Simulation of the Process Step Polymer Removal in Indirect Metal Laser Sintering

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Reviewed, accepted August 31, 2004

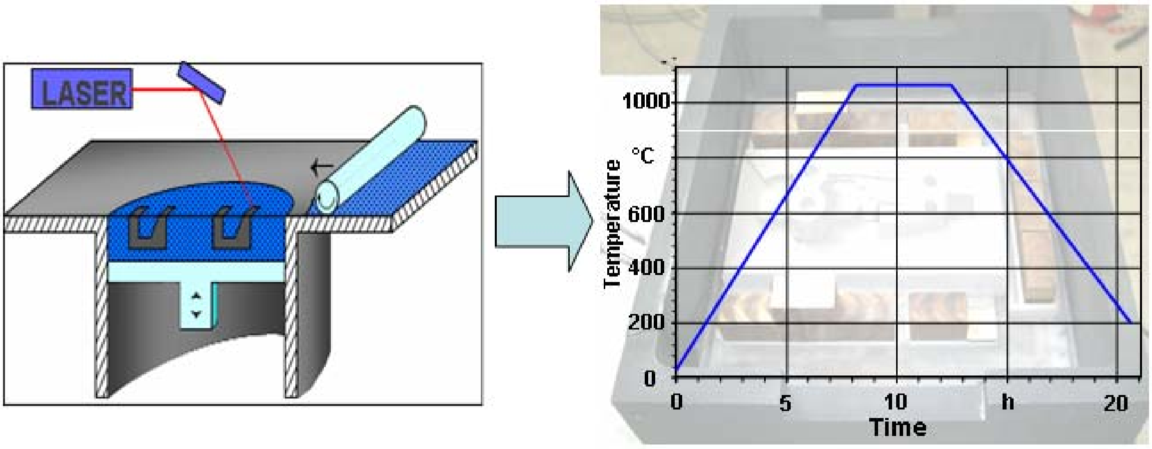
Abstract

With the Indirect Metal Laser Sintering and by means of a heat treatment in an oven process metal components can be produced. In the first step the polymer is transformed from the solid state into the gas phase. This takes place all over the component at different velocities depending on the local temperatures and temperature gradients. The creation of the gas phase develops a pressure inside of the component because the diffusion of the polymer within the part has a finite velocity. The pressure may contribute to a damage of the component. This essay deals with the procedure to simulate the gas pressure on the basis of the implementation of kinetic models in the Finite-Element-Analysis.

Introduction

The Selective Laser Sintering (SLS) process and the derived manufacturing process known as Indirect Metal Laser Sintering (IMLS) to produce metal parts were invented at the University of Texas in Austin [1].

The method is divided in two steps, the Selective Laser Sintering and the following oven process (Fig 1).



1. Selective Laser Sintering (SLS)

2. Oven Process

Fig. 1: Process flow of Indirect Metal Laser Sintering – Oven process

The base material is a metal powder coated with polymer. During Selective Laser Sintering a mechanism applies the powder layer by layer on a working stage. Subsequently a CO_2-Laser melts the polymer and agglutinates the particles within the layer. This procedure is repeated on the following layer whereas the laser agglutinates the particles within the new and also with the subjacent layer. Therefore a so called green body arises gradually.

Because of the metal particles being agglutinated only by the polymer, the green body is not rugged. A further step in the process, the oven process, is essential to reach mechanical strength properties similar to those of aluminum.

Thereby the green body is treated by heat. In the beginning the used temperature program heats with a heating rate of 2 Kelvin per minute up to 1070°C. This temperature remains for three hours before it is cooled down with a rate of 2 Kelvin per minute.

In doing so, different physical procedures take place during which a component is generated with a weight proportion of 60 % stainless steel and 40 % bronze. The green body contains approximately 2.5 % polymer, which are transformed into the gas phase and diffuse out of the metal component during the oven process.

Initial Situation

During a test series at the *iwb* application center in Augsburg near Munich to investigate the step polymer removal one test item was damaged (Fig. 2).

