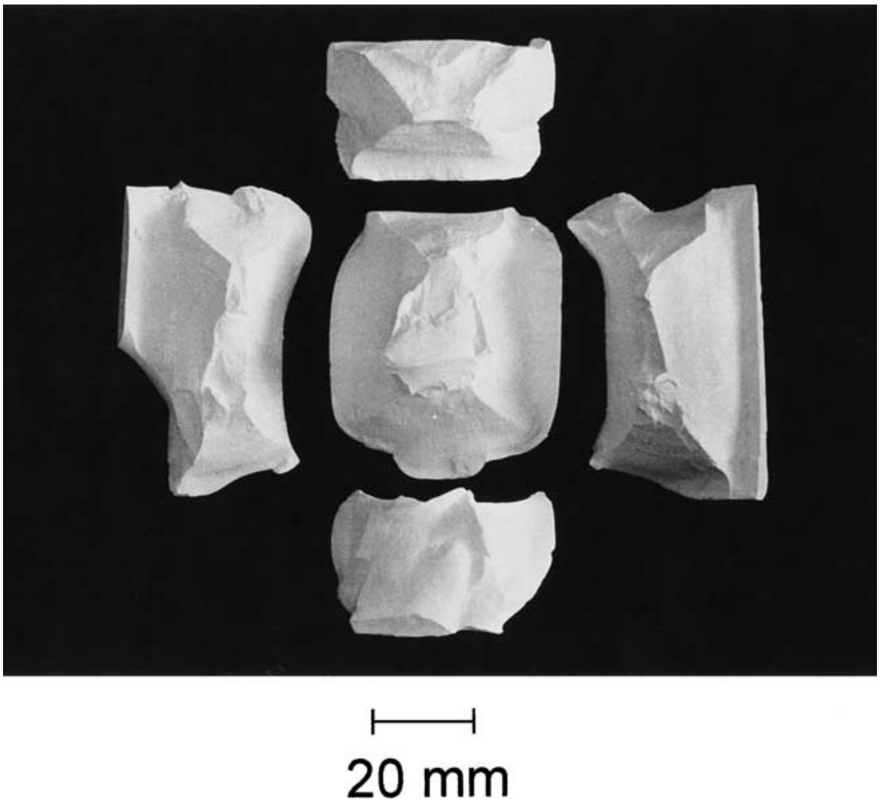

Figure 5 The 45° crack pattern in a 25 mm thick insulated sprue moulding after binder removal (100 MPa).

temperature as is practically possible. Fig. 4 plots the temperature difference between the surface and centre of mouldings as a function of time for different thicknesses. The graphs are calculated by using a finite difference method [36] for a 45 mm wide, infinitely long moulded bar with thicknesses from 1 to 25 mm. The injection temperature was 180°C and the mould tool temperature was 135°C (as used in this work). In these calculations, contact of the moulding to the die wall is assumed and so a constant surface heat transfer coefficient of 1000 $\mathrm{Wm}^{-2}\,\mathrm{K}^{-1}$ was used. For high pressure insulated sprue mouldings, this assumption is safe since the mouldings stay in contact with the die wall during solidification [3]. At lower holding pressures however, the moulding surface separates from the die wall leading to pronounced reduction of the heat transfer coefficient. During such separation the surface temperature of the moulding has been found experimentally to increase [27]. Firstly, this may lead to stress relaxation in layers close to the surface. Furthermore, a lower temperature difference during solidification is expected and this may reduce stress development.

Each of these effects; the reduction of restricted shrinkage, the narrower temperature distribution and the raised surface temperature may influence the stress distribution. Further experiments applying controlled cooling rates in the mould cavity need to be done to distinguish the magnitude of these effects and to clarify the influence of the moulding thickness.

During binder removal, catalytic decomposition of the polyacetal starts at the moulding surface and gradually moves into the moulding. Since this is a gas-solid reaction, it occurs exclusively at the inward moving reaction interface until the remaining core disappears.

In prior work [3] the binder was removed from 35 mm and 25 mm thick insulated sprue mouldings produced at hold pressures from 40–120 MPa. A distinctive defect pattern appeared (Fig. 5) in which cracks started from the moulding corners and entered the moulding at 45° to the walls. Interrupting the binder removal process showed that these cracks appeared at an early stage. This crack pattern, which is clearly distinguished from defects which appear in conventional mouldings [3, 4] during binder removal, indicated the presence of tensile stresses at the surface and this has been confirmed [15].

