

Analysis and Optimization of the Binder Burnout of 3D-Printed Ceramic Components

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The production of sophisticated ceramic components by means of 3D printing is becoming increasingly important in modern industry. Thanks to this method, prototype production or the manufacture of small series can be realised much faster and more efficiently compared to alternative or traditional ceramic manufacturing processes. Customer specific mass production of complex ceramic components was already realised, as well. The worldwide technology and market leader in the field of lithographic 3D-printers of ceramic components is Lithoz GmbH/AT. Through interdisciplinary collaboration between specialists from the fields of mechanical engineering, process engineering and chemistry, Lithoz has succeeded in developing a manufacturing system with which ceramics for industrial and medical applications can be generatively manufactured.

Introduction

In Lithography-based Ceramic 3D Manufacturing (LCM), a dispersion is manufactured by mixing a ceramic powder with a light-curing liquid binder. This dispersion is then exposed to light layer by layer so that a three-dimensional ceramic green body is obtained over time. The green body is then heat-treated in a furnace, where the organic binder is burned out. Subsequently, the debinded green body is sintered at a higher temperature and the final ceramic component is obtained. Examples for 3D-printed ceramic parts are shown in Fig. 1 [1]. The heat treatment has decisive influence on the structure and properties of the final product. Too fast debinding can lead to cracks in the structure, which will not anneal during sintering. In this work; a nearly pure alumina green body was investigated using thermal analysis techniques to gain deeper insight into the binder burnout. The results obtained can be used to optimize temperature control, avoid structural damage during heat treatment and thus design efficient manufacturing processes.

Ceramic 3D printing is becoming increasingly important in various applications today. For example in the production of ceramic implants in medical technology or special applications in aerospace. Com-



Fig. 1 Components, manufactured by means of a Lithoz 3D printer (Source: Lithoz) [1]

plex ceramic parts need to be produced in low quantities. However, highly specific components with low volume cannot be manufactured efficiently using conventional ceramic mass production processes such as slip casting, injection moulding or dry pressing. This is where 3D printing delivers clear advantages. CAD drawings or other three-dimensional data models can be transferred directly to the printer and the ceramic green body is produced in just a few hours. Beside the printer, no special tools or moulds are required. In addition, prototypes and modifications can quickly and easily be produced to check whether the part fits optically or is suitable for future applications.

One of the world's leading manufacturers of corresponding printers is Lithoz GmbH from Austria [1]. Designed for industrial manufacturing, the Lithoz 3D printer, applying

LCM technology, allows for reliable production of additively manufactured ceramics. The mechanical performance, dimensional accuracy, and reproducibility of ceramic components meet or even exceed those of conventionally manufactured components.

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Keywords: binder burnout, simulation, thermal analysis, thermogravimetry, 3D-printing



Fig. 2 Lithoz CeraFab multi 2M30 3D printer (Source: Lithoz) [1]



Fig. 3 Netzsch STA 449 F3 Jupiter model with mass spectrometer coupling

Powered by LCM technology, Lithoz's industry-oriented 3D printers are the answer to the reliable serial production of additively manufactured ceramics. An example of a Lithoz printer is shown in Fig. 2. The CeraFab printer systems fulfil even the toughest requirements of high-performance ceramics. Mechanical performance, dimensional accuracy and the reproducibility of ceramic parts have proven to meet and exceed conventional ceramic methods.

Starting with a CAD model, the first step of the process is the job preparation and optimization. The information for the job is digitally transferred to the 3D printer directly from the computer. The ceramic-loaded liquid (or slurry) is automatically dosed and coated on top of a transparent vat. The movable building platform is dipped into the slurry, which is then selectively exposed to light from below the vat. The layer image is generated via a Digital Micromirror Device (DMD) coupled with a state-of-the-art projection system. By repeating this process, a three-dimensional green part can be generated layer-by-layer.

