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# Powder-binder separation in injection moulded green parts

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**Abstract**

For powder injection moulding (PIM) the ceramic powder is mixed with a thermoplastic binder system to achieve an injectable feedstock. In contrast to injection moulding of polymeric components, the binder must be removed after the shaping step before sintering the ceramic part to full density. During the mould filling process shear forces act on the blend that might cause separations of powder particles and binder. In this case polymer films form at the mould surface and at internal interfaces which induce microstructural defects in the debinded part. In particular for multi-component parts this effect is critical since binder films in the joining zone weaken the bonding strength between the two components that might even lead to delamination.

For detecting binder separations within the injection moulded bulk material and at joining zones of two-component parts the microstructure of green samples has been studied. Since conventional machining techniques like grinding and polishing modify the original structure, e.g. when particles are pulled out of the matrix and binder smears onto the surface, a special ceramographic method for the preparation of cross-sections was applied. This approach bases on broad ion beam techniques and enables the simultaneous polishing of hard ceramic particles and soft polymer molecules without destroying the structure or producing a relief at the surface. In the analysed samples binder accumulations were found along flow lines, at weld lines, at boundaries of so-called dead water regions and at the interface of two-component parts.


*Keywords:* Injection moulding; Defects; Electron microscopy; Non-destructive evaluation; Powder-binder separation

## 1. Introduction

For complex shaped ceramic components injection moulding (CIM) is the technology of choice since it is capable of producing near-net-shape parts in highly automated serial production. Four manufacturing steps have to be carried out: compounding of feedstock, injection moulding, debinding and sintering.

The feedstock composition is the basis of the whole manufacturing route and therefore the critical factor for defect-free components. In order to enable plastic forming the powder is mixed with a binder system which is usually composed of several constituents attributed to different tasks. The feedstock has to combine apparently opposite demands: Excellent flowability and high solids loadings. Therefore the binder system has to show low viscosity and good wettability of the powder. After shaping it has to be removed without destruction of the green body before sintering the component to fully dense ceramic parts.

The mouldability of a feedstock depends strongly on the powder content since viscosity of the mixture increases with solids loading and reaches infinity at the critical powder concentration.[1] Therefore successful feedstock formulations contain about 2–5 vol% more binder than needed for filling the interstices between the particles.[2] However, too low powder loadings can cause defects in debinding stage when insufficient mechanical strength leads to deformation or sagging.[3] Furthermore, defects can be created in the microscopic scale, too. During mould filling the feedstock is sheared and powder–binder separations may occur that produce inhomogeneities in the particle packing. Variations in the density distribution will lead to non-uniform sintering which results in anisotropic properties in the final product.[4,5] The probability for such separation effects in a specific part depends on the mould filling characteristics. Critical locations are the result of two feedstock streams meeting or moving relative to each other, e.g. forming weld lines. For multi-component parts this is of upmost importance since two feedstocks have to be joined at the interface. A close contact in green parts is essential for achieving a good compound strength.

In order to investigate the effect of the shaping process on the powder–binder mixture the microstructure of green samples has been studied. By the liquid immersion method not only pow-

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der agglomerates were found but also matrix particles oriented in flow direction.[6,7] The magnitude of texturisation depends on feedstock composition, injection moulding parameters and mould design which could be shown using polarized light optical texture analysis.[8] For both methods thin slices of sintered or pre-sintered specimens had to be cut out altering the original structure. For the investigation of density differences local binder concentrations in test geometries were analysed by X-ray radiography and DSC on small cut-outs.[9] Unfortunately, the resolution was too low for both experimental methods. Electron microscopy offers the possibility to resolve the microstructure in detail and fractured cross-sections are often used to study homogeneity or debinding progress. But the rough surface makes it difficult to gain reliable information.

In this study a special ceramographic technique allowing the preparation of micro-sections of injection moulded green samples has been developed. Broad ion beam technique was used to simultaneous polishing of soft binder matrix and hard ceramic particles without destroying the original conditions and without achieving a relief at the surface.