Some mouldings were fractured after binder removal but before sintering and they revealed a sound and smooth fracture surface. The example shown in Fig. 6 was subjected to a hold pressure of 0.5 MPa. From extensive industrial experience discussed in previous work [3, 4, 15, 20, 37, 38] the authors expect defects which will lead to the initiation of cracks during sintering to present a similar pattern of defects on this fracture surface. Indeed this assessment by fractography can sometimes be more reliable than contact radiography because of the resolution and orientation problems of the latter.

To investigate the effects of the early stage of sintering, two sound 20 mm thick mouldings made at 0.5 MPa were subjected to a stepwise heating during sintering. One of these mouldings was broken in half before sintering. During the sintering schedule the mouldings were slowly heated ($1^{\circ}\mathrm{C\,min}^{-1}$) to 600°C. At this stage additives (3 wt%) which are not removed by the binder removal process are pyrolysed from the mouldings. The inspection of the moulding after this stage did not reveal signs of cracking.

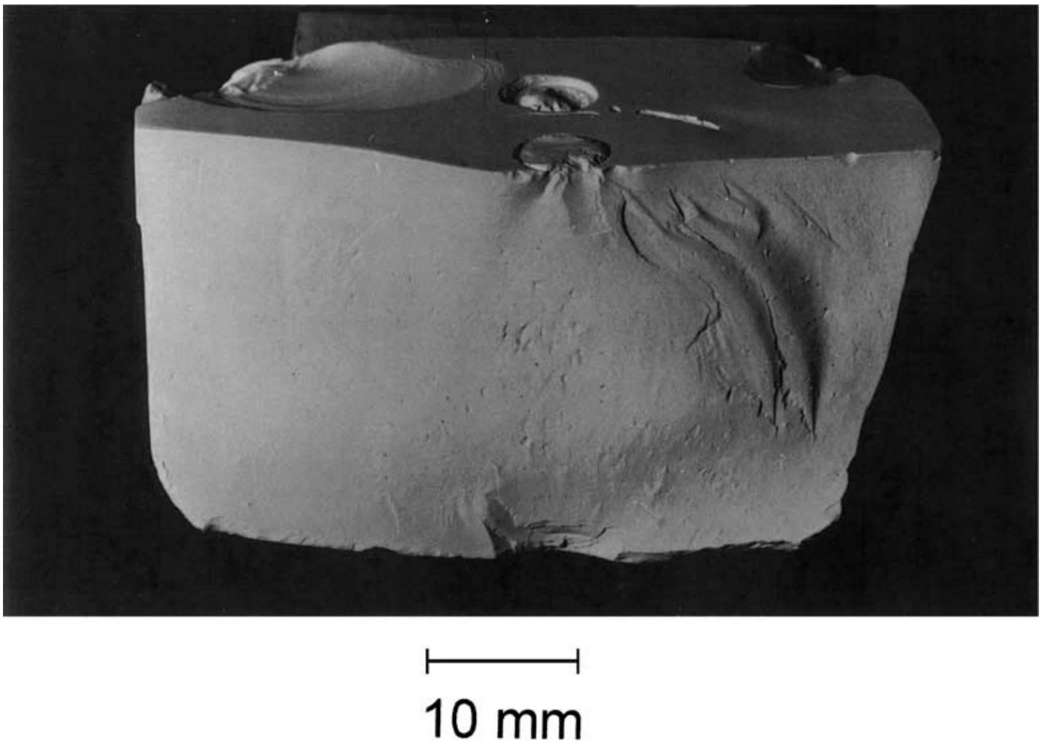

Figure 6 Fracture surface of a sound 20 mm thick moulding (0.5 MPa) broken after binder removal.