The LCM technology leverages decades of ceramic powder processing experience. By using the same powders and furnaces as injection moulding, ceramic parts with outstanding mechanical properties and surface quality can be produced. Following thermal post-processing steps, the binder is removed and the green parts are sintered, resulting in fully dense ceramic parts [2].

Netzsch-Gerätebau GmbH from Selb/DE, develops, manufactures and distributes measuring instruments for thermal analysis and measurement of thermophysical properties. Especially in the field of high-temperature applications and ceramics, Netzsch is the global technology and market leader. By means of Netzsch thermobalances and STAs (Simultaneous Thermal Analysers), mass losses during burnout of organic binders and/or the release of energy during combustion of the binder can, for example, be exactly characterised. In connection with a mass spectrometer coupling, the composition of the gases released can be also be investigated. By varying the size and shape of the green body, the heating rate during debinding and by changing the gas composition, details of the binder decomposition/ and combustion process can be determined. An example of a thermobalance, coupled to a mass spectrometer, is presented in Fig. 3. By using mathematical post-processing of the measurement data, the kinetic parameters of the debinding process can be evaluated and simulations are possible to determine the material behaviour in a real production kiln.

Within the scope of this work, 3D-printed green bodies of nearly pure alumina were investigated. During the tests in the thermobalance, the influences of the sample shape (crushed or solid test specimen) on the binder burnout were examined.

Additionally, decomposition/burning of the binder was measured at different heating rates. Those results were analysed using a Thermokinetics Software package.

Based on this, temperature profiles allowing for efficient and damage-free removal of the binder from the green body can be determined. For more information on the measuring techniques employed, see, for example, [3, 4].

Results and discussion

First, thermogravimetric studies on the samples were performed between room temperature and 800 °C under air. The measurements were carried out at a heating rate of 5 K/min in a dynamic air atmosphere at a flow rate of 40 ml/min. Fig. 4 shows the results on a printed rectangular block (solid sample) with an edge length of about 5 mm.

Initially, small amounts of surface water are released up to ~100 °C, followed by further evaporation effects (humidity, low molecular hydrocarbons) up to 180 °C. The mass fraction here is approximately 0,5 %. This means that a large part of the water present during printing has already evaporated due to the subsequent storage at room temperature. Right after this, the multiple-step decomposition of the organic binder can be seen between approximately 180 °C and 550 °C.

Three clear mass loss steps of 8,33, 10,56 and 1,74 % respectively, could be evalu-

ated. Anyhow, the structure of the steps indicate that the binder decomposition and oxidation might be even more complex. Above 550 °C, evaporation and decomposition of the binder is completed and the mass of the green body remains stable. Compared to conventionally manufactured ceramic green bodies, the binder content of approximately 21,2 % is very high.

Fig. 5 shows the comparison of two measurements on the same alumina material, once as the formerly shown solid material and once as a crushed powder. The first step again corresponds to the dehydration of slight amounts of water. In both cases, decomposition starts at approximately 180 °C and occurs in multiple steps. However, the decomposition reactions, particularly in the second step, run much faster for the crushed material. The larger surface area of the powder allows for faster evaporation of the binder components and decomposition products. Additionally, oxygen accessibility is increased and oxidation reactions take place faster. This means for industrial manufacturing that oxygen restrictions and wall thicknesses of the components can shift binder degradation to higher temperatures. In both cases, however, the binder is entirely removed from the component at 550 °C, resulting in approximately the same mass losses.

In further investigations, the powder samples, where the decomposition reactions occurred earlier, were examined at different heating rates between 2,5–20 K/min (Fig. 6). As expected, all decomposition and oxidation reactions are shifted to higher temperatures with increasing heating rate. However, neither the course nor height of the steps reveal significant differences. Thus, the heating rate has no relevant influence on the reaction flow. For all tests, nearly the same final mass loss was achieved. Of course, this is expected as in no case residual binder should remain in the ceramic green body.