## 2. Experimental

### 2.1. Feedstock preparation

Three feedstock couples have been developed for two-component injection moulding. In each of these couples one component consisted of alumina (CT3000SG, Almatis, Germany) with $d_{50} = 0.8\ \mu m$ and a specific surface of $6.5\ m^2/g$. The partner material, zirconia toughened alumina (ZTA), was created by addition of 7 wt% nano-structured zirconia (Evonik-Degussa, Germany) which had a primary particle size of $0.02\ \mu m$ and a specific surface of $43.3\ m^2/g$ to the alumina matrix.

The commercially available binder system Licomont® EK 583 (Clariant, Germany), on basis of polyethylene wax and polyethylene glycole, was used for feedstock preparation.

To evaluate the influence of the binder content three feedstock couples (GW1–3) with differing solids loadings had been prepared. To verify the powder content the mass loss during thermal debinding was determined (Table 1).

Compounding was performed on a shear roll compactor (BSW135-1000, Bellaform, Germany) in three passes to assure good homogenisation.

### 2.2. Injection moulding

There are several critical sites in injection moulded parts at which binder separations can be expected. The two-component hollow gear wheel discussed in this study is an example part having weld lines and dead water regions which are sensitive to demixing. In comparison to one-component parts multi-component parts do not only demand defect-free bulk material but also flawless interfaces. Avoiding defects at the interface over all processing steps is the special challenge of multi-component injection moulding. The gear wheel (designed by Robert Bosch GmbH, Germany) consists of two concentric rings whereby the inner alumina ring holds the gears and the ZTA is the outer ring with a diameter of 27 mm.

Injection moulding had been conducted at a two-component injection moulding machine (320S, Arburg GmbH, Germany). The inner ring was injected first. After it had been transferred by rotation to the second cavity the outer ring was injected.

### 2.3. Debinding

Often defects introduced in the shaping process are not visible in the green state and they become obvious only after binder removal. To evaluate the consequences of binder separations on crack evolution the samples were debinded thermally in air up to a temperature of 500 °C.

### 2.4. X-ray computed tomography

Debinded samples were examined by X-ray computed tomography (CT Compact, ProCon X-Ray, Garbsen, Germany and Fraunhofer Development Centre for X-ray Technique, Fürth, Germany) to evaluate internal defects. Samples containing X-ray sensitive tracers were used for the visualisation of flow lines as explained below.

### 2.5. Flow line detection

The mould filling characteristics can influence the properties of the final product. In order to visualize the flow pattern in the gear wheel a method has been developed which allows marking flow lines with X-ray sensitive tracers.[10] The chosen zirconia tracer particles had a higher X-ray attenuation coefficient compared to the base material giving a suited contrast. Due to the limited lateral resolution single particles could not be detected. Therefore they were introduced into a feedstock having the same binder system to achieve similar rheological properties. Both feedstocks were fed in small alternating quantities into the injection barrel. Since the materials did not mix homogeneously during dosage flow lines could be detected using X-ray computed tomography.

Table 1
Solids loadings of the feedstocks determined by ashing.

| | $Al_2O_3$ | | ZTA | |
|---|---|---|---|---|
| | Solids loading [wt%] | Solids loading [vol%] | Solids loading [wt%] | Solids loading [vol%] |
| GW1 | 82.28 | 55.6 | 82.67 | 55.7 |
| GW2 | 82.82 | 56.7 | 83.40 | 57.0 |
| GW3 | 84.60 | 59.7 | 85.34 | 60.5 |

