Quantitative study of powder binder separation of feedstocks

Martin Jenni (1), Lukas Schimmer (1), Rudolf Zauner (2), Juergen Stampfl (3) and Jeff Morris (4)

(1) Austrian Research Centers GmbH – ARC, A-2444 Seibersdorf, Austria
(2) Verbund – Austrian Renewable Power GmbH, A-1010 Wien, Austria
(3) Vienna University of Technology, Institute of Materials Science and Technology, A-1040 Vienna, Austria
(4) City College of New York, Levich Institute & Chemical Engineering, NY 10031 New York, USA

The rheological properties of feedstocks and their flowability and tendency for powder binder separation have a strong influence on the successful manufacturing of PIM components. A systematic comparison of the filling behaviour of different tungsten and aluminium feedstocks has been carried out experimentally. Using specially designed moulds, designed experiments (DOE) with variations in the nozzle temperature, mould temperature an injection speed of feedstocks with extremely different physical and thermal properties (tungsten and aluminium) were carried out. The results were statistically analysed. The observed effects are explained and implications for optimised PIM processing are suggested. Furthermore parts of the samples are analysed for powder separation and compared to predictions made by the pseudo-continuum separations model named: Balance Model.

Introduction

Powder injection moulding (PIM) is a relatively new processing technology used in powder metallurgy and ceramic processing industries. This process is especially cost-effective and beneficial for manufacturing small and complex components in large quantities. Powder injection moulding is used in an increasing range of different fields, including automotive, medical and telecommunication industries. It includes four basic steps consisting of (1) mixing the powders and binders, (2) injection moulding, (3) debinding and finally (4) sintering [1]. Both injection moulding and sintering are the most important steps related to forming the green part and the final part, respectively. In particular, the injection step often requires expensive and time consuming trial and error methods to resolve design problems associated with raw material, product dimensions, tooling factors and process issues during manufacturing. A direct relationship between input and output parameters is often not obvious and a lot of testing is needed to find empirical relationships for the influence of feedstock properties, processing conditions and mould properties on the mould filling behaviour. Today's computer aided engineering tools for plastic injection moulding and PIM have shown promising results in resolving problems of material, part and mould design.

Similar to injection moulding of thermoplastic feedstocks, defects such as jetting, air traps, dead zones, or welding lines can also occur in PIM. The available simulation software addresses these points already. However, the powder binder separation, also called phase segregation, is a phenomenon which is frequently observed in PIM and happens during the high speed and high pressure injection moulding process due to the different densities associated to powder and binders. These can induce inhomogeneities of green parts. After the debinding step, the binder is removed and the remaining component results in a porous brown part. In the consecutive sintering step, the debinded parts shrink substantially. The shrinkage between the green component and resulting net component is typically in the range of 10 to 20% and the final density in the range of 95 to 100% [2]. After sintering some finishing operations may be needed. The dimensional tolerances of PIM components

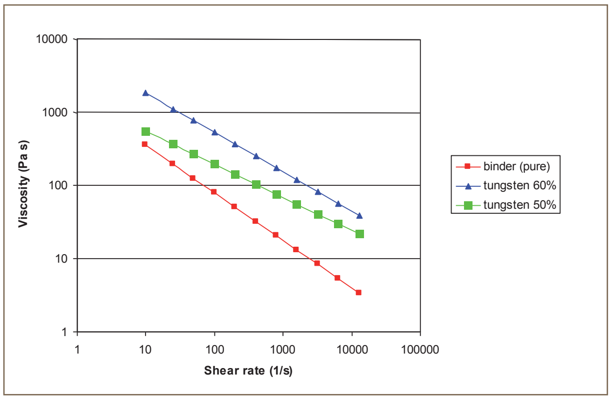

Fig. 1 Viscosity measured with capillary rheometry for different loadings. The material was tungsten with ARC binder

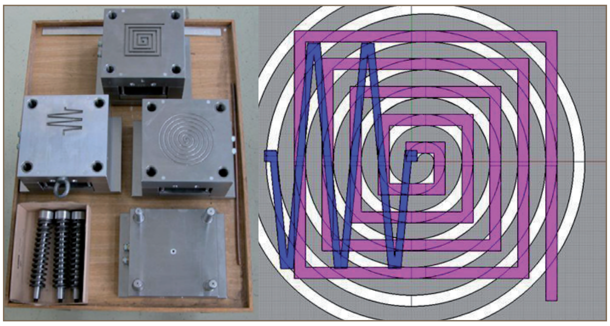

Fig. 2 Characterisation moulds; three different forms: spiral (white), square spiral (pink) and zigzag (blue)

are in the range of 0.3 to 0.4%, which is large compared with the tolerances achieved by other near net shape technologies [3] but small considering the substantial shrinkage from green to sintered dimensions. Therefore it is essential to control defects such as inhomogeneous shrinkage, distortions, cracks, etc. to get the final components with the required dimensional accuracy and specified mechanical properties.