Using the measurement data at different heating rates, the kinetic parameters of the decomposition reaction can then also be determined by means of the Netzsch Kinetics Neo Thermokinetics Software Package [6]. The results of the kinetic model are depicted in Fig. 7, together with the measurement results. As can clearly be seen, the test results (symbols) can be described ac-

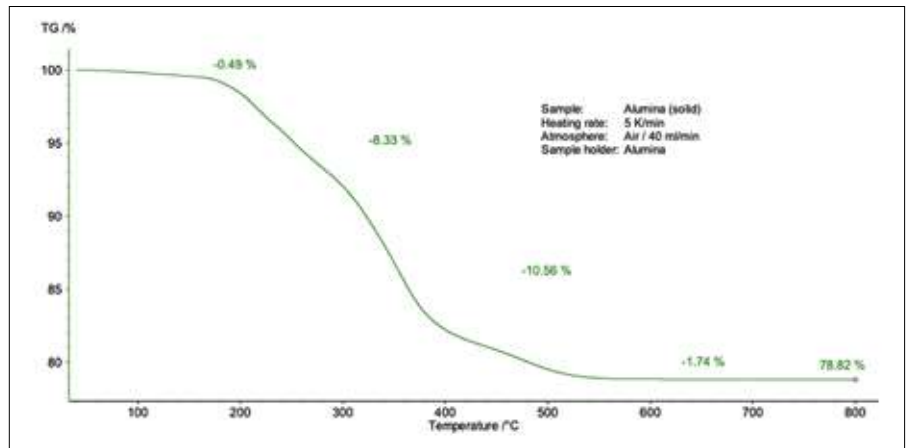


Fig. 4 Mass change of a 3D-printed, solid rectangular alumina green body (approximately 5 mm edge length) between room temperature and 800 °C

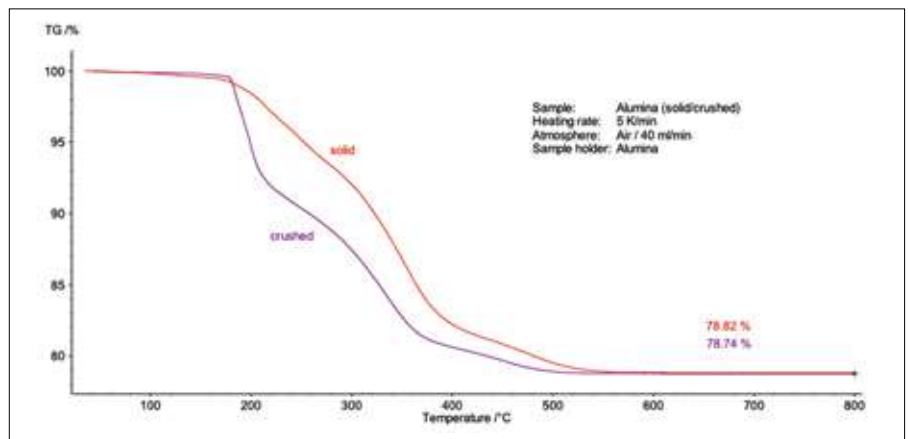


Fig. 5 Mass change of a 3D-printed alumina green body, 5 mm, between room temperature and 800 °C (comparison of a solid and a crushed sample)