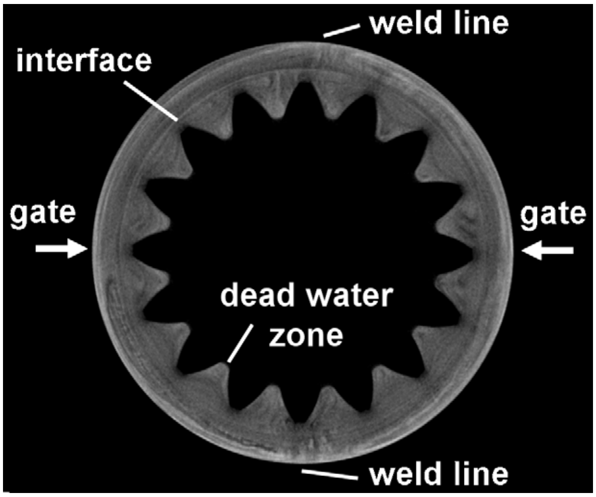


Fig. 1. X-ray CT reconstruction image of a two-component gear wheel with tracer feedstock showing the flow pattern.

### 2.6. Microscopic detection of powder-binder separations

For investigating the microstructure of green injection moulded parts the samples were polished by broad ion beam technique. By sputtering with argon ions the atoms or atom clusters of both the hard ceramic particles and the soft polymer molecules are removed from the surface simultaneously without destroying the structure. For the preparation an ion etching system BAL-TEC RES 101 (Bal-Tec AG, Liechtenstein) was used. The micrographs were taken on a field emission scanning electron microscope NVision 40 (Carl Zeiss AG, Germany). For better contrast between the ceramic particles and the organic matrix a backscattered detector was applied.

Low magnifications showed the extent and orientation of macroscopic binder segregations. The distribution of particles was studied at 10,000-fold magnification for the sample GW3. Micrographs were taken with a spacing of 100 μm along the centerline of a gear tooth starting at the tip and continuing until the interface. The porosity was determined using the image analysis software Leica QWinV3.

## 3. Results

### 3.1. Flow pattern

When injecting the tracer-mixed feedstock into the mould the two original feedstocks proved to be not completely homogenised. Therefore there are separate layers in the stream with differing X-ray attenuation coefficients moving parallel. After solidifying in the mould, they reveal the history of filling in CT measurements (Fig. 1).

Each component of the gear wheel is injected simultaneously through two gates. Thereby weld lines are created perpendicular to the gates where the feedstock fronts collide. When filling the inner ring dead water regions are formed in the gear teeth. While material has already deposited in the tip of the gears new feedstock flows along forming a boundary. The interface around the whole circumference as well has to be considered as a potential defect site.

