Radical Time Reduction of Debinding Processes by Combined in-situ Measurements and Simulation

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Debinding is a crucial process step in the production of almost all powder based materials. The low mechanical strength during debinding requires careful heating to avoid component damage due to pressure by gaseous products or thermal gradients. In consequence the debinding is often conducted in a considerably too careful way leaving a huge potential for minimizing energy consumption and process time. In this paper, a combined approach using experiments and simulation to systematically optimise debinding processes is presented. The method is based on measuring precisely different material properties in situ during the heat treatment. A finite element model utilizing these in situ data predicts the debinding behaviour of green bodies, including the resulting internal stresses. The feasibility of this approach is demonstrated on the example of a refractory material.

Introduction

The debinding of green bodies is an important topic for the preparation of almost every powder-based ceramic material. The amount of binder used can vary quite strongly depending on the shaping process. Binder content of up to over 25 vol.-% is not unusual. During the heat treatment, especially during the debinding of green bodies with a relatively high amount of binder, not only the intended but also many unwanted material changes can occur. Furthermore, if binder burnout or pyrolysis are not complete, residual carbon can affect sintering and lead to damage or distortion of the component.

Heating rates and dwell times applied for debinding processes are typically determined by purely empirical methods. As such an approach is very time-consuming and costly, empirical optimization is usually focused on avoiding defects and distortions which can occur during debinding when too high heating rates are used. Latter cause high vaporization rates of the binder leading to high thermal stresses and overpressure in the green body. Therefore, industrial heating cycles are often far away from the minimal possible processing time. In order to systematically optimise a debinding process and shorten the process time, the most important chemical and physical mechanisms in the green bodies must be well known.

To get the knowledge about these mechanisms, the debinding process is reproduced at Center HTL in special laboratory-scale furnaces, which allow reproducing the industrial process conditions in particular temperatures and atmosphere.

The most crucial parameter is the debinding rate, which can be quantified by measuring the mass loss in situ by using Thermogravimetric Analysis (TGA). Additionally, it is possible to determine simultaneously the heat of reaction by Differential Scanning Calorimetry (DSC) and the chemical composition of evolved gases by Mass Spectroscopy (MS). For the process simulation, further parameters have to be measured, in particular thermal diffusivity and gas-permeability of the green compact. With these experimental data it is possible to set-up a Finite Element Model (FEM) for parts of arbitrary shape, which can accurately predict debinding behaviour. The FE-simulation is used to optimise the process by changing different kind of parameters and variables, at the first place the time temperature cycle. In this way the process time can be systematically minimized without decreasing the quality of the components. As instructive example for such an optimization the in situ characterization and simulation of the debinding of a refractory brick is discussed in the present paper.

Experimental characterization

The refractory material under consideration in this work is a fireclay usually used for lightweight bricks. The basic material composition and some general material parameters are summarized in Tab. 1. Green bodies of such fireclay bricks have been used for the experimental work.

In general the debinding processes of a material depend on the binder and its decomposition products as well as on the refractory microstructure. In an effort to minimize the amount of experimental work needed,

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Tab. 1 Material properties of used refractory bricks

Parameter	Symbol	Unit	Value
Bulk density	ρ	g/cm³	2,2
Apparent porosity	ε	vol.-%	17
Cold crushing strength	f	F	40
Amount SiO_2	W_{Sio_2}	%	52
Amount Al_2O_3	$W_{Al_2O_3}$	%	42
Amount Fe_2O_3	$W_{Fe_2O_3}$	%	1,8

the approach discussed in this article is based on four measuring methods which will be shortly explained below:

Debinding kinetics

Debinding comprises a variety of interacting chemical and physical processes. Trying to identify and understand all these processes in detail would require a huge amount of experiments to be performed.

As has been shown in previous work of the Center HTL, it is much more effective to characterize the debinding kinetics in a generalized way: by creating and using a so called kinetic field one can describe and predict the debinding of ceramic green bodies from a small number of experiments [1]. Such a kinetic field can be created by measuring in situ the mass loss during debinding of green body samples at different constant heating rates.

