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Residual stresses and cracking in large ceramic injection mouldings subjected to different solidification schedules

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Abstract

In ceramic injection moulding, the moulding dimensions and the residual stresses are related to the hold pressure history during solidification in the cavity. In conventional moulding, the residual stresses are generally compressive at the surface. In this work, an insulated sprue device was made. It allows prolonged pressure transmission to the moulding and this can result in residual tensile stresses at the surface of thick section mouldings. At very low holding pressures (< 9 MPa) or under conditions of premature gate solidification, a reversal of the sign of surface stresses occurs with compressive stresses near the surface. The appearance of cracks during binder removal was related to these residual stresses. For 25 mm thick mouldings which were subjected to a low but persistent hold pressure of 5 MPa no defects developed during the binder removal stage.

Keywords: Al_2O_3; Failure analysis; Injection moulding; Residual stresses

1. Introduction

The successful manufacturing of ceramics by injection moulding is still limited to components of relatively small cross-section. Various defects occur with increasing frequency in thicker mouldings.[1] The appearance of voids and shrinkage deformation can be successfully prevented by the use of modulated pressure moulding,[2] heated sprue[3] and insulated sprue moulding.[1] Problems also attend the binder removal stage in thick sections. The invention of a polyacetal based binder for powder injection moulding[4–6] has enabled the gradual removal of the polymer vehicle from 35 mm thick moulded sections.[1] Unfortunately cracks developed in these mouldings during binder removal and sintering. The incidence and form of these cracks revealed a systematic relationship to the injection moulding conditions. Non-uniformity set up during solidification, in particular residual stresses, are thought to cause this cracking even though it appears at a later stage in the manufacturing route.[1]

Residual stresses have been widely investigated particularly in the case of unfilled polymer moulding. Earlier theoretical work accounted for cooling-related stresses, assuming free quenching and predicted compression at the moulding surface and tension in the moulding centre with a parabolic distribution.[7–9] The stresses are attributed to sequential cooling and modulus increase in successive layers. Later investigations[10–14] accounted for changes in the hydrostatic pressure of the molten core in the moulding and reported a pronounced influence on residual stresses and a possible reversal of the stress distribution at higher and longer holding pressures giving rise to tension on the moulding surface and compression in the moulding centre.[10] The effect of pressure history on residual stresses in injection moulding in the case of constrained shrinkage has also been considered.[15] A large enough pressure in the moulding centre, or a geometrical barrier is assumed to restrict cooling shrinkage of the solid layers. The model predicts a stress distribution consisting of a small tensile zone near the surface, a compressive minimum, and a second tensile zone in the moulding centre. Ejection of the moulding too soon or gate solidification before the molten core solidifies results in a reduction of the surface tensile stress.[16]

Experimental studies describe the influence of various moulding conditions on residual stresses in polymer mouldings.[17–22] Residual stresses are usually measured by the layer removal technique[23] and are in the region 2–20 MPa with compression at the moulding surface and tension in the moulding centre. The use of high holding pressure or long holding times can change this distribution. Close

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to the gate, the surface stresses changed from compression to tension at higher holding pressures.[20,21]

A study of residual stresses in particle-filled polypropylene revealed generally lower stresses in the filled polypropylene compounds. Storage and ageing led to a reduction of residual stresses. But unlike the unfilled polypropylene, a reversal of the stress distribution occurred in some of the filled mouldings during storage and annealing so that compression prevailed at the moulding centre and tension at the moulding surface.[24]

Fewer investigations on residual stresses have been carried out in powder injection moulding.[25,26] The theoretical and experimental reports correlate with the stress distributions reported in polymer mouldings. Surface stresses up to 4 MPa are reported in ceramic injection mouldings with compression at the moulding surface and tension at the moulding centre at a holding pressure of 108 MPa. At a lower holding pressure of 43 MPa the stress maxima were reduced to around 1.7 MPa and by using a heated sprue at a hold pressure of 43 MPa extremely narrow stress distributions not exceeding 0.5 MPa were measured.[25] However, these stresses were measured 600 ks after moulding when the stress state had stabilised and do not represent the maximum stress developed during or immediately after moulding.