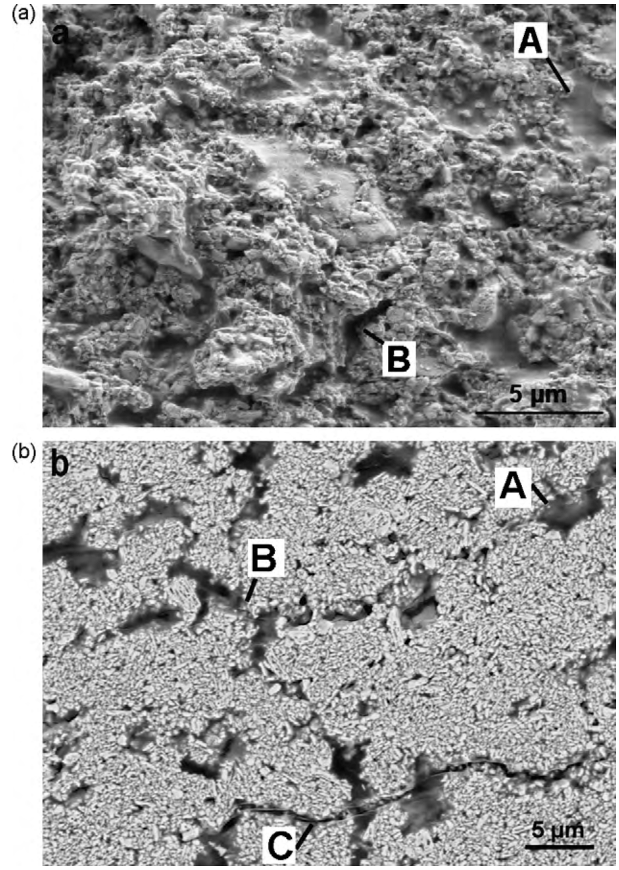


Fig. 2. SEM images of (a) the fracture surface and (b) ion beam polished surface of a green sample of GW1. (A) Bulk binder separations, (B) elongated pores filled with binder and (C) crack.

### 3.2. Preparation method

Injection moulded green parts cannot be treated with conventional micro-secting techniques, because during the grinding and polishing step the hard ceramic particles are pulled out of the binder matrix and the original structure is changed.

Fracture surfaces provide a first impression of the unaltered state. Fig. 2a shows the powder embedded in the polymer matrix. Between the single particles binder bridges formed as plate like sheets standing upright. Binder agglomerations appear as smooth areas within the particle packing. Nevertheless, information about their dimensions and occurrence can hardly be gained due to the rough surface. Furthermore, global structural attributes like porosity or position of cracks cannot be characterised.

In the broad ion beam polished surface (Fig. 2b) the microstructure can be observed independently from the fracture topography. Binder agglomerations were identified as round shaped bulk segregations with an approximate diameter of 5 μm. Polymer filled elongated pores are potential origins of crack initiation.

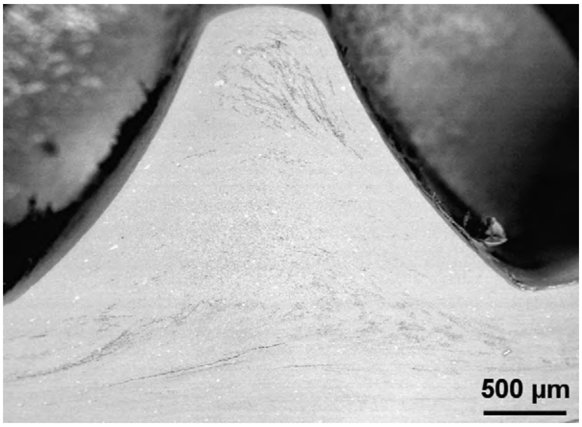


Fig. 3. Binder segregations in a gear tooth of GW1.

### 3.3. Binder segregations

Binder segregations as described in Fig. 2 were found at several locations in the gear wheel. The overview of a gear tooth (Fig. 3) shows characteristic orientated binder exclusions. In the tip which is the end of a flow path and thus the deposition site binder segregations are aligned in flow direction. Next to this dead water zone a curved line has formed where continuing feedstock passes the cooling material.

Between the inner and the outer ring (Fig. 4) there is a large gap which is filled with a 30–40 μm thick binder layer weakening the bonding strength of the compound.

Prior to sintering the binder is decomposed by thermal treatment. That implies that all binder exclusions leave pores or cracks behind. Due to the weakened green strength macroscopic cracks develop in the debinded part. These cracks can be detected by X-ray CT (Fig. 5). The comparison of the crack formation with the tracer image (Fig. 1) points out that they are aligned as the flow pattern.

### 3.4. Particle distribution

The process of cavity filling influences the particle packing density in the green part. The porosity, i.e. the interspace between the solids which is filled with binder was determined along a gear tooth of GW3 spatial resolved. The lowest porosity was found in the tip (Fig. 6). With increasing distance the particle packing density decreased and left 39–40% pores which is close to the nominal binder content of 40.7%. The high particle packing observed in the dead water region indicates that the deposited feedstock was compressed while feedstock streamed past. Excessive binder was then carried away or deposited as binder segregation.