In general, binder removal can take place via two different types of reaction, depending on the amount of oxygen in the furnace atmosphere. If enough oxygen is available, the binder burns out, otherwise it is pyrolised. Pure pyrolysis is expected for inert atmospheres only, while even in presence of oxygen mostly both types of reaction occur simultaneously depending, e.g. on local oxygen content within the part during debinding. Therefore, two kinetic fields for the limiting cases were prepared measuring the debinding of a fireclay green brick under air as well as under inert atmosphere. Subsequently an interpolation between these two kinetic fields was used in the FE-model.

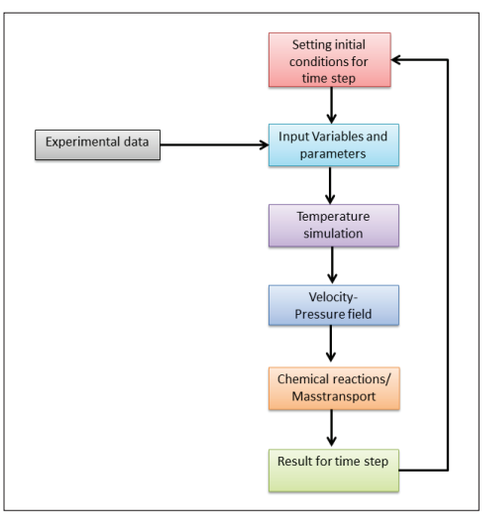

Fig. 1 Simulation flow chart

Binder composition

To describe the chemical reactions occurring in the debinding process of the refractory, basic information about reaction educts and products is needed. Since the actual chemical composition of the binder is often not known a simple elemental analysis of organic carbon-, hydrogen-, oxygen- and nitrogen content in the green sample was performed. In addition the evolved gas species during debinding were identified by mass spectrometry. These data are used in the FE-simulation to consider the chemical reaction products during the debinding process.

Thermal diffusivity

A key parameter to describe the debinding in the simulation model is the current temperature distribution. For that, it is necessary to measure the thermal diffusivity of the green component as a function of temperature. This quantity was measured in situ by the well known laser flash technique.

Gas permeability

The permeability describes the propagation of a fluid through a solid material; it is apparently related to the porosity, but also depends on other microstructure parameters. The permeability of the considered refractory material was measured using a small sample of the material, where the flow of a test gas through the sample as a function of pressure gradient was determined. To consider the increasing permeability with decreasing amount of binder, permeability was measured before and after debinding; a linear interpolation between these two values was used for the FE-model.

FE-model

To describe the debinding numerically, a FE-model was developed in COMSOL Multiphysics using the results of the experimental characterization as input. As different kinds of physical mechanisms and chemical reactions are affecting each other during debinding, a coupled multiphysical formulation of the problem is required.

Firstly, an energy conservation formulation is used to describe the heating of the sample and the distribution of temperature during the heat treatment. The energy conservation is then combined with the Darcy equation for porous media to describe the flow of gaseous reaction products through the material and pressure buildup during the vaporization of binder.

Next, mass transfer due to interdiffusion effects and due to chemical reactions was considered in the model. Therefore, the above-mentioned coupled phenomena were combined for the numerical simulation with two additional equations for diffusive mass transfer and appropriate chemical reactions. In total, three different physical interfaces were used.

As shown in the flow chart of the simulation process in Fig. 1, each calculation loop (time step) starts with the temperature simulation, followed by finding the current solutions for gas flow and pressure, ending with chemical reactions and interdiffusion and an evaluation of mechanical stresses. The number of time steps used for the simulation of a given time-temperature cycle is balanced between the needed accuracy of the prediction of the debinding process and the calculation time. To keep the latter as short as possible, an efficient model which can be used for optimisation had to be created.