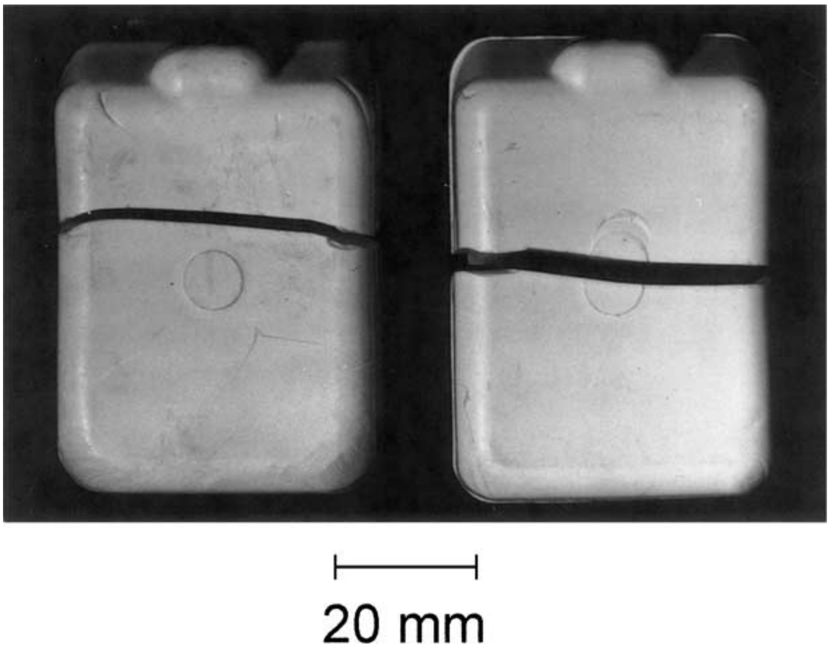

Figure 7 Cracks developed in 20 mm thick mouldings during sintering.

The subsequent stepwise heating into the sintering region followed by visual inspection did reveal the appearance of cracks in these mouldings. In the sectioned moulding, a crack appeared in the moulding centre at 1100°C. At 1250°C a crack became visible on the surface of the complete moulding (Fig. 7). At 1100°C, densification of the alumina powder had just begun and the mouldings had shrunk by about 4.5% from their moulded size by 1250°C.

All those mouldings that did not show any signs of defects after binder removal developed cracks during sintering. In related work on alumina injection mouldings having thick sections, a pronounced effect of differential sintering associated with the orientation of the alumina powder became evident [38]. Linear shrinkage during sintering varied from about 15% to 20% attributed to flow-induced alignment of non-uniform shaped particles. Such differential sintering was shown to cause loss of moulding shape [38] and is held to be responsible for the crack growth during sintering observed in the present study.

4. Conclusions

The use of constant applied hold pressure in a range 0.1–120 MPa in conjunction with an insulated sprue allowed the production of 15 mm, 20 mm and 25 mm thick mouldings without the creation of voids or pronounced sinking deformation. Mouldings made at a hold pressure below 10 MPa displayed significant overall shrinkage whereas at higher pressures (10–25 MPa) the temperature-corrected dimensions were close to those of the cavity. It is suggested that this difference is because at low hold pressures, shrinkage of surface layers cannot be opposed by the pressure in the liquid core acting on the projected areas of the solidified wall of the moulding.

During binder removal, mouldings made with the pneumatic injection method at a hold pressure of 0.1–1 MPa did not develop cracks. This is related to the reduction of residual stresses in large section mouldings made at low hold pressures. Mouldings made at higher hold pressure revealed a distinct crack pattern that appeared during binder removal.

Fracture faces of sound, binder-free mouldings were observed at various stages during sintering and they developed cracks which initiated at 1100°C. These can be attributed to differential shrinkage caused by the alignment of anisotropically shaped alumina particles.