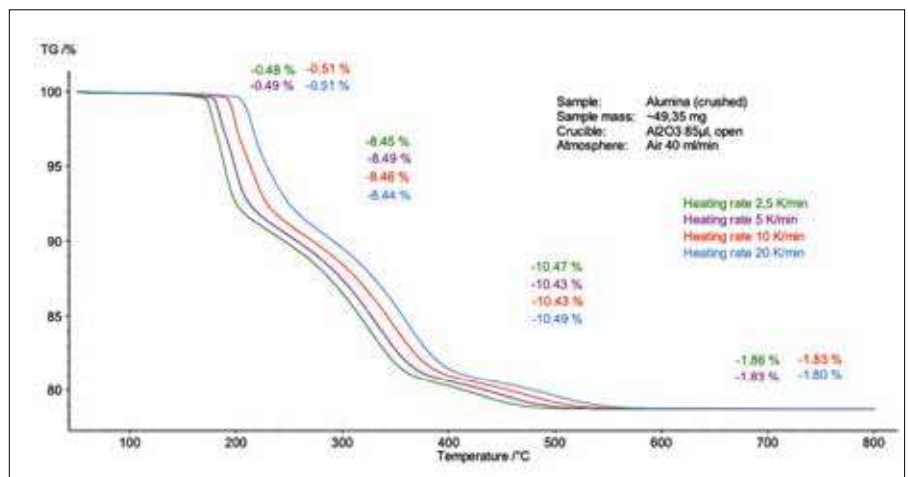


Fig. 6 Mass change of a 3D-printed alumina green body at different heating rates between room temperature and 800 °C (powderized sample)

curately by means of a five-step reaction (solid lines). Applying less reaction steps did not allow for accurate description of the measurement results.

This data is in line with the mass loss results and the results of the simultaneous thermal analyser shown later. The reaction types used to describe the measurements consist

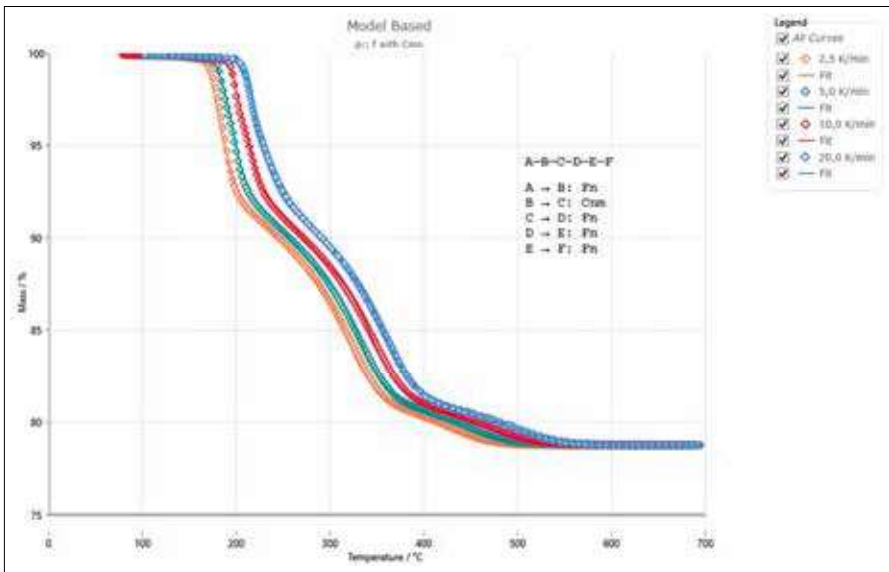


Fig. 7 Description of the binder burnout by means of thermogravimetry and thermokinetic analysis