Conventional trial and error methods are widely used in the PIM industry to obtain the required products by adapting and adjusting tooling and processing parameters iteratively. The numerical simulation of PIM is now in development and promises a cost-effective tool to optimise the process and avoid the trial and error approach. Often, thermoplastic injection moulding software is used as a base for modelling the process from feedstock to green part. These "plastic injection software" tools do not address PIM-specific problems like powder density distribution of green parts.

In this paper, the main focus will be on the powder-binder separation of the PIM process, because of its importance for the following sintering process. Therefore the influence of injection parameters for different materials on the process and resulting separation is discussed. Because of the lack of a powder binder separation model in present injection simulation software for thermoplastics, alternative simulation approaches were investigated. So calculations with the Balance Model for Separation of Suspension which includes a powder binder separation model were carried out and compared to the real parts to check the quality of the results.

Experimental investigation

With the main focus on the powder binder separation, first a procedure to quantify the local powder content had to be found. The method had to be simple and fast because of the large number of samples that were expected. Different approaches were tried and in the end measurement with a differential scanning calorimeter (DSC) worked out best. After measuring reference material with different loadings, a correlation could be found and used for the measurements. For example tungsten feedstock with 30% , 50%, 60% powder was produced. Then the material was measured with DSC and the change of enthalpy of one feedstock ingredient (binder component) compared. With the resulting curve the correlation between powder content and enthalpy change could be defined.

To compare different materials and processing parameters, three characterisation moulds (Fig. 2) are produced. These characterisation moulds were designed in a way to exaggerate powder-binder separation. Moulds used to test the mouldability of plastics are similar in design.

Mouldability is expressed as the length of the characterisation mould filled under a set of conditions. Because the mould is cold, a frozen layer continuously forms along the mould wall. This means that continued filling of the mould depends on the flow through the partially frozen channel. The process is termed fountain flow. As heat is extracted through the walls, the center channel progressively closes and eventually halts flow [4]. This mouldability test shows good results for plastic injection, however, the predictions for PIM feedstocks are difficult. Near the critical solids loading, small changes in solid content have large effects on flow.

The experimental runs are performed the same way for all different materials to get comparable results. Furthermore, the tests are designed to fit a "Design of Experiments" approach to visualise the outcome. The dependent variable for the mouldability is the flow length and the input variables are nozzle temperature, mould temperature and injection speed. Because of three variables at two values a full test (8 runs each session) was made. Tested materials are ARC tungsten and ARC aluminium, each with 60% and 50% loading.

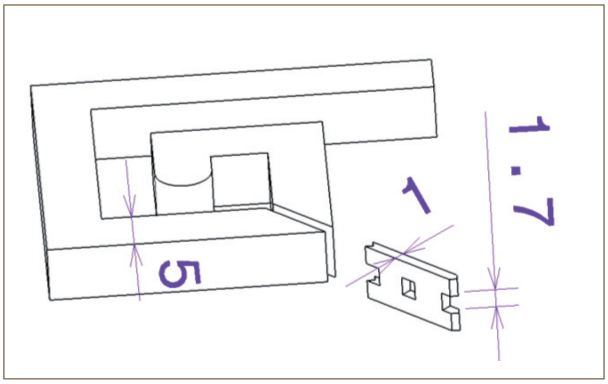

Fig. 3 Position of the three samples for powder content measurements

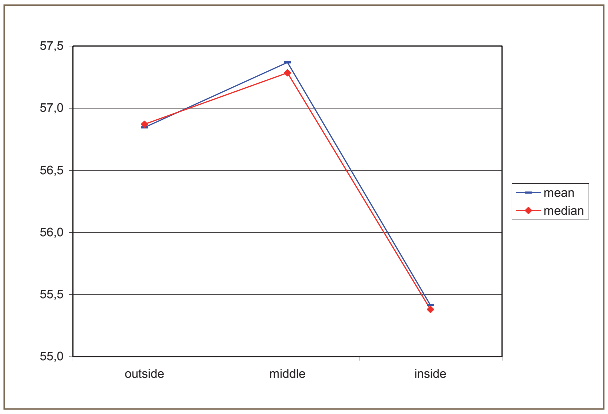

Fig. 4 Influence of the nozzle, mould temperature and injection speed on the powder content; mean and median powder content over the experiment series