Factors affecting residual stresses and the development of cracks in ceramic injection moulding have been investigated mainly in the moulded state before binder removal.[1,25–29] The present work investigates the relationship between holding pressure or time and residual stresses in thick ceramic injection mouldings and describes their relevance to the development of cracks which appear during binder removal. The moulding procedure used in this work allows low hold pressures to be applied and the insulated sprue enables them to be held for the duration of solidification.

2. Experimental details

2.1. Materials

The alumina powder was grade CT 3000 SG (Alcoa Chemie GmbH, Ludwigshafen, Germany) being a fine pure alumina with average particle size (d_{5o}) of 0.6–0.8 μm and BET specific area of 6–8 $m^2 g^{-1}$. The powder was provided in suspension in a powder injection moulding grade of polyoxymethylene at 56 vol.% ceramic which had been prepared by high shear mixing. It is available commercially under the designation Catamold AO-F (BASF, Ludwigshafen, Germany).

2.2. Processing conditions

The suspensions were injected into a 25×45×60 mm rectangular mould. The cavity was direct-gated from a 10 mm thick conventional sprue which served as the gate. Insulated sprue mouldings were made by replacing the sprue bush with a 12 mm diameter (10 mm long) polyetheretherketone sprue which reduced radial heat loss and allowed a significant contribution from axial heat flow. A Negri Bossi NB90 injection moulding machine was used, operating with the settings given in Table 1. An external pressure reducing valve was adapted to the injection unit to achieve holding pressures below 12 MPa.

The polyoxymethylene was removed by catalytic degradation in the solid state at 110°C in an oven (Model VT6060-MU-2 Heraeus Instruments, Hanau, Germany). The furnace was supplied with oxygen-free nitrogen at 500 l/h and liquid fuming nitric acid at a rate of 30 ml/h from a metered pump (Constrakron 3, Kron-lab Sinsheim, Germany). The 25 mm thick mouldings were catalytically degraded for 72 h, and afterwards sintered in air. The alumina 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.

2.3. Mechanical testing

Deformation at the surface of large ceramic mouldings resulting from residual stresses was observed by a modified layer removal technique.[23] Samples of 7×12×45 mm were cut from the surface region of 25×45×60 mm thick mouldings using the sectioning scheme shown in Fig. 1. The surface opposite the mould wall and originally inside the moulding was carefully ground to give a

Table 1
Injection moulding conditions

Parameter	Settings
Barrel temperature profile	170–170–170-175°C (nozzle)
Mould temperature	135°C
Injection speed	$8\times10^{-5} m^3 s^{-1}$
Maximum injection pressure	95 MPa
Hold pressure	5–120 MPa for 400 s

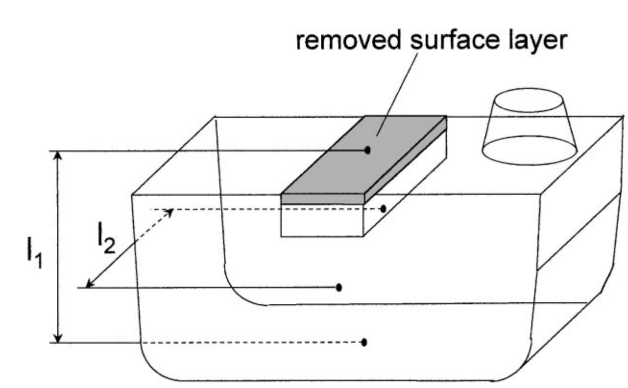

Fig. 1. Schematic diagram of a 25 mm thick moulding showing the section taken for layer removal and defining directions l_1 and l_2.

reference plane (designated the reference surface). The samples were then partially immersed in a silicone-oil bath with the reference surface downwards and the bath was placed in the binder removal oven. During binder removal, the polymer fraction near the exposed moulding surface was gradually removed to a depth of approximately 2 mm in the nitric acid containing atmosphere at 110°C. During this catalytic binder removal stage no external mechanical stresses were applied to the sample. In the next step, the residual ceramic powder layer left by polymer loss from the surface was removed with water. The resulting deformation of the sample was recorded by dial gauge at an accuracy of 0.01 mm and observed by illumination of the gap between a flat gauge plate and the reference surface.