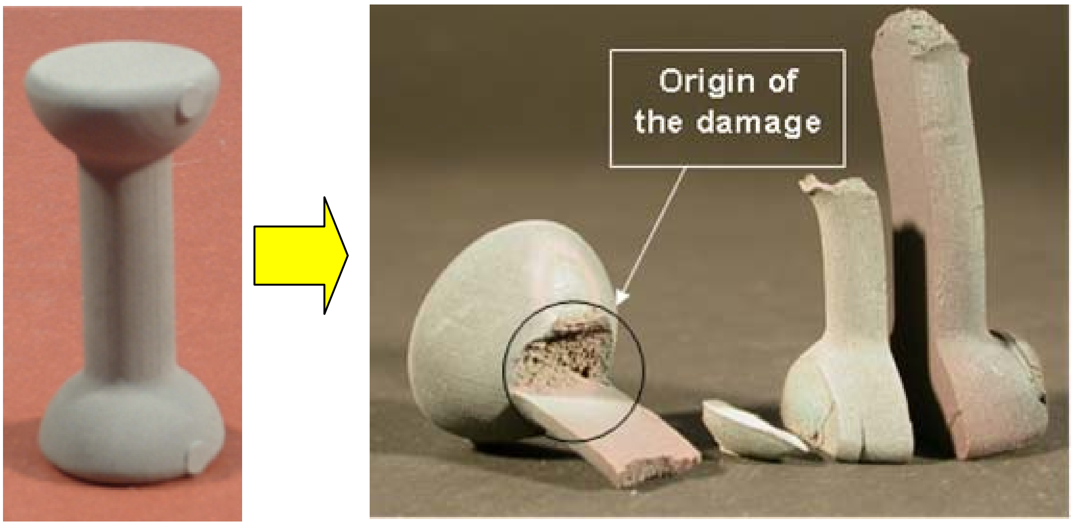


Fig. 2: Damage of a test item [2]

The following points were assessed as results from a more precisely examination of the damage:

- The origin of the damage is situated at the bottom of the component.
- The damage spreads out along the contact surface between two layers. Due to SLS there is only low strength at the contact surface.
- A formation of pores can be observed at the beginning of the damage (Fig. 3).

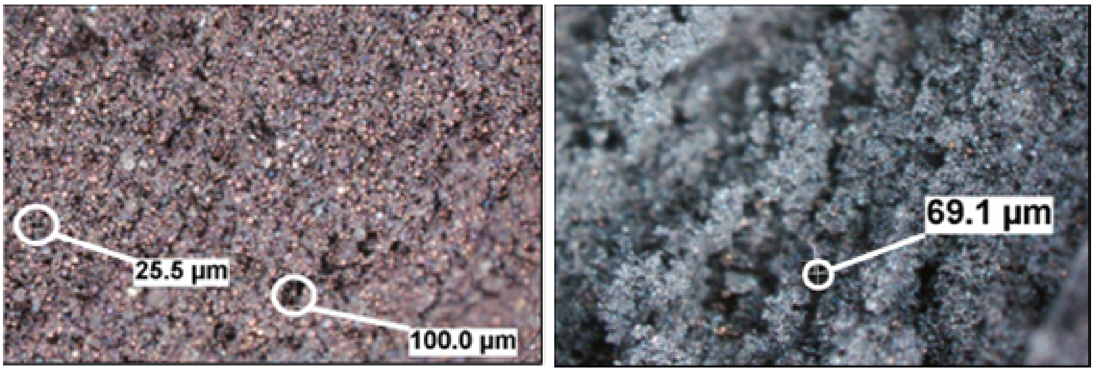


Fig. 3: Formation of pores at the fractured surface [2]

The reason for the formation of pores is to be found in the gasification of the polymer and the closely connected increase of the gas pressure within the component.

In the following it will be shown how the gas pressure leads to a damage of the component. Furthermore a procedure to predict the gas pressure within the component with the Finite-Element-Analysis will be described.

By gravimetric measurements a basis for a kinetic model of the process polymer removal must be established. For a better understanding of the formation of the kinetic model some basic principles of the reaction kinetic will be resumed.

Reaction Kinetic

For kinetic analysis of the chemical reaction equation (1) is generally assumed by

$$A_{solid} \rightarrow B_{solid} + B'_{gaseous} \quad (1)$$

with A_{solid} as edukt, B_{solid} as produkt 1 and $B'_{gaseous}$ as produkt 2.

In this case, it means that the source material of the green body turns into a solid and gaseous product. By using this equation no conclusions can be drawn about the course of the reaction. A description of the reaction kinetic is possible by means of mathematical models. The context between the conversion function U, depending on the reaction time t, the temperature T and the concentration of the reactant e and product p and the conversion of the reactant is the basis for the mathematical model.

$$\frac{de}{dt} = U(t, T, e, p) \quad (2)$$

Furthermore the conversion function can be described by two separated subfunctions:

$$U(t, T, e, p) = k(T(t)) \cdot f(e, p) \quad (3)$$

The Arrhenius-equation is supposed to be valid to describe the first subfunction:

$$k(T) = A \cdot \exp\left(\frac{-E}{RT}\right) \quad (4)$$

The differential equation for the concentration of mass reads as follows:

$$\frac{de}{dt} = -A \cdot \exp\left(\frac{-E}{RT}\right) \cdot f(e,p) \quad (5)$$