number	nozzle temp. [°C]	mould temp. [°C]	injection speed [cm³/s]	length of flow [mm]
1	150	150	35	246
2	150	150	30	239
3	150	140	35	235
4	150	140	30	230
5	140	150	35	240
6	140	150	30	227
7	140	140	35	236
8	140	140	30	222

Table 1 Data sheet for DOE measurements; material: ARC tungsten feedstock with 60% loading; mould: square spiral

Initially, the standard conditions for the process were determined. The successful determination depends very much on the experience of the operator of the moulding machine. After finding the best parameters, the variables are shifted up and down. After the first test a shifting of +/- 10 K for nozzle and mould temperature and +/- 5 cm^3/s for injection speed are defined. More than +/- 10 K shifting leads to cracks, overheating of the feedstock and general problems during injection and ejection.

After performing the DOE for the above mentioned materials, the influence of the variables on the mouldability is discussed. The feedstock behaviour is as expected. Within the parameter window for good results, increasing temperature and energy (injection speed) leads to better flowability of the feedstock. Also the flow length for different loadings changes significantly. The mean

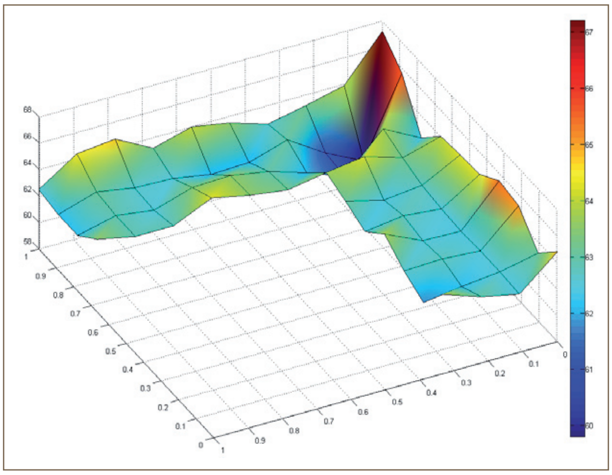

Fig. 5 Powder distribution along a corner; material: tungsten feedstock with 60% loading

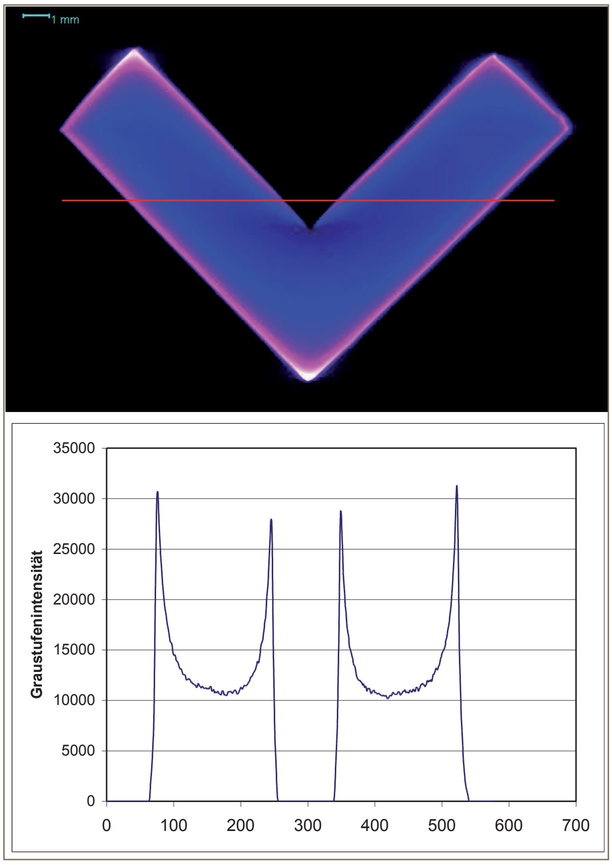

Fig. 6 Measurement with computer tomography (top) and presentation of the greyscale intensity (bottom) along the marked line 60% loading (intensity in the middle)

difference for tungsten with 60% and 50% loading and square spiral is about 108 mm or 68 %.