This was realized by (i) modeling only one eighth of the refractory brick using symmetrical constraints, and (ii) simulating the refractory brick without an explicit model for the surrounding environment (furnace). Instead, the interaction with the surroundings was modelled with well-established empirical equations.

Results

The measurements described in section 2 have been performed using small samples prepared from the fireclay green bodies to determine the required material parameters. With these as input, a FE-model as shortly described in section 3 has been set up. To verify the prediction of this model, an example debinding process of the fireclay material was performed applying a full-size brick in a special furnace, which was equipped with a weight sensor to determine sample weight in situ. The refractory brick was heated up to 800 °C applying a defined heating profile (see below) and the weight loss was measured continuously. In Fig. 2, the weight loss is shown and compared to the simulated results.

The graph shows that the simulation and experiment are in good agreement. The deviation in the first 2–3 h is explained with drying effects, which were not included in the simulation model.

Due to the successful validation of the FE-model, it can now be used to gain process details, which are needed to develop an efficient debinding process without deterioration of the product properties. In particular, the model enables the prediction of local state and progress of the debinding at any time and any position within the brick. Moreover, it is possible to analyse the evolution of local pressure throughout the process. In Fig. 3 the progress of debinding of the refractory brick is shown for four different times; the colour represents the binder content. Due to the chosen symmetry conditions, the bottom left corner of the shown cuboid is the center of the full brick.

It can be clearly seen how debinding proceeds from the outer to the inner regions. Simultaneously the permeability of the refractory material increases and the built-up pressure decreases. The evolution of the pressure with time can be used to predict possible damage within the material. As an example an alternative heating profile was created and the resulting prediction for the debinding process was simulated. In Fig. 4 the results of two simulations are compared. On the left side, the two different temperature profiles are shown. Temperature profile (a) is the original temperature profile, which was run during the validation experiments. Profile (b) is an example for a profile reducing process time considerably.