For one-step reactions (A→B) the function f(e,p) can be rephrased with the degree of conversion to the function F(x) [3]. There are presently 16 types of reactions available for a mathematical description of one-step reactions. Reaction types are e. g.

n^{th} order reactions: f(e,p) = e (6)

or

the Jander´s Type: $f(e,p) = 1.5*e^{1/3}(e^{-1/3}-1)$. (7)

The parameters, like the pre-exponential factor and the activation energy of each one-step reaction, are determined via a hybrid regularized Gauss-Newton method (Marquardt method) integrated into a Price-Dormand-Method (Runge-Kutta-Method 5th degree) with an automatic optimization of supporting points [4].
Combining more one-step reactions multiplies the describing possibilities (Fig. 4).

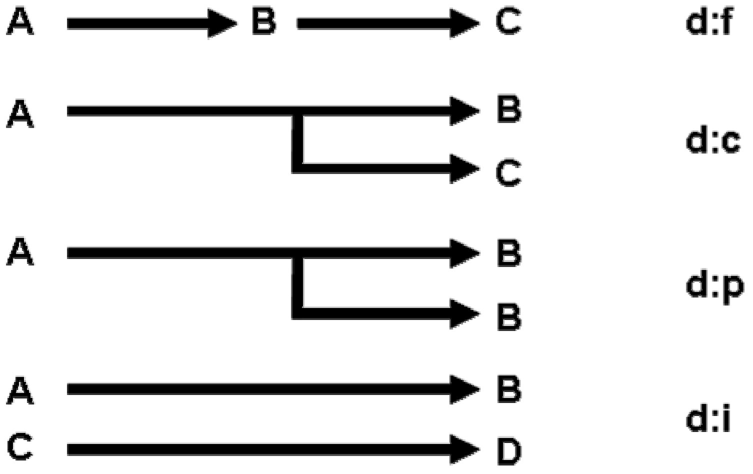


Fig. 4: Possibilities to combine one-step reactions

For a better handling each combination is represented by characters. The first character represents the number of subreactions (d=double). Due to software limitations only models with a maximum of 6 subreactions can be described at the moment [4].
The second and other characters provide information about the course of the reaction. The character f means follow. The start reaction from reactant A to product B is followed by a subsequent reaction. At present time 4 different subsequent reactions can be distinguished.

Abundant possibilities result from the combination of sub reactions with the different courses of subsequent reactions. 68 alternatives can be implemented into the Finite-Element-Analysis by means of the software Kinetics for Ansys [4].

For the evaluation of thermogravimetrical measurements the method of multivariate kinetic analysis can be applied.

The courses of mass loss versus temperature are not identical with different temperature gradients. Fig. 5 shows thermogravimetrical measurements of a green body with temperature gradients of 2.5 and 20 Kelvin per minute. Thus the reaction course of the gasification of the polymer depends on temperature gradients.

The multivariate kinetic analysis method allows to associate different courses of mass loss over the temperature with a kinetic model (Fig. 5). The software Thermokinematics (Fa. Netzsch, Germany) iteratively assigns a mathematical model to the real course of the chemical reaction of the process step polymer removal. According to the method of a genetic algorithm the mathematical model is enhanced to a supposable optimum.