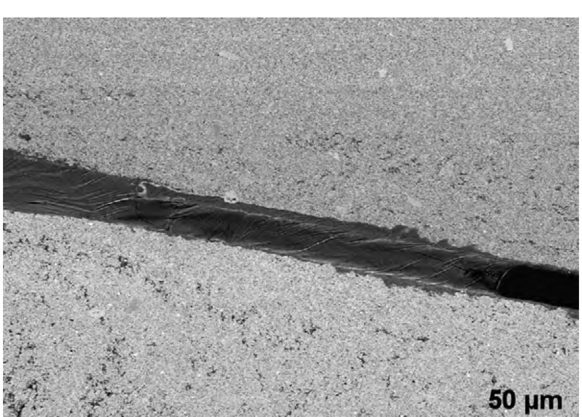


Fig. 4. Interface between inner and outer ring of GW1.

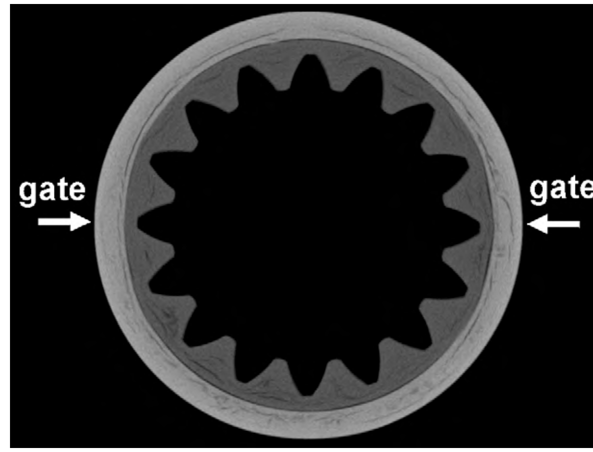


Fig. 5. X-ray CT reconstruction image of debinded sample GW1.

### 3.5. Solid content

In injection moulded parts weld lines are one of the most critical sites. When the melt fronts meet frontally they have to join closely. Any binder exclusions will break up the weld line and lead to failure of the part.

In Fig. 7 the weld lines are shown at different solids loadings. At the lowest powder content (GW1) strong binder segregations formed along the flow lines. Additionally, a large polymer agglomerate is situated at the weld line between inner and outer ring which was possibly created when binder on the surface of the inner ring was pushed ahead the melt front. For GW2 the quality of the interface improves. However, flow lines are still

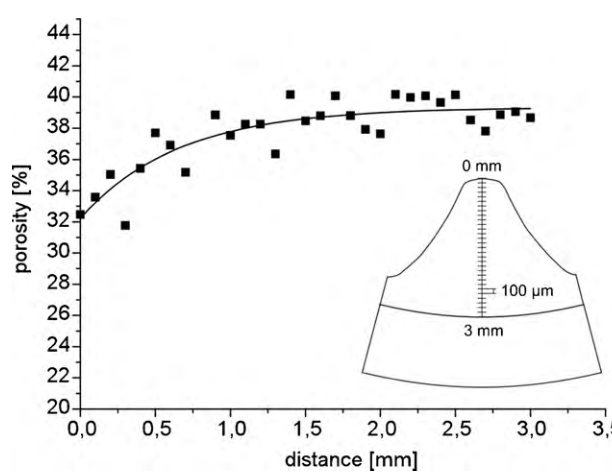


Fig. 6. Porosity in a gear tooth of GW3 in green state determined by image analysis of SEM micrographs.

