Voxeljet AG

3-D-printed sand core (left) and final casted part (right).

Additive Manufacturing

Slurry-based 3-D-printing of Casting Cores

Additive Manufacturing (AM) allows for the production of complex casting cores e.g. made from sand. Especially the Binder Jetting technique enables a production in an efficient way. However, the part produced generally exhibits a high surface roughness and limited mechanical strength. Slurry-based AM, however, offers the potential for producing mechanically stable, complex and filigree casting cores with a low surface roughness for the investment casting of complex hollow shapes such as e.g. cooling channels.

By Joachim Vogt and Marina Stepanyan, Bayreuth, Patricia Erhard and Daniel Günther, Garching, Sebastian Schmalzl, Friedberg, and Sven Gläser, Neukirchen

In the ZIM-project „Development of a digital production process for the economical production of systems for close-contour printing“ funded by the German Ministry of Economics, the whole process chain ranging from material development to prototype printers is set up. Quartz slurries have been developed as the feedstock material. These have been processed in self-developed test and prototype 3-D printers in order to produce homogeneous, dried powder bed layers as a building material. In parallel, green samples have been produced via slip casting, which were then analyzed concerning sintering behavior, density, and mechanical strength.

Introduction

Modern demands on technical constructions are largely derived from the energy consumption of the end products and from environmental aspects. The foundry technology, as a production method of mass production, accommodates this. Due to the high possible complexity of the parts, lightweight constructions are achievable that can save large amounts of energy during the use of the product. In addition, with skillful process management, the number of reheating of material and components can be reduced and thus production energy can be saved. [1] The topology optimization, which can essentially only be envisaged with casting techniques in series, represents a lightweight construction stage, in which composite components can also be reduced in the future. This means that foundry technology can also pro-

Photo: Fraunhofer Center HTL

Figure 1: Thermooptical measurement device TOM_air.

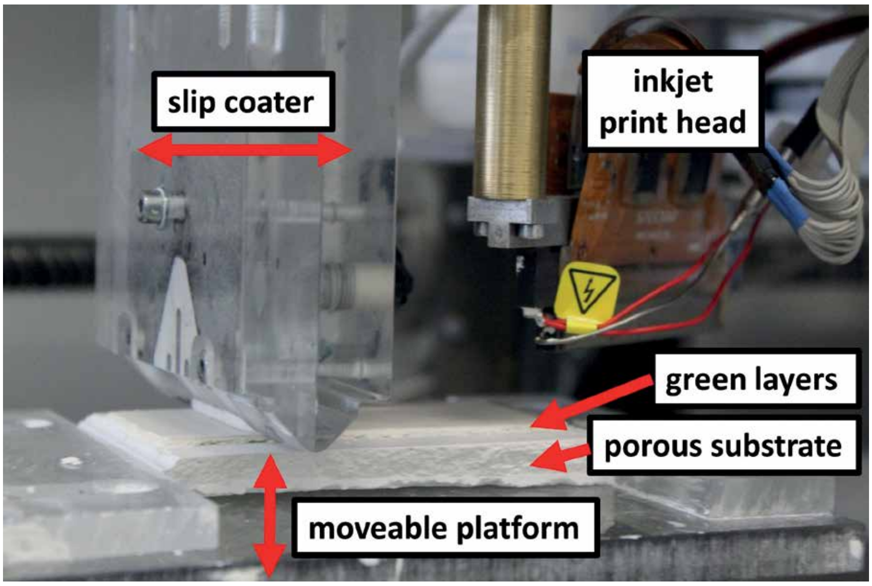

Figure 2: Production of 50 µm thick slurry layers on a porous substrate with the slurry-based 3-D printer test setup at the Fraunhofer IGCV.

cess material systems that have a very high cycle potential.

The constructions of the components are becoming increasingly complex in the course of this trend. Conventional shaping in the sand molding process using molds and cores reaches its limits. This concerns the possible complexity, surface quality and heat resistance. Here, the binders on which most systems are based, are a major limitation. Ceramic bonds, as in the investment casting process, are superior in all characteristic parameters, but the manufacturing route in investment casting is complex and costly. [2]

Additive Manufacturing processes are