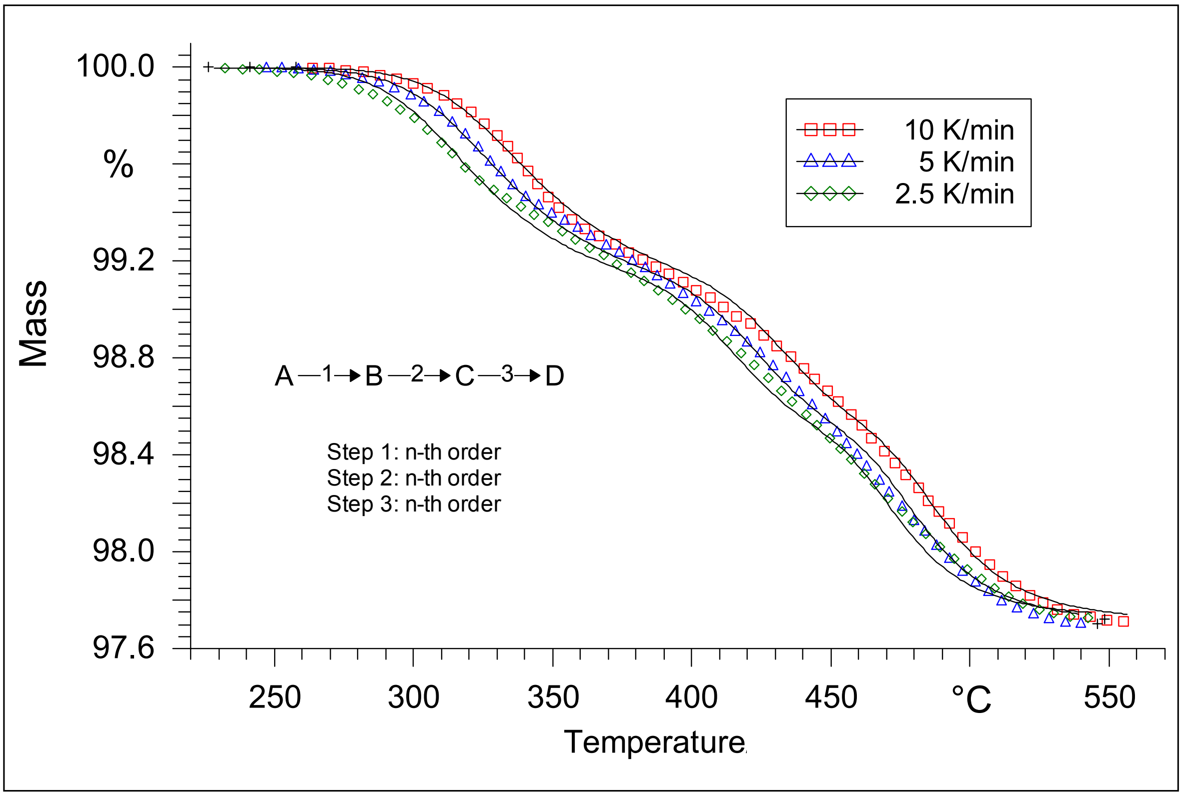


Fig. 5: Thermogravimetric measurements with different temperature gradients and the reaction kinetic model [2]

Thereby a kinetic description of the course, which is approximated to reality, is calculated. An exact chemical model cannot be generated as only one step reactions can be described due to limited mathematical possibilities. However, it is possible to determine the state of the chemical reaction at any time and with any temperature gradients within the limits of the measurements.

Implementation of reaction kinetics into the Finite-Element-Analysis

The software Kinetics for Ansys implements the kinetic model into the Finite-Element-Analysis (FEA). The kinetic model from the thermogravimetrical measurements (Fig. 5) belongs to a three-step reaction with two following subreactions (**t**riple – **f**ollow – **f**ollow) [1].

$$A \rightarrow B \rightarrow C \rightarrow D \tag{8}$$

To clarify the situation the model can be implemented in Ansys and transferred to a single element of the FEA software. The element is charged with a temperature gradient according to a measurement (Fig. 6).