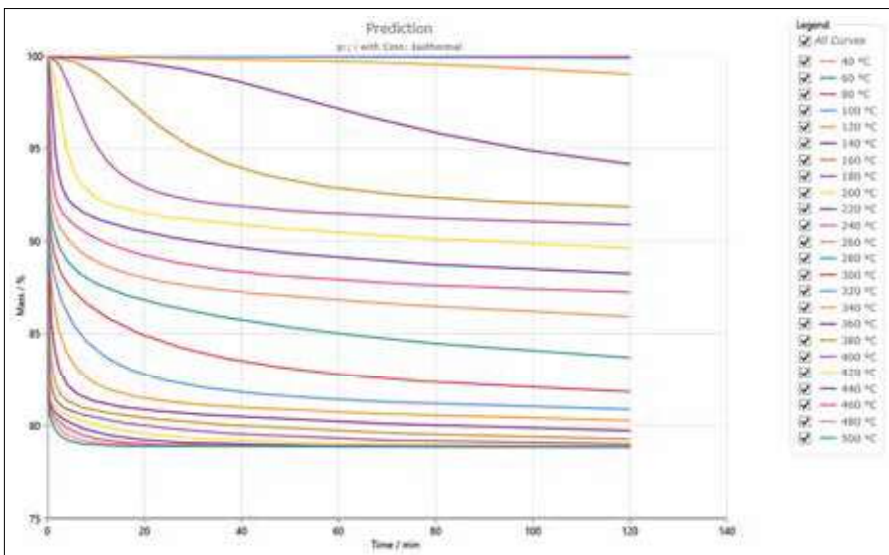


Fig. 8 Simulation of debinding at different isothermal steps between 40–500 °C, calculated with the Netzsch Kinetics Neo software package

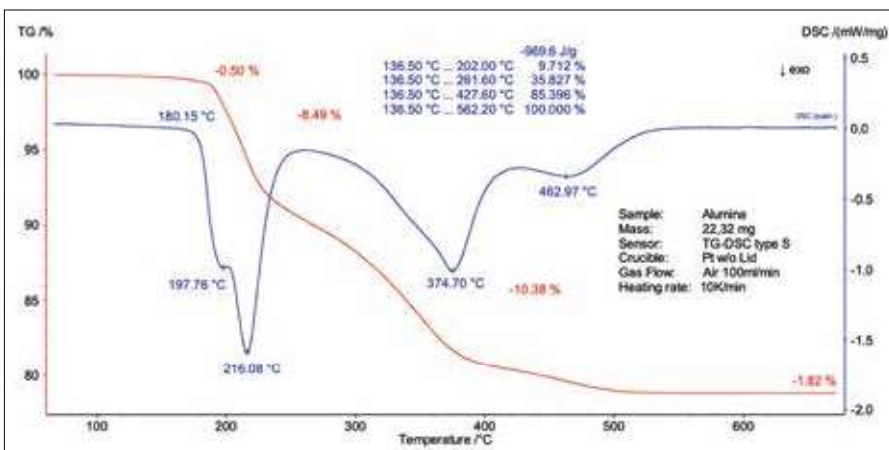


Fig. 9 Mass change and energetic effects (DSC signal) of a solid alumina green body, measured with an STA

of nth order and autocatalytic reactions. This reaction types are typical for decomposition or oxidation reactions of organics. Based on this data, optimum firing profiles can be established in order to remove the binder from the green body as effectively and gently as possible.

It is feasible, for example, to simulate how debinding proceeds at a step-wise isothermal temperature profile or a complex temperature program with various heating and isothermal steps. Examples for this can be found in [6].

Fig. 8 depicts a simple example for a simulation of debinding at different isothermal temperatures. The mass loss was simulated between 40–500 °C in steps of 20 K for a period of 2 h. As expected, only the water release is visible up to 100 °C, which is related only to a small mass loss. With increasing isothermal temperature, the mass loss increases significantly. At high temperatures, the mass loss happens nearly immediately. From such simulation, a temperature profile, where debinding occurs slowly enough at each step in order to avoid structural damage (cracks in the component), can be estimated. For example, isothermal temperatures at 160, 260, 300 and 400 °C respectively, would allow smooth debinding of the material in a production furnace. Of course, depending on the production furnace type and control, estimated temperature regimes can be pre-checked in the software and optimum heating steps and isothermal temperatures can be calculated.

Fig. 9 illustrates a measurement on a solid sample by means of Simultaneous Thermal Analysis (STA) [4]. Along with the mass change, also the DSC signals on the same sample and under the same conditions are obtained. The measurement was carried out at 10 K/min in a dynamic air atmosphere between room temperature and 700 °C. A higher gas flow rate of 100 ml/min was applied for the measurement to compensate differences in the inner size of the measurement system and thereby achieve comparable conditions as for the former thermogravimetry tests. The contribution of the specific heat capacity to the DSC signal was removed from the curve by subtracting a second measurement on an already debinded sample.