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References

1. J. R. G. EVANS, in "Materials Science and Technology Series," edited by R. J. Brook (VCH Weinheim, Germany, 1996) p. 268.
2. J. S. REED, "Principles of Ceramic Processing" (John Wiley, New York, 1995) p. 477.
3. S. KRUG, J. R. G. EVANS and J. H. H. TER MAAT, *J. Amer. Ceram. Soc.* **82** (1999) 2094.
4. *Idem.*, in Proc. PIM98, Powder Injection Moulding Technologies (1998) p. 407.
5. T. ZHANG and J. R. G. EVANS, *J. Mater. Res.* **8** (1993) 187.
6. M. S. THOMAS and J. R. G. EVANS, *Br. Ceram. Trans. J.* **87** (1988) 22.
7. N. J. MILLS, *Plast. Rubb. Proc. & Appln.* **3** (1983) 181.
8. T. ZHANG and J. R. G. EVANS, *J. Mater. Res.* **8** (1993) 345.
9. K. N. HUNT and J. R. G. EVANS, *J. Mater. Sci. Lett.* **10** (1991) 730.
10. J. WOODTHORPE, M. J. EDIRISINGHE and J. R. G. EVANS, *J. Mater. Sci.* **24** (1989) 1038.
11. J. K. WRIGHT and J. R. G. EVANS, *ibid.* **26** (1991) 4897.
12. J. EBENHOCH, J. H. H. TER MAAT and H. J. STERZEL, in "Adv. Powder Met," Vol. 2, Powder Injection Moulding, edited by L. F. Pease and R. J. Sancoury (Metal Powder Industries Fedn., Princeton, N. J., 1991) p. 159.
13. J. H. H. TER MAAT, J. EBENHOCH and H. J. STERZEL, in Proc. 4th Int. Symp. Ceramics Materials and Componemts for Engines, edited by G. R. Carlsson and T. Johansson (Elsevier, London, 1991) p. 544.
14. J. H. H. TER MAAT and J. EBENHOCH, in Proc. 3rd Congr. Euro. Ceram. Soc., Madrid, edited by P. Duran and J. F. Fernandez (Faenza Iberica, Castellon, Spain, 1993) p. 437.
15. S. KRUG, J. R. G. EVANS and J. H. H. TER MAAT, *J. Euro. Ceram. Soc.* **20** (2000) 2535.
16. I. PELTSMAN and M. PELTSMAN, *Ceram. Eng. and Sci. Proc.* **3** (1982) 865.
17. T. KOSMAC and R. JANSSEN, *J. Mater. Sci.* **32** (1997) 469.
18. I. KOTSIS, T. KORIM and M. ENISZ, *Hungarian J. of Ind. Chem.* **24** (1996) 61.
19. S. J. KWAK, E. KRUG and S. C. DANFORTH, *J. Mater. Sci.* **26** (1991) 3809.
20. S. KRUG and J. R. G. EVANS, *Ceram. Int.* **25** (1999) 661.
21. S. KRUG, J. R. G. EVANS and J. H. H. TER MAAT, *J.Mater. Res.* in press.
22. G. MENGES, A. DIERKES, L. SCHMIDT and E. WINKEL, *SPE Tech. Pap.* **26** (1980) 300.
23. N. J. MILLS, *J. Mater. Sci.* **17** (1982) 558.
24. L. C. E. STRUIK, *Polym. Eng. Sci.* **18** (1978) 799.
25. G. TITOMANLIO, V. DRUCATO and M. R. KAMAL, *Int. Polym. Proc.* **1** (1987) 55.
26. K. M. B. JANSEN and G. TITOMANLIO, *Polym. Eng. Sci.* **36** (1996) 2029.
27. G. TITOMANLIO and K. M. B. JANSEN, *ibid.* **36** (1996) 2041.
28. A.I. ISAYEV and D. L. CROUTHAMEL, *Polym. Plast. Technol. Eng.* **22** (1984) 177.
29. M. RIGDAHL, *Int. J. Polym. Mater.* **5** (1976) 43.
30. L. F. A. DOUVEN, F. P. T. BAAIJENS and H. E. H. MEIJER, *Prog. Polym. Sci.* **20** (1995) 403.
31. A. I. ISAYEV and D. L. CROUTHAMEL, *Polym. Plast. Technol.* **22** (1984) 177.
32. G. J. SANDILANDS and J. R. WHITE, *Polymer* **21** (1980) 338.
33. L. D. COXON and J. R. WHITE, *Polym. Eng. Sci.* **20** (1980) 230.
34. A. SIEGMANN, A. BUCHMAN and S. KEMIG, *ibid.* **22** (1982) 560.
35. B. KOSTIC, T. ZHANG and J. R. G. EVANS, *J. Amer. Ceram. Soc.* **75** (1992) 2773.
36. T. ZHANG and J. R. G. EVANS, *ibid.* **75** (1992) 2260.
37. S. KRUG, J. R. G. EVANS and J. H. H. TER MAAT, *J. Euro. Ceram. Soc.* **21** (2001) 2275.
38. *Idem.*, *ibid.* **22** (2002) 173.

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