Fracture stress was recorded for the injection moulding suspension and the sintered ceramic using test machines models, 4206 and 1195 (Instron, High Wycombe, Bucks, UK). The (4×13×100 mm) injection moulded bars were loaded in three point flexure with a span of 72.6 mm and a crosshead speed of 3.3×10^{-5} m s^{-1}. The sintered (3.3×10.8×85 mm) bars where tested at the same speed with a 40 mm span. The fracture stress of the ceramic powder assembly after binder removal was measured from the same (4×13×100 mm) bars in three point flexural loading with a span of 60 mm using a Rheometrics Solids Analyzer RSA II (Rheometrics, Inc., NJ, USA) having a maximun force of 9.8 N and a sensitivity of 9.8×10^{-3} N.

3. Results and Discussion

3.1. Mechanical properties

The ceramic injection moulding suspension passes through several stages during manufacturing. In order to understand and assess the development of cracks in this sequence it is helpful to know the mechanical properties and the stress at failure for the solidified material.

During cooling in the mould, the mechanical properties of the ceramic–polymer composite are strongly influenced by temperature. The maximum stresses at failure was 13 MPa at 30°C falling to 7 MPa at 110°C. During binder removal, the polymer fraction undergoes a catalytical degradation resulting in a dramatic loss of mechanical strength. It leaves a ceramic powder layer which also incorporates a proprietary processing aid, present at 3 wt.% which is not removed by the nitric acid containing atmosphere at 110°C. The flexural strength of this layer was 1.0±0.2 MPa at 110°C and 0.8±0.07 MPa at 30°C. During sintering, the ceramic undergoes a second progressive change in strength. The final sintered ceramic presents a fracture stress of 350 MPa. The results demonstrate the fragility of the ceramic powder layer and indicate why cracks preferentially develop during binder removal even if their antecedents were established in earlier stages.

3.2. Restricted shrinkage

The moulding dimensions were measured in the two perpendicular directions defined by Fig. 1. Fig. 2 shows the dimensional changes in conventional and insulated sprue mouldings as a function of the applied hold pressure. In order to interpret these it is helpful to consider the onset of pressure decay during solidification. In the case of insulated sprue mouldings, the hydrostatic pressure applied to the molten core by the holding pressure on the barrel was transmitted for about 240 s. Most of the insulated sprue moulding solidified at a constant applied pressure and only a small molten section in the moulding centre was sealed from the sprue.[30] In conventional moulding, the sprue solidified after approximately 26 s and this led to pronounced and rapid pressure decay in the remaining molten core.[31]

In insulated sprue mouldings, the moulding dimensions were almost constant in the hold pressure range from 120 down to 10 MPa. At pressures lower than 10 MPa the mouldings contracted during packing and solidification and this contraction appears at almost constant moulding density.[30] These mouldings shrink during solidification without the creation of voids, pronounced sinking marks or deformation. The reason for this contraction is that there is insufficient pressure in the molten core during low pressure solidification to oppose the contraction of the solid shell. Fig. 3 illustrates this schematically by showing the molten core surrounded by the solid layer of thickness, s, during solidification in the mould cavity. The constant applied hold pressure, p, in insulated sprue moulding acts on the projected area of the surrounding solid layer causing it to stay in contact with the moulding wall and thus overall shrinkage is restricted. During solidification, the solid layer grows and the projected

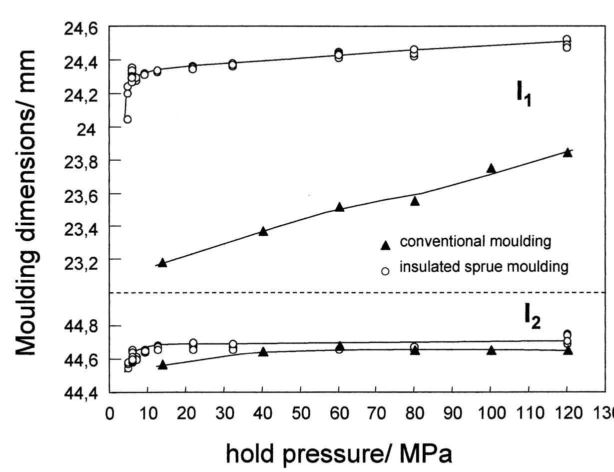

Fig. 2. Moulding dimensions as a function of hold pressure for insulated sprue and conventional mouldings.