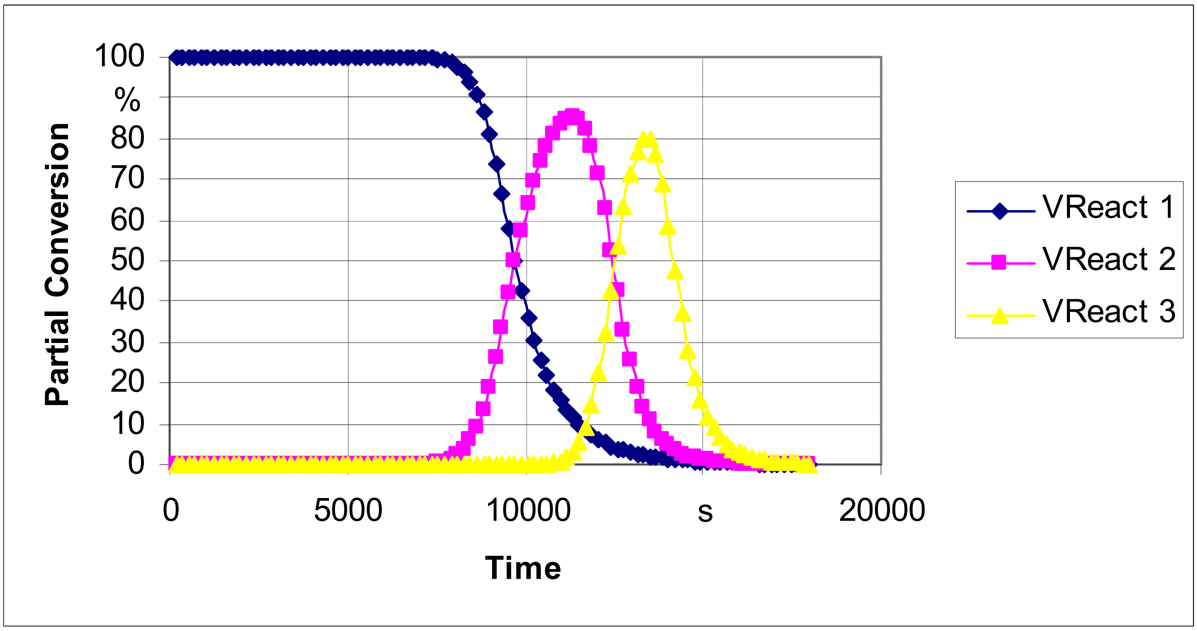


Fig. 6: Course of the kinetic model

Fig. 6 shows that the reactant (VReact 1) changes into a first interstage product (VReact 2) according to the three-step model. At a certain temperature this interstage product turns into a second interstage product (VReact 3). Every subreaction and thus the whole reaction is finished. Remaining is the final product shown as the character D in (8). This proves that the course of the calculated chemical reaction by FEA remains the reaction kinetic model in (8).

However, this is only the reaction course of an approximately described reaction and it is not possible to draw a conclusion concerning the real chemical reaction during the process step polymer removal.

The mathematical description allows to represent the state of the chemical reaction at any time (Fig. 6). In addition it is possible to describe the gradient of mass loss as well (Fig. 7).

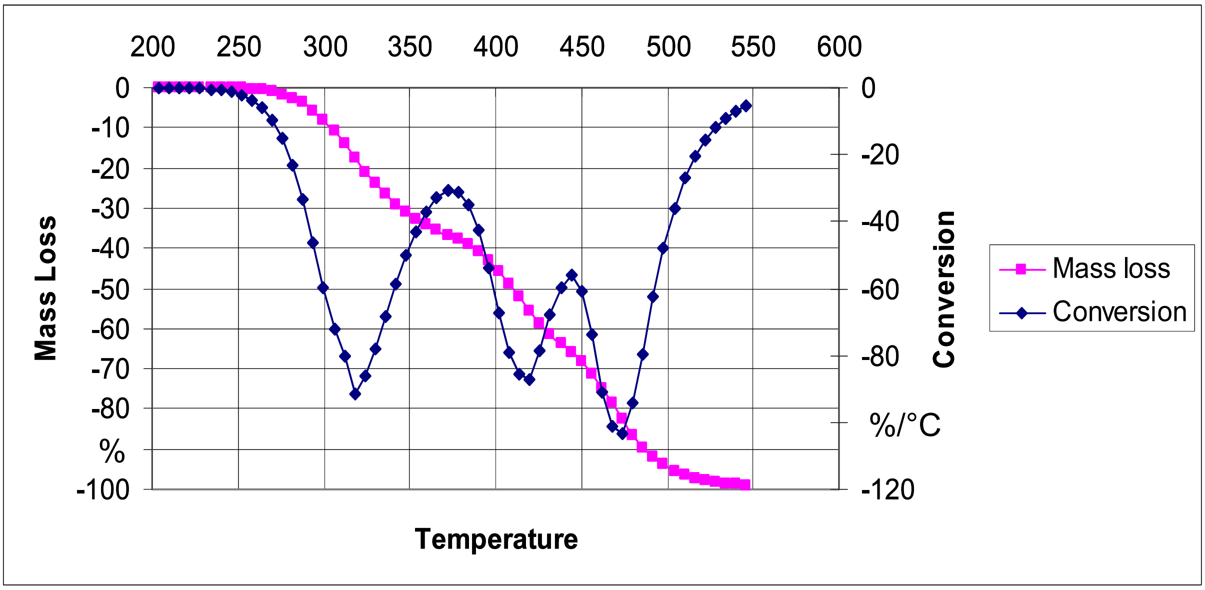


Fig. 7: Conversion and mass loss versus time correlated to temperature

Fig. 7 shows the conversion and the mass loss of the kinetic model implemented in Ansys versus time. The kinetic description of the chemical reaction during the process step polymer removal allows predicting the conversion and mass loss with any temperature gradient. Upper and lower limits are constrained by the maximal and minimal heating rates of the measurements.

The qualitative course of the mass loss in Fig. 7 is identical to the thermogravimetric measurement with a temperature gradient of 2 K/min in Fig. 5. The conversion is the mass loss per time. The mass loss is calculated through integration of the conversion.

Because of the formal description of mass loss by the multivariate kinetic analysis the qualitative course of mass loss can be predicted with different temperature gradients. For the ordinate scale changing between 0 and 1 it is not possible to display the absolute course of the mass loss. The mass loss and the conversion will be used to predict the concentration of the gas within the test item.

Temperature field simulation

The thermogravimetrical measurements reveal the mass loss and therefore decomposition of the polymer as a thermal activated reaction. Calculating conversion and mass loss within the test item requires modelling the temperature field in order to carry out the polymer removal simulation afterwards (Fig. 8).