Furthermore, not only the flow length but also the powder content at a defined location was measured for each sample [Fig. 3]. The third corner of the square spiral was horizontally sliced and resulted in a one millimetre thick L-shaped geometry. Then a one millimetre wide bar was cut out from the inner corner to the outer corner. This bar was then divided in 5 parts and the number one, three and five is taken for measurements.

After a closer look at the results and comparison with other materials and powder loadings, the development of a fountain flow becomes more significant with higher temperature and speed.

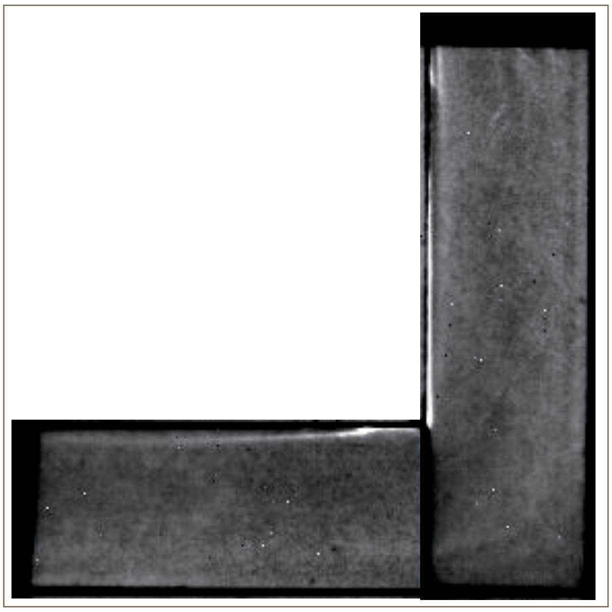

Fig. 7 Measurement with radiography (greyscale)

On the wall of the mould, the material freezes and the mould and feedstock temperature has a good influence on the powder content. Also the increasing flow length and the small increase of the mean powder content at the third corner of the square spiral (constant distance from entrance) predict the fountain flow phenomenon. The binder is fluid and will therefore flow more easily while the powder will follow behind. Therefore in a characterization mould like the square spiral the general powder content will sink somewhat with raising number of corners. Furthermore, note the small or marginal influence of the injection speed on the powder content in the middle of the corner point at this fountain or channel flow. Also the higher mean and median powder content over a series of eight runs support this behaviour.

With main focus on the powder-binder separation, a feedstock with less variation of the mouldability (flow length) gives better results when the temperatures are changed. Also the induced energy by temperature and velocity should be as small as possible in the window of useful parameter settings for each feedstock.

Two dimensional measurements

Besides performing analytical tasks two and three dimensional pictures of the powder distribution are produced. In order to get a qualitative comparison between real parts and simulation, two and three dimensional pictures of the powder distribution are produced. For a two dimensional picture a part was divided into small pieces and the powder content measured. For example, a tungsten corner was first cut horizontally into 3 pieces to get a plate with 1mm height out from the middle. This thin plate in the shape of the corner was afterwards cut into 64 pieces with 1mm side length. After measuring a picture of the distribution over the corner can be made.

Further radiographic and computer topographic measurements were carried out. Unfortunately, because of its high density and absorption tungsten is very complicated to measure so the quality of the results is not satisfying at the moment. The influence of the edges is too dominant.

Simulation models of suspension flows

In reality PIM feedstock consists of two phases one of which (binder) undergoes phase transformation during the moulding stage, while the other (powder) one remains solid. Besides the fact that the properties of the constituents are different, the distribution of the powder in the binder may be changed during the moulding process. Efforts undertaken in modelling of specific PIM-related phenomena like the powder binder separation is based mainly on two physical models for suspension flows: Diffusive-flux models [5] and the suspension balance models [6-7]. Both models are continuum based models, in which the particle phase is approximated as a pseudo-continuum. Other methods of study like experimental investigation and particle tracking simulations provide valuable insight into specific systems, but are time consuming and the results are not easily generalised.

Balance model

The model is developed for the flow of suspensions of rigid, spherical particles in a Newtonian fluid. The dominant interaction between the particles is hydrodynamics, viscous conditions and non-Brownian particles with no external field except gravity is assumed. The Reynolds number for the flow is considered to be vanishingly small.