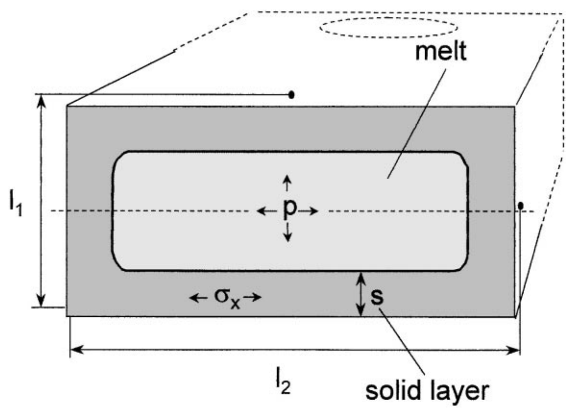

Fig. 3. Schematic diagram of the solidification stage in ceramic moulding.

area of the molten core decreases until the imbalance of forces allows the moulding to shrink and to separate from the die wall.

Fig. 2 shows that in conventional mouldings, a change in hold pressure causes dimensional changes in direction l_1. The moulding dimensions increase with increasing hold pressure monotonically over the whole pressure range. In direction l_2, the pressure influence is almost absent and only at very low pressures is some moulding shrinkage visible. The difference in dimensional changes in directions l_1 and l_2 is due to a larger area of the shrinking core acting in direction l_1 which leads to an amplified effect of pressure changes. The fact that the l_1 dimension does not change with increased pressure (upper curve in Fig. 2) indicates that clamp opening was not responsible for the changes seen in the case of conventional mouldings.

The insulated sprue mouldings are generally around 0.8 mm bigger than the conventional mouldings in direction l_1, a difference caused by the different pressure histories of the mouldings as expressed in Fig. 3. In direction l_2, which, as discussed above, shows less pressure sensitivity, the conventional mouldings are less than 0.1 mm smaller. Although these differences are small they are consistent with the practical observations made during moulding. In the pressure range from 120 MPa down to approximately 10 MPa the insulated sprue mouldings were still tight in the mould cavity at the ejection stage. In contrast, all conventional mouldings separated easily from the mould cavity during ejection and this was also true for the insulated sprue mouldings made at hold pressures lower 10 MPa.

3.3. Residual stresses

Fig. 4a and b shows photographs of the deformation of 7×12×45 mm bars cut from 25 mm thick insulated and conventional mouldings, respectively. They have been subjected to binder removal from one side only. The bending is made visible by the gap between reference surface of the sample (lower bar) and the gauge plate (upper bar) and is developed during gradual layer removal of polymer from the original surface of the moulding. The gaps visible on these photographs clearly distinguish concave and convex deformation of the samples. During binder removal, an unbalancing of the compressive and tensile stresses in the bars takes place; an effect which is comparable to layer removal. The bending, therefore, indicates the existence and sign of residual stresses in the mouldings. The deformation was recorded by dial gauge from various mouldings and is displayed in Fig. 5. The concave bending of the bars visible in conventional mouldings indicates compressive stresses on the moulding surface. The convex bending of some bars cut from insulated sprue mouldings made with a hold pressure greater than 9 MPa indicates tensile stresses in the moulding surfaces. All conventional mouldings revealed compressive