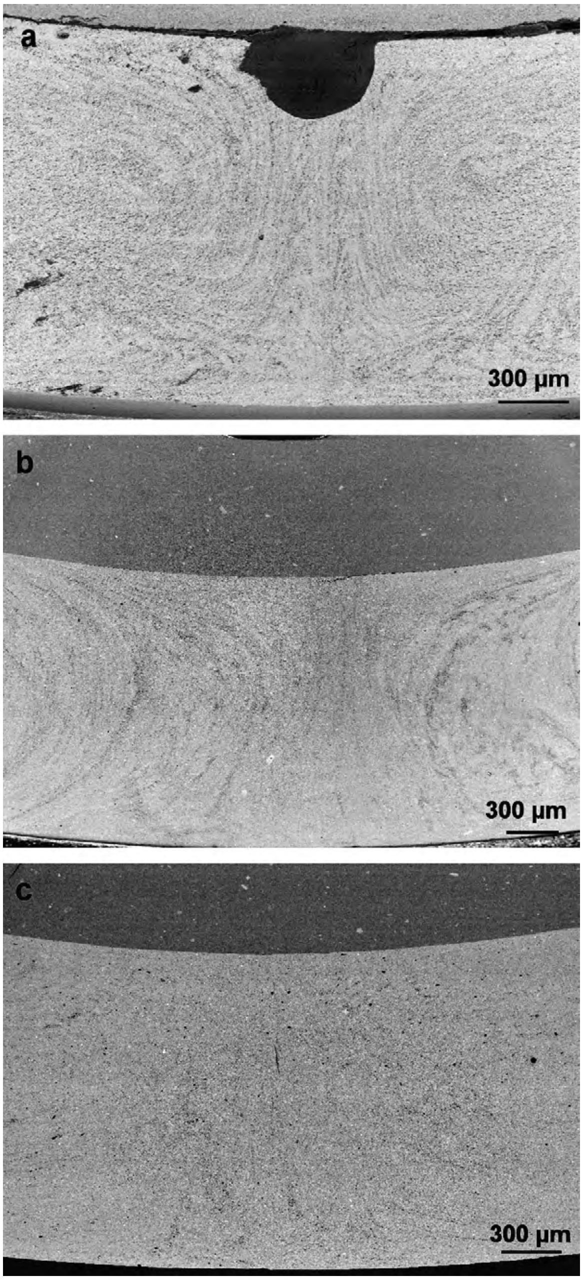


Fig. 7. Weld line at different solids loadings: (a) GW1, (b) GW2, and (c) GW3.

clearly visible. Only at the highest solids loading (GW3) separations at the flow lines disappear and an intact interface can be formed. For this sample the prerequisite of a defect-free green sample for successful sintering was met.

The risk of forming binder segregations decreased with increasing powder content since separation effects of solids and polymers were less probable.

## 4. Discussion

During the injection phase the particles move within the binder matrix. To allow relative displacement and rotation of solids each particle has to be coated by a binder layer which supplies the necessary distance between neighbours.[11] A defor-

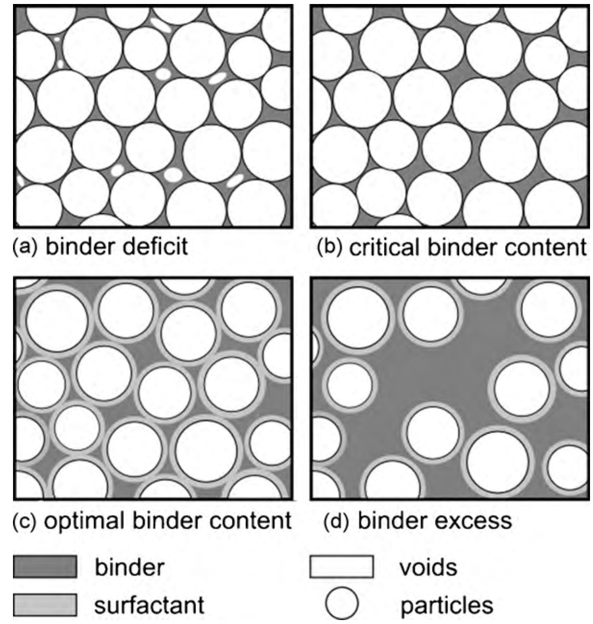


Fig. 8. Particle packing in feedstocks.

mation mechanism is introduced in a model in Ref. [12]. Layers of mobile binder are created between particle stacks that form slip bands. If the flow direction changes the initial slip band system becomes inactive and binder molecules have to migrate to a new one. The mobility and availability of mobile molecules determine the rheological response. At high binder contents the viscosity decreases while the number and the thickness of binder layers increase.