Most important equations

Assuming that the particle phase can be approximated as continuum, the following equations are developed.

$$\nabla \cdot u = 0$$
$$\nabla \cdot \Sigma = 0$$

u is the bulk suspension velocity and Σ the bulk suspension stress. These equations describe the suspension mass and momentum balances.

The particle-phase mass balance is

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi u_P) = 0$$

where $\phi(x)$ is the particle volume fraction and u_P is the particle phase average velocity. By defining an overall particle flux $j := \phi u_P$ the equation can be written as

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot j$$

The bulk suspension stress Σ is divided into the fluid phase contribution Σ_f and the particle phase contribution Σ_P . Σ_f is a function of the fluid phase averaged pressure P, the local rate of strain E and the viscosity of the suspending liquid η_0 .The constitutive law for the particle stress is that suggested by Morris and Boulay [7] and contains both shear and normal stress portions. To model these terms it is necessary to calculate the shear viscosity

$$\overline{\eta_S} = \eta_0 \eta_s = \eta_0 (1 + \eta_p)$$

where η_p is the particle phase viscosity. For the development of a computational tool it is actually the relative viscosity, $\eta_s = \frac{\overline{\eta_s}}{\eta_0}$ which is important.

To match the shear thinning nature of the ARC feedstock the model changed from the powder concentration depended viscosity $\eta(\phi)$ to shear induced viscosity models $\eta(\dot{\gamma})$. The viscosity of the feedstock was measured by capillary rheometry and then fitted into viscosity models. Because of availability the Carreau-Yasuda model was used for the binder viscosity:

$$\eta_0(\dot{\gamma}) = \mu_\infty + (\mu_0 - \mu_\infty) \cdot (1 + (\lambda \dot{\gamma})^a)^{(n-1)/a}$$

and the Power Law model for viscosity of the feedstock.

$$\overline{\eta}_s(\dot{\gamma}) = \frac{B}{1 + \left(\frac{B\dot{\gamma}}{\tau}\right)^{1-m}} \qquad B = D_1 \exp\left(\frac{-A_1(T - D_2)}{A_2 + (T - D_2)}\right)$$

The normal stress portion of $\sum_P$ contains the "normal stress viscosity", which is built by the Carreau-Yasuda model and data from normal stress measurements in a rotational viscometer.

Computational tool

The computer code is built from a series of MATLAB script files run in a PC environment. The program is mainly for testing purpose and works for Cartesian geometries (x,y) as well as for two dimensional, axisymmetric flows (z,r). For the spatial discretisation of the balance equations (suspension mass and momentum) the finite volume method (FVM) is utilised.

The solution domain is divided into a finite number of elements. The arrangement of these so called cells utilises a structured Cartesian grid with the capability of refinement in regions of interest. Due to numerical reasons ϕ and P are solved at the central node of each cell, whereas the velocity components $u = (u, v)^T$ are solved at the wall node normal to the velocity direction.

The flowfield and the particle migration equations are coupled in the following way: In one computational step the flow field is determined for a given particle volume fraction $\phi(x)$. This flowfield solution then provides the necessary stress information to determine the change in the ϕ field over a single explicit time step. This sequence of steps is repeated to provide the solution of the u and ϕ flow fields as they evolve over time.