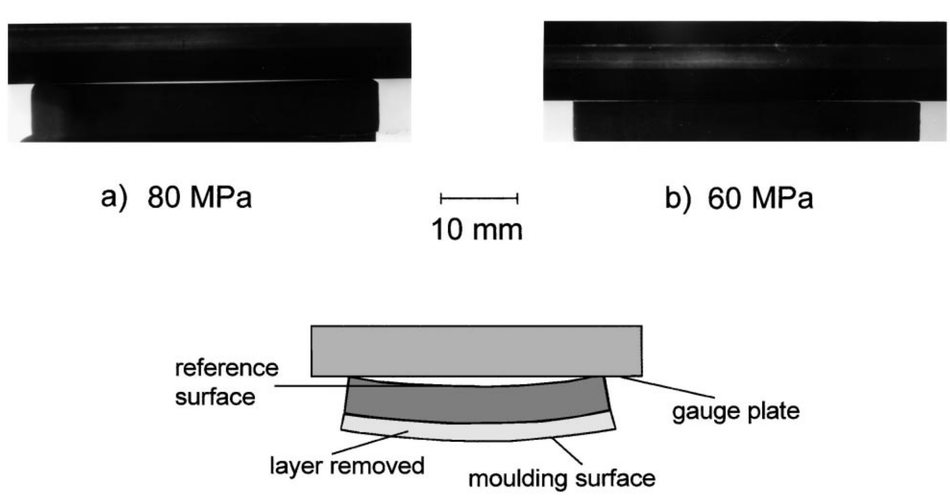

Fig. 4. Photographs of bars after layer removal; (a) conventional moulding and (b) insulated sprue moulding. Inset defines the surfaces.

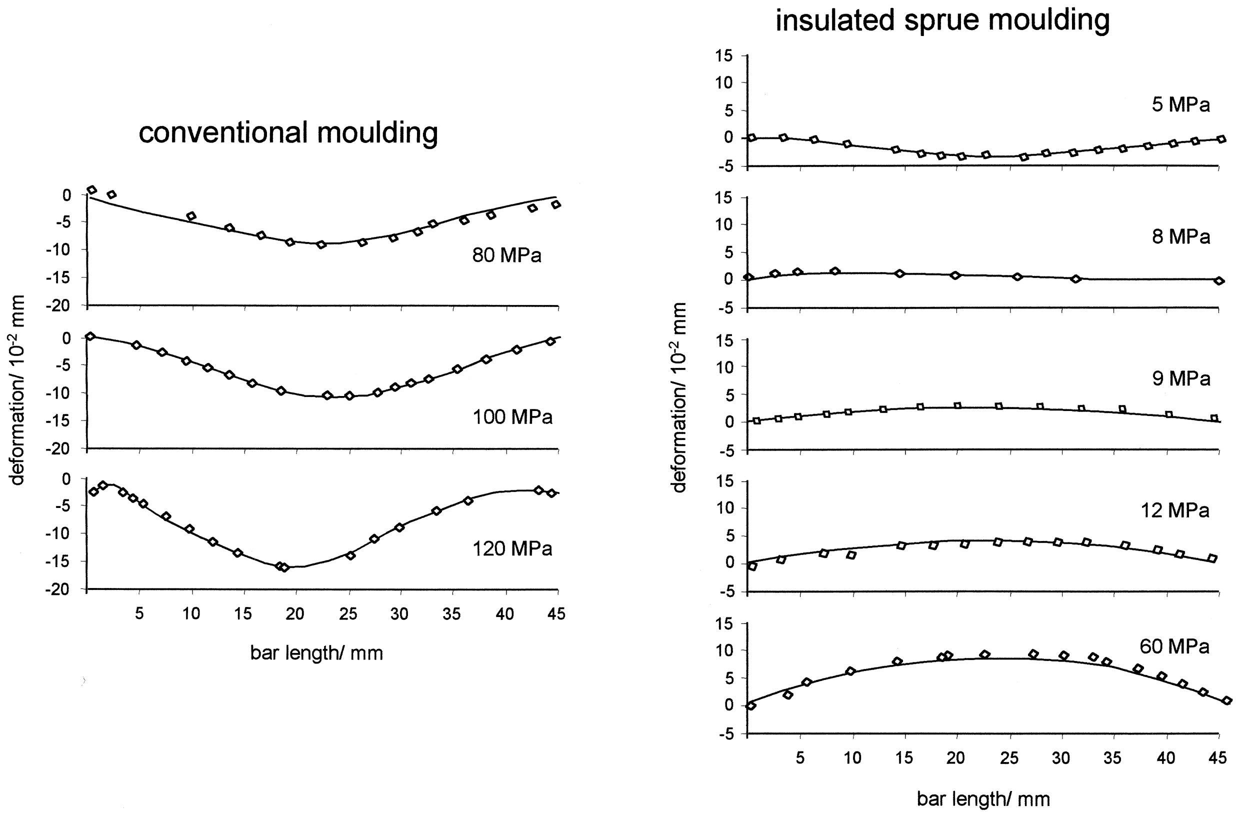

Fig. 5. Deformation of the bars after layer removal.