According to the binder content different states can be distinguished in feedstocks. Assuming randomly dense packed particles, in case of lacking binder voids remain which hinder particle movement (Fig. 8a). At the critical binder content the polymer fills the spaces between the particles completely (Fig. 8b). But since the particles are still in contact with each other the binder is immobilized and cannot work as lubricant. Adding binder increases the particle distance and allows the system to form a polymer layer attached to the powder covering the whole surface (Fig. 8c). In this way the particles can easily glide against each other and are able to form slip bands. When the optimal binder content is exceeded (Fig. 8d) the distance between the solids increases too much so that the particles cannot stabilize each other mechanically in debinded state.

Under pressure excessive binder will move relative to the particle packing. At critical shear rates the solids act like a filter through which the polymer molecules pass.[13] In rheological measurements this is associated with flow instabilities which are often accompanied by the slip phenomenon. In particle filled systems thin, binder rich layers are formed at the wall.[14,15] The bulk feedstock is then gliding in plug flow onto the slip layer without an inner velocity gradient or inner deformation.

This has serious consequences for the injection moulding process. As the feedstock is injected into the mould shear forces act, thus powder and binder can separate. That might happen in contact with external surfaces like the tool wall, but it can also

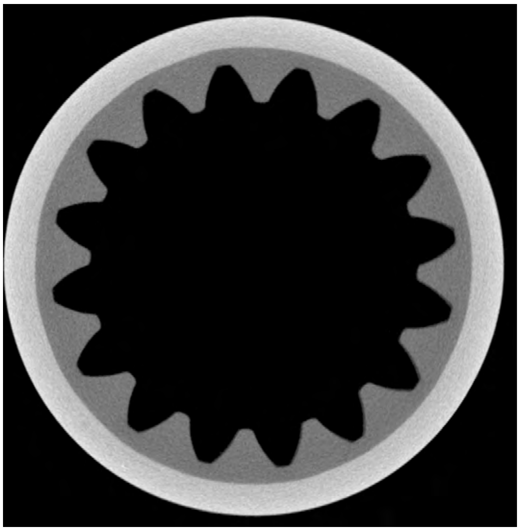

Fig. 9. X-ray CT reconstruction image of debinded sample GW3.

appear within the feedstock at boundaries between two gliding feedstock layers.

During the production of the first gear wheel component, binder is pressed to the surface while the feedstock passes the narrow gates at high shear rates. The created binder layer solidifies at the tool wall. In one-component parts this could be tolerable, since it is removed in debinding, but in multi-component parts the former outer surface now becomes the interface. If the separated polymer molecules are accumulated by the flowing second feedstock, defective joining zones as shown in Figs. 4 and 7a would occur.

In addition, inside the bulk feedstock flaws can be created by a similar effect. If during cavity filling the feedstock flows next to areas already cooled, binder layers can form at the boundary. They will deposit for example at dead water zones like shown in Fig. 3. The separated binder then solidifies dividing dense packed particle regions and causes cracks after binder removal.

If the excessive binder is kept at an optimal degree, separation effects can be suppressed and defect-free parts can be obtained (Fig. 9).

## 5. Conclusions

Broad ion beam technique as a new ceramographic method for the preparation of injection moulded green samples has been introduced. Polished cross-sections of two-component parts showed segregated binder in the interface as well as in the bulk material. To visualize the mould filling, tracer feedstocks were applied to mark flow lines in X-ray CT. Comparision of the binder segregations with the flow pattern revealed that powder and binder are separated along flow lines. By increasing solids content less excessive binder is available leading to decreased separation effects.


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