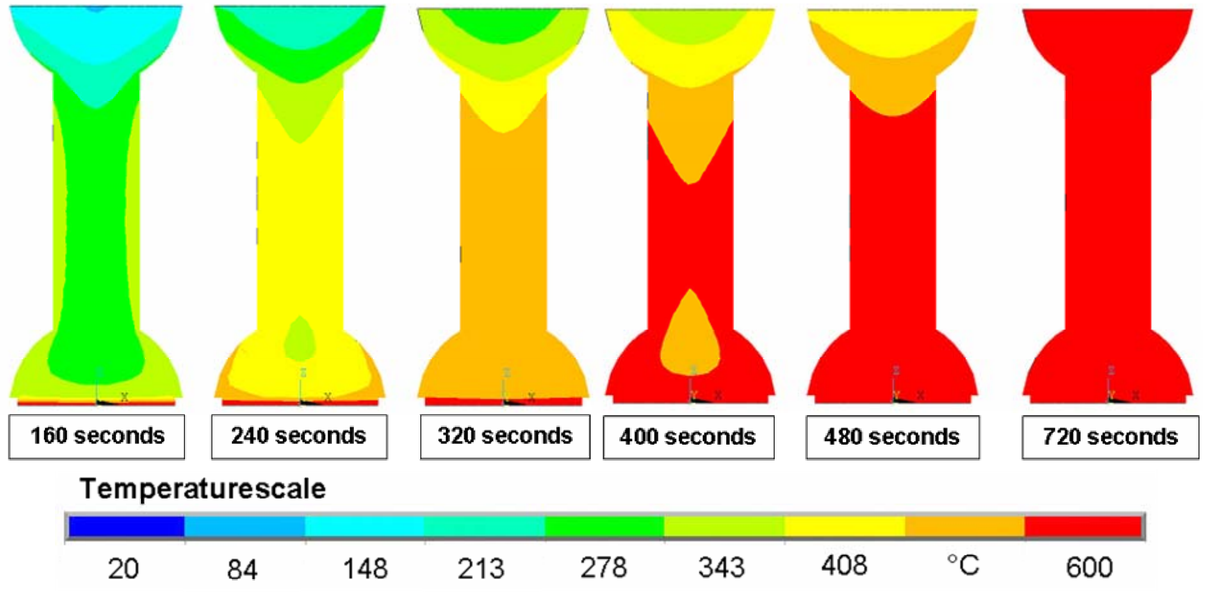


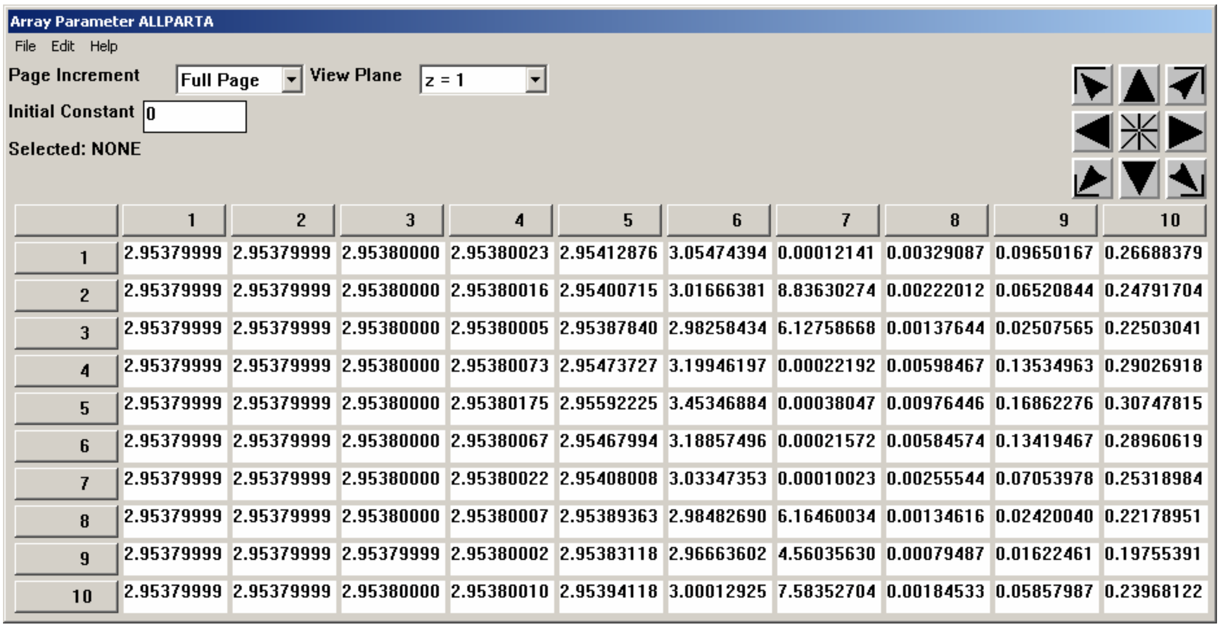
Fig. 8: Temperature field simulation on the test item

Fig. 8 shows the temperature field simulation on the test item from Fig. 2 represented in the section through the rotation axis. Heat transmission was adapted to the real situation. The bottom of the test item was located on a ceramic plaque standing on the ground of the oven. The outer face of the test item is only affected by radiation. The radiator temperature corresponds to the oven temperature.