stresses at the moulding surface with a tendency to higher values at higher holding pressures which is consistent with both experimental[25] and theoretical work.[12,13]

In insulated sprue mouldings, an influence of pressure on reversal of residual stresses is clearly visible. At high pressures, the removal of the surface layer caused convex deformation of the reference surface, which indicates tensile stresses at the moulding surface. Below 9 MPa, the stress distribution changed and at 8 MPa the bar showed no bending. At 5 MPa the bending of the reference surface was concave indicating compressive stresses in the surface layers. These experimental observations are in good agreement with the theoretical work of Jansen and Titomanlio.[15,16] They described the stress distribution in injection mouldings caused by restricted shrinkage and revealed tension at the moulding surface and compression in the moulding centre.

The sudden appearance of moulding shrinkage at an applied hold pressure of about 10 MPa corresponds to reversal of the sign of the surface stress. Applying a high holding pressure during solidification inhibits shrinkage of the surface layers as shown in Fig. 2 and tensile residual stresses result. At a lower melt pressure which, in the present case was around 10 MPa, the surrounding solid layer is able to contract during cooling. In the same way, the surrounding solid layer of conventional mouldings is free to contract during cooling after 26 s when the internal pressure starts to decay. Further thermal contraction of the moulding centre in conventional moulding led to shrinkage deformation and compressive stresses appeared at the moulding surface balanced by tension in the moulding centre. This was accompanied by the appearance of shrinkage voids in mouldings made at $P < 80$ MPa.

3.4. Effect of residual stress on cracking

More evidence for the existence and sign of residual stresses is revealed in Fig. 6. These X-ray radiographs show a conventional moulding before (Fig. 6a) and after (Fig. 6b) an annealing treatment of 26 h at 145°C. In Fig. 6a, showing the as-moulded stage, the cracks are near the centre and do not intersect the surface of the moulding which is characteristic of a centre-tensile, surface-compressive stress distribution. The existing cracks grew in length and thickness and some new cracks became visible on the radiographs after the annealing treatment consistent with the observations of Thomas[27] on wax-based ceramic mouldings. The pattern and location of the crack development indicates that the polymer fraction underwent a relaxation of residual tensile stresses in the moulding centre. Similar cracks initiated in the interior during annealing treatment and were attributed to compressive stresses in quenched and

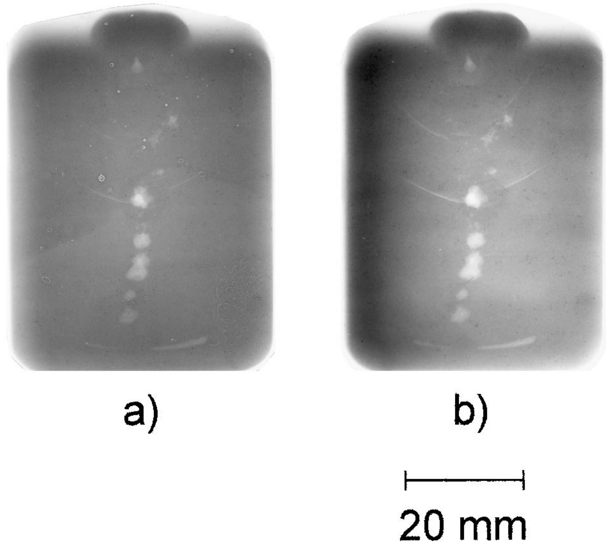

Fig. 6. X-ray radiographs of 25 mm thick conventional mouldings: (a) as moulded and (b) after heat treatment.

moulded bars.[32] The shrinkage voids associated with hydrostatic tension in the melt preceded the cracking.

Fig. 7 shows X-ray radiographs of 25 mm thick ceramic injection mouldings after binder removal. Fig. 7a shows a conventional moulding injected at a hold pressure of 100 MPa. The melt pressure decay associated with the premature gate solidification encouraged shrinkage voids to form in the melt. The incidence of cracks was dependent on the applied hold pressure and at high hold pressures they had already appeared after injection moulding.[1] During binder removal, the existing cracks grew and "new" cracks previously undetected by X-ray radiography developed in all conventional 25 mm mouldings, over the whole hold pressure range.