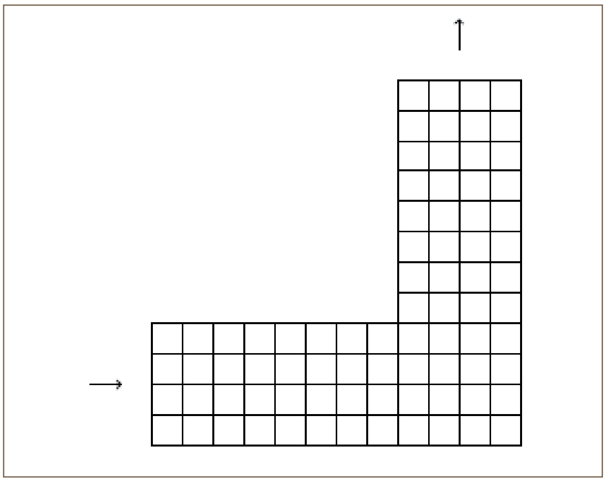

Fig. 8 Typical geometry with computational grid

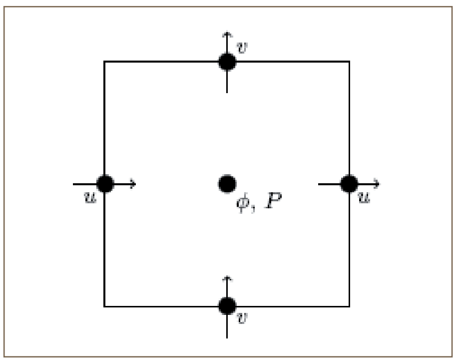

Fig. 9 A cell with nodes at the center and wall-mid points

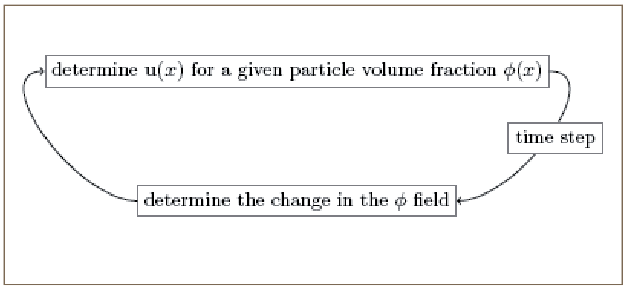

Fig. 10 "Solver-Evolver" method

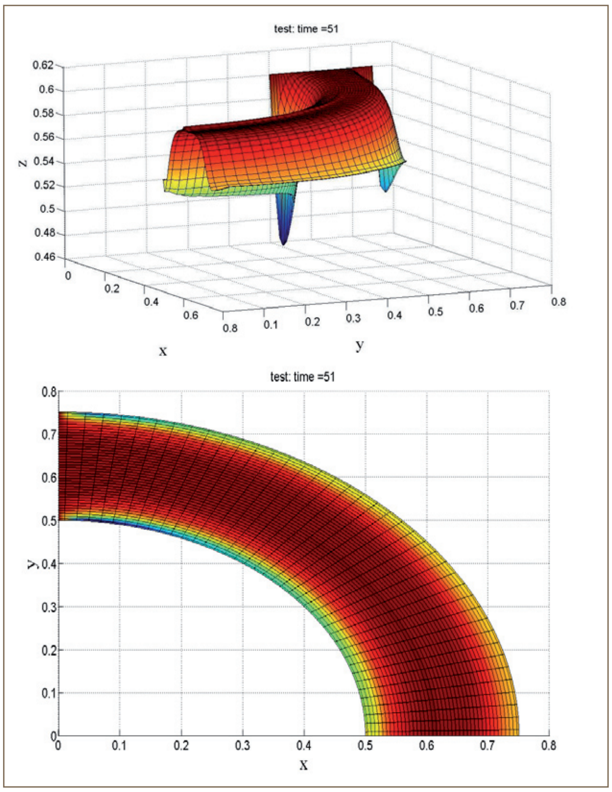

Fig.11 Powder concentration in a curved channel with tungsten feedstock (60% loading)

Conclusion

To minimise the powder dissemination or powder binder separation, several approaches have been investigated. Reduction of the nozzle and mould temperature decreases the separation. So optimising with reducing of process temperatures (nozzle and mould temperature) to working limits of the feedstock can be useful. The same is true for the injection speed. Furthermore a feedstock with little mouldability shifting over the processing parameter window and parameter values shows less powder binder separation. In particular the influence of temperatures changes on the flow behaviour should be small. A feedstock with a rapid change between solid and fluid should be preferred. Also the thinning of the feedstock should be small while using adequate process parameters.

The suspension balance approach for separation of suspensions is a good starting point for modelling of powder binder separation. The code gives a good picture for migration of particles in basic geometries. Problems are slip effects at the wall and the "fountain flow", which are not addressed by the code. The code, which has been successfully applied for 3D geometries, has potential to accommodate additional physical phenomenon to reflect the reality in more detail. The measurements with the DSC are useful for a quantitative verification of pictures made by other processes like computer tomography and radiography. For a detailed picture of the flow and powder distribution the resolution is too little. But the weak spots like the wall effects can be seen. So further investigation of wall effects like slip, rolling of particles, layer with a lot binder is necessary.