The highest temperature gradients and therefore the highest thermal stress are situated at the top of the test item after about 400 seconds. Besides it is known that the green bodies have the lowest strength at the glass transition temperature of the polymer. In the current simulation the glass transition temperature is reached after about 160 seconds. At this time the highest temperature gradients are located at the top of the test item as well. Thus the thermo mechanical stress does not deliver any explanation for the damage at the bottom of the test item.

Calculation of the kinetic reaction within the test item

Based on the thermal simulation and the kinetic model of the test item it is possible to determine the actual state of the reaction and thus the conversion and mass loss at any time for any element of the model. For a later utilization the software accumulates all data in a three-dimensional vector, an array (Fig. 9).



Page Increment Full Page View Plane z = 1

Initial Constant 0

Selected: NONE

	1	2	3	4	5	6	7	8	9	10
1	2.95379999	2.95379999	2.95380000	2.95380023	2.95412876	3.05474394	0.00012141	0.00329087	0.09650167	0.26688379
2	2.95379999	2.95379999	2.95380000	2.95380016	2.95400715	3.01666381	8.83630274	0.00222012	0.06520844	0.24791704
3	2.95379999	2.95379999	2.95380000	2.95380005	2.95387840	2.98258434	6.12758668	0.00137644	0.02507565	0.22503041
4	2.95379999	2.95379999	2.95380000	2.95380073	2.95473727	3.19946197	0.00022192	0.00598467	0.13534963	0.29026918
5	2.95379999	2.95379999	2.95380000	2.95380175	2.95592225	3.45346884	0.00038047	0.00976446	0.16862276	0.30747815
6	2.95379999	2.95379999	2.95380000	2.95380067	2.95467994	3.18857496	0.00021572	0.00584574	0.13419467	0.28960619
7	2.95379999	2.95379999	2.95380000	2.95380022	2.95408008	3.03347353	0.00010023	0.00255544	0.07053978	0.25318984
8	2.95379999	2.95379999	2.95380000	2.95380007	2.95389363	2.98482690	6.16460034	0.00134616	0.02420040	0.22178951
9	2.95379999	2.95379999	2.95379999	2.95380002	2.95383118	2.96663602	4.56035630	0.00079487	0.01622461	0.19755391
10	2.95379999	2.95379999	2.95380000	2.95380010	2.95394118	3.00012925	7.58352704	0.00184533	0.05857987	0.23968122

Fig. 9: Array of conversion of mass loss

Fig. 9 shows a two-dimensional sector of a three-dimensional array of the FEA-software Ansys which contains the conversion of mass loss. Further considerations are essential for predicting the gas concentration and pressure within the test item: Both heat transport and diffusion can be calculated with the Poisson differential equation. Further descriptions can be found in the literature [5; 6; 7].

$$\boxed{\nabla(\lambda\nabla\Phi) = R} \qquad (9)$$

∇	Nabla-Operator
λ	Conductivity
Φ	Power function
R	Right side

Further reading gives hints on the analogon of the presented physical principles [5; 6; 7]. Taking the units into account it is possible to calculate the diffusion analog to the temperature field. The following is to be considered:

Analogon

Temperature field

$$\dot{q} = \frac{\dot{Q}}{A} = \frac{\lambda}{\delta}(T_1 - T_2) \qquad (10)$$

Diffusion

$$j = \frac{J}{A} = \frac{D}{d}(C_1 - C_2) \qquad (11)$$

$\dot{q}$	Heat flux density	j	Diffusion density
$\dot{Q}$	Heat flux	J	Diffusion amount
A	Area	A	Area
λ	Thermal conductivity	D	Diffusion coefficient
δ	Length	d	Length
T	Temperature	C	Concentration

Thus it is possible to calculate the gas diffusion at the step polymer removal analog to the temperature field. Thermogravimetrical measurements reveal mass loss of the polymer. With a weight of approximately 40 mg the test parts are small enough to assume an immediate gasification of the polymer. As a consequence mass loss can be set equal to the polymer gasification.

Implementing a kinetic model in the Finite-Element-Analysis allows to determine the mass loss and the conversion degree of mass loss at any time. Therefore the conversion degree of mass loss corresponds to polymer gasification. As a result of integrating each degree of conversion this can be assumed as well for mass loss and gasification of polymer.

Simulation of Diffusion

Calculating the gas concentration inside the test item requires a simulation of diffusion with a gas creation which depends on the temperature of the elements. Thus, the outer nodes of the test item elements are loaded with the concentration zero. This signifies no existing gas concentration in the surrounding area.

Temperature field calculation can take heat into account, which is produced within the test item e.g. by an electric resistance. The denomination is heat generation in watt/volume.

Analogously gas production can be assigned to an element in the diffusion calculation. The denomination here is the gas production rate in diffusion amount/volume.

Each element obtains a gas production rate as body-force-load. The kinetic model and the temperature field simulation with a subsequent calculation of the state of the chemical reaction at any time allow assigning a qualitative course of its gas production rate to each element. The results of the simulation of diffusion are shown in Fig. 10:

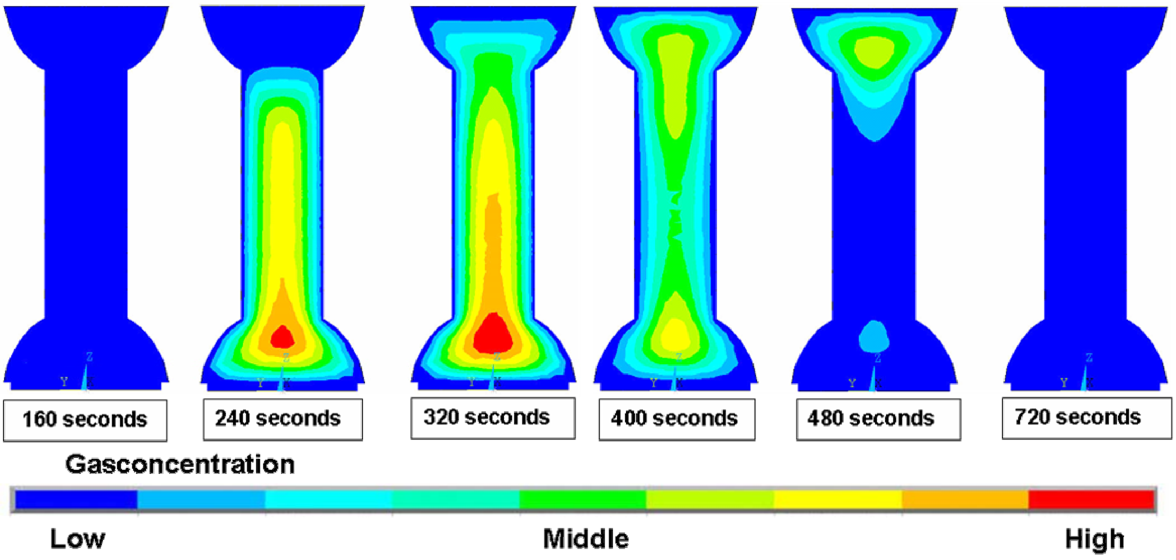


Fig. 10: Results of the diffusion simulation

Fig. 10 shows the gas concentration within the test item represented in a section through the rotation axis. The ideal gas behaviour assumes a direct proportionality between gas concentration and pressure within the test item. Applying kinetic analysis and the consequent qualitative evaluation of the gas production no more conversion between gas concentration and pressure is required, but it is not possible to determine the absolute gas pressure. Only its qualitative course can be predicted. Fig. 10 reveals the remarkable fact that the inner gas pressure reaches its highest level after about 320 seconds at the same position as the real test item was damaged. At the top of the test item the maximum pressure remains considerably lower.

Conclusions and future developments

The presented procedure allows predicting the course of gas pressure within a component during the process step polymer removal. Thereby it is possible to analyse any temperature program. Method limitations are given by the kinetic model and the extremes of temperature gradients during thermogravimetric measurements. Heating rates of 50 K/min were used. A very high gas pressure and a high thermal load damaged the green body. Damages as shown in fig. 2 are generally not known because the conventional oven process has heating rates of 2 K/min. From an economic point of view it is essential to reduce the entire process time. This means higher heating rates and a higher gas pressure within the part. This essay shows a procedure to optimize temperature programs concerning the gas pressure inside the component.
Furthermore the process can be applied to any thermal reaction in which a part of the basic substances is turned to gas and subsequently diffused out as e. g. during the production of ceramics.

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The present work was promoted by the German Research Society (DFG), by CADFEM GmbH (Germany) and Netzsch Gerätebau GmbH (Germany).