Fig. 7b shows a 25 mm thick insulated sprue moulding injected at a hold pressure of 100 MPa which reveals a crack pattern representative of insulated sprue mouldings injected at high holding pressures. The moulding revealed no cracks in the as-moulded state. The cracks appeared during binder removal and started from the moulding corners at 45°. Interrupting the binder removal process showed that these cracks started from the moulding surface at an early stage of binder removal. The compressive internal forces in the insulated sprue moulding cause a dilation of the unreacted core and induce cracks in the surrounding ceramic powder layer.

Fig. 7c shows an insulated sprue moulding injected at a constant hold pressure of approximately 5 MPa. A small crack in the moulding centre which is caused by a premature pressure decay in the moulding[30] is not visible on this print of the X-ray radiograph. The crack was detected in the as-moulded stage and in the sintered ceramic but no macroscopic defects developed during binder removal. The crack pattern in these mouldings shows a good correlation with the observed stress distribution in Fig. 5. In conventional mouldings cracks appeared in the moulding centre where tensile stresses prevail. In insulated sprue mouldings, the cracks started from the moulding surface during binder removal where tensile stresses were observed and in low pressure insulated sprue mouldings no crack development was detected during binder removal.

4. Conclusions

The pressure history during solidification of large ceramic injection mouldings has pronounced effects on the incidence of cracks which appear after binder

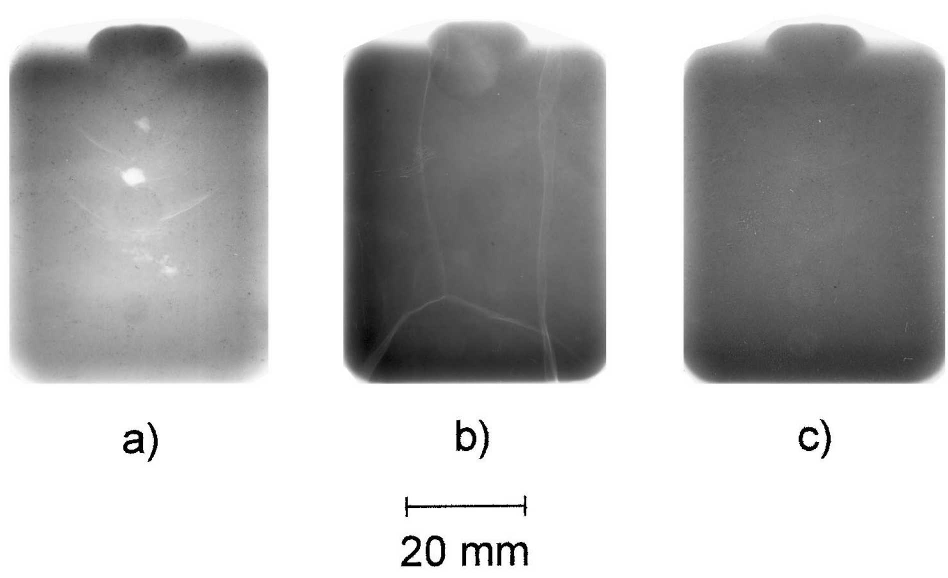

Fig. 7. X-ray radiographs of 25 mm thick mouldings: (a) conventional moulding as moulded, (b) insulated sprue moulding after binder removal, and (c) low pressure insulated sprue moulding after binder removal.

removal. Different solidification conditions can reverse the residual stress distribution and this in turn changes the incidence and pattern of defects. Compressive stresses were present in the surface of conventional mouldings which experienced a short hold time due to sprue solidification. A long applied holding time in insulated sprue mouldings gave rise to residual tension in the surface layers of 25 mm thick mouldings. At a low and constant applied hold pressure of around 8 MPa the residual stresses were considerably reduced. This residual stress behaviour correlated with overall moulding shrinkage data. Thus, in the insulated sprue mouldings made with pressures lower than 10 MPa, a pronounced moulding shrinkage appeared. From the insulated sprue mouldings subjected to a low and constant hold pressure of 5 MPa, the binder could be removed without the creation of cracks. Thus not only can the arrangement of defects be related to the solidification history but solidification conditions can be devised which do not subsequently induce defects.

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