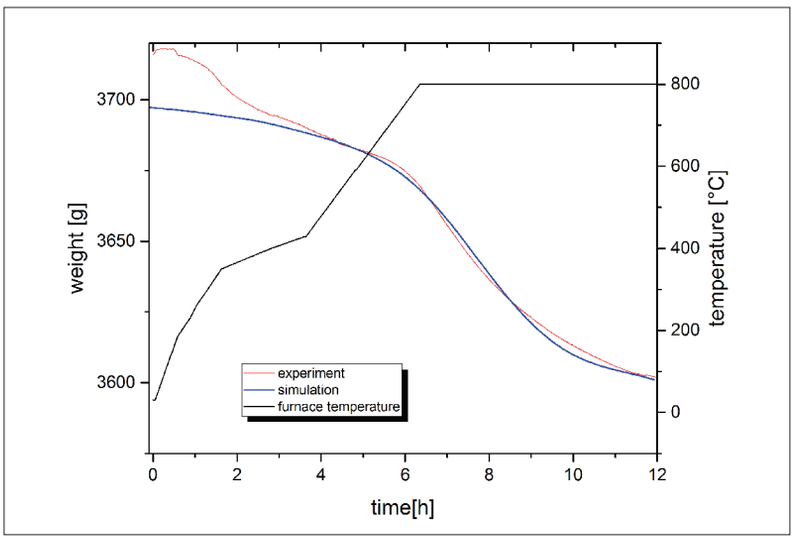

Fig. 2 Validation of the simulation model

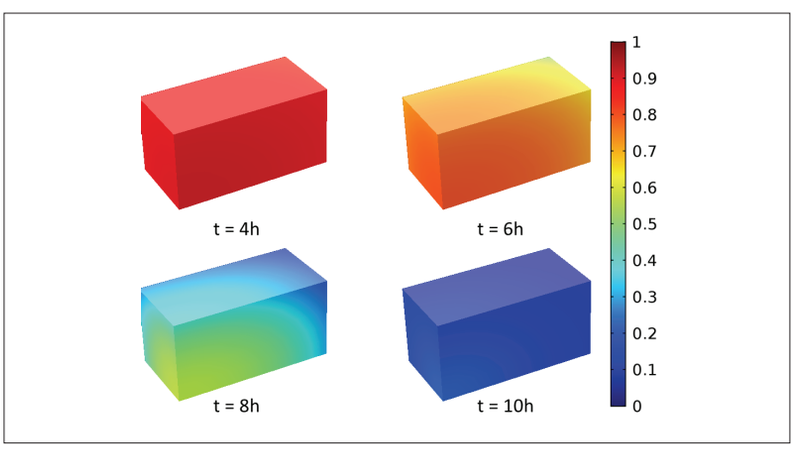

Fig. 3 Normalized binder content at different states of debinding

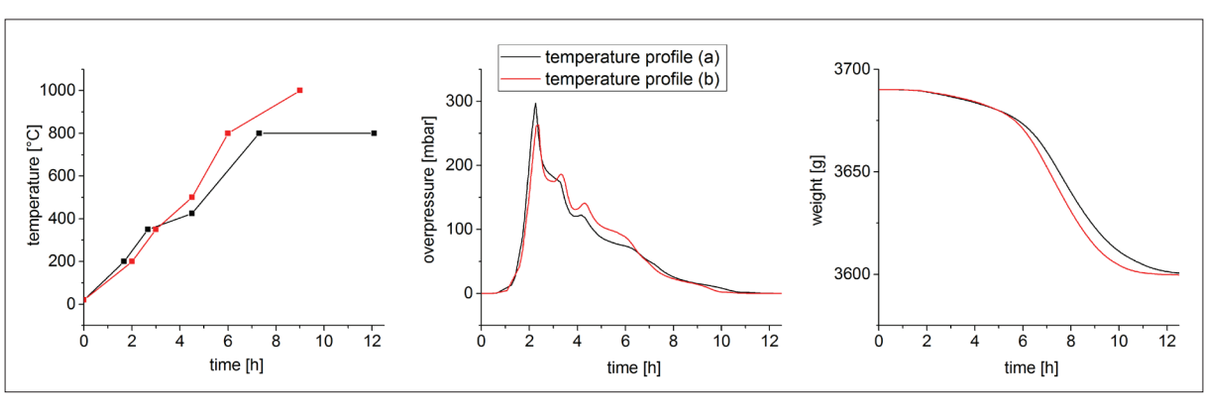

Fig. 4 Comparison of two different heating profiles

The concept for the new temperature profile (b) was developed by analysing in detail the modelling results. In a purely empirical approach one would argue that the occurring overpressure is directly related to the temperature profile, so that, simply spoken, higher heating rates will result in higher pressures.

Consequently, the overall heating rate would be decreased in case of material damage problems. By help of the FE-model it becomes possible to identify the critical time intervals with maximum pressure. In the example of temperature profile (a) a pressure peak occurs at around 3 h after the start of heating (graph in the middle of Fig. 4, black curve). The idea for temperature profile (b) was to increase the heating rate at stages with a lower pressure buildup, but to decrease the heating rate at time stages with a higher pressure buildup.

As seen in the figure, this approach leads even to a reduction of the maximum pressure.

The total process time, however, is reduced drastically: the calculated curves of weight loss for the two temperature profiles (right-hand side of Fig. 4) indicate a 20 % reduction of process time for complete binder removal.

Summary

It was shown by means of the example of a refractory brick that the debinding of green bodies of ceramic materials can be predicted by using a combination of in situ measurements and FE-simulations.

This example shows a systematical approach to determine the behaviour of ceramic samples during the debinding process. With this method, it is possible to enhance the performance of the debinding processes drastically by reducing the process time under consideration of occurring pressures within the sample.

References

[1] Raether, F.: The kinetic field – a versatile tool for prediction and analysis of heating processes. High Temperatures – High Pressures 42.4, 2013