The finding presented in this work can help both feedstock designers and PIM manufactures to identify important parameters to optimise their materials and processes, respectively. Further

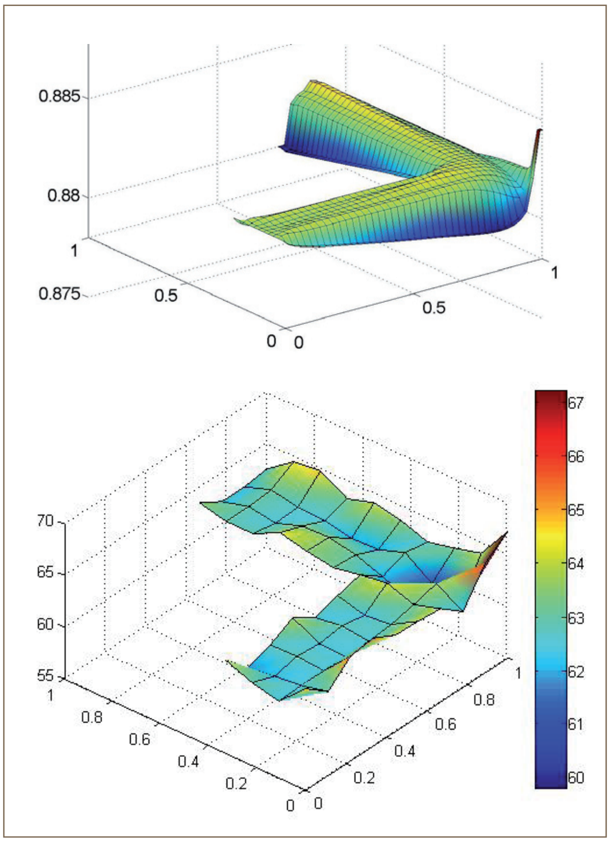

Fig. 12 Corner with tungsten feedstock (60% loading);
Top: "balancemodel"; powder content is shown here as a fraction of maximum flowable solid content, assumed as 68%; 0.6/0.68 = 0.88
Bottom: measured with DSC method

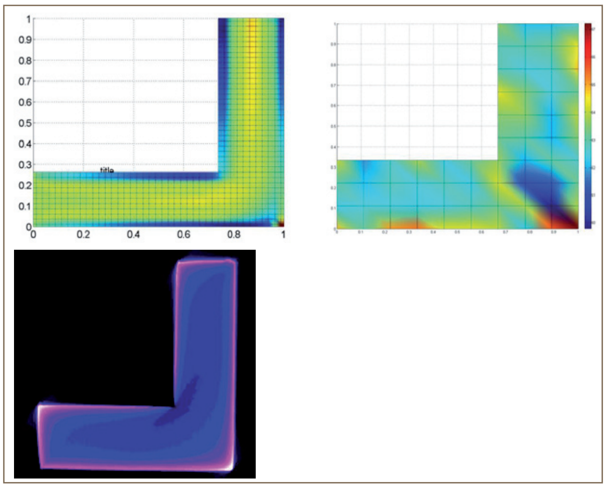

Fig. 13 Powder distribution along a corner; material: tungsten feedstock with 60% loading. Top left: Balance model; Top right: measured by DSC; Bottom left: measured by computer tomography

work will be needed to quantitatively relate the findings to shrinkage and distortion effects observed during debinding and sintering.

References

[1] S. V. Atre, S.-J. Park, R. Zauner, R.M. German, "Process simulation for powder injection moulding: identification of significant parameters during mould filling phase", 2006, *Powder Metallurgy*, vol. 49, no. 3.
[2] J.C. Gelin, Th. Barriere, J. Song, "Processing defects and resulting mechanical properties after metal injection moulding", 2007, FEMTO-ST Institute, Department of Applied Mechanics, ENSMM Besançon, France.
[3] V. V. Bilovol, "Mould filling simulations during powder injection moulding", 2003, PH.D. Thesis, Delft University of Technology, Delft, The Netherlands.
[4] Randall M. German, Animesh Bose, "Injection Moulding of Metals and Ceramics", 1997, Metal Powder Industries Federation, Princeton, New Jersey.
[5] Ronald J. Phillips, Robert C. Armstrong, Robert A. Brown, Alan L. Graham, James R. Abbott, "A constitutive equation for concentrated suspensions that accounts for shear-induced particle migration", 1992, *Phys Fluid A*, vol. 4, pp. 30-40.
[6] Ryan M. Miller, "Continuum Modelling of Liquid-Solid Suspensions for Nonviscometric Flows", 2004 PH.D. Thesis, School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia.
[7] Jeffrey F. Morris, Fabienne Boulay, "Curvilinear flows of noncolloidal suspensions: The role of normal stresses", 1999, *J. Rheol.* 43(5), pp. 1213-1237.