The mass changes (red line) correspond to the results of the thermogravimetry meas-

urements, shown earlier (Fig. 1). The blue curve shows the DSC results, in which energy absorption and release can be seen. At 180 °C, the exothermal combustion of the binder component starts. The decomposition and oxidation takes place in several steps, which can clearly be seen from the overlapping DSC peaks. Maxima in energy release are shown at 198, 216, 375 and 463 °C respectively. The peak at 375 °C is preceded by a shoulder in the range of 320 °C.

This is an indicator that two decomposition effects are overlapping here, which, in turn, is in good agreement with the results achieved by the kinetic analysis.

These, as stated above, already verified that the description of the binder burnout required more than four steps. In total and related to the original weight, an amount of heat of 970 J/g is released during combustion. This value must also be taken into consideration in the industrial process since this can possibly (if sufficient oxygen is available) lead to local hotspots, which could cause structural damage to the green body. Fig. 10 depicts a measurement carried out with an STA coupled mass spectrometer (only mass changes and the most important mass spectrometer signals are depicted here). This measurement delivers a deeper insight into the nature of the gases released during binder burnout. The measurement was carried out up to 800 °C at 10 K/min under synthetic air. It vividly shows that mainly carbon dioxide and water are released during combustion.

Water (mass number 18) can primarily be seen during the first decomposition steps up to 420 °C. Carbon dioxide (CO₂, mass number 44) is visible during each step. However, the release of organic molecular fragments

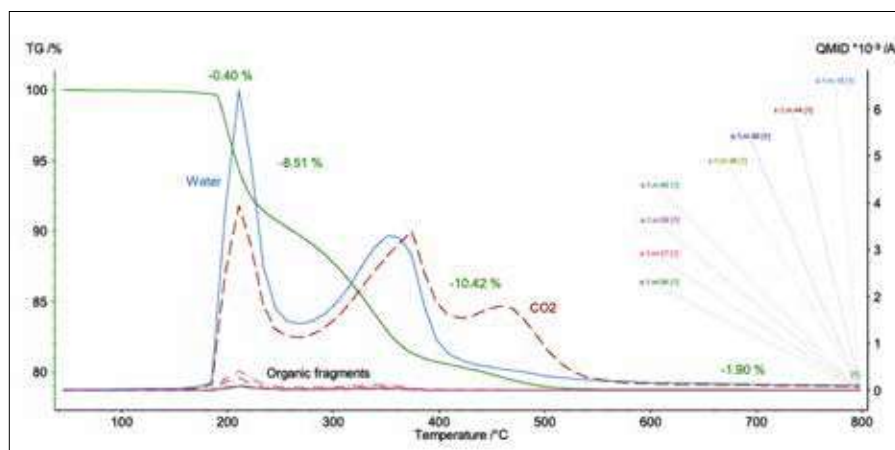


Fig. 10 Mass change and mass numbers from a mass spectrometer

(mass number 38, 39 or 56–60 respectively) is also evident in the temperature range between 180–400 °C. Associated fragments or trace gases are, of course, visible, as well, but not shown in this picture. The fact that some organic volatiles are not completely oxidized and simply evaporate is important in practice when larger amounts of such ceramic parts are fired simultaneously.

Summary

By means of thermal analysis (Thermogravimetry, Simultaneous Thermal Analysis, Evolved Gas Analysis), the burnout of organic binder from 3D-printed alumina components, can be comprehensively investigated. The results obtained deliver deep insight into the exact course and temperature range of the binder decomposition and oxidation.

With extended analysis methods such as a thermokinetic analysis software, it is also possible to determine the decomposition kinetics, which, in turn, allows for simulations and predictions on the alternative temperature traces or simulation of decom-

position/combustion in the production furnace. Along with the investigation of mass changes, simultaneous thermal analysis allows for determination of the heat release during binder burnout. Using evolved gas analysis, the gases released during binder burnout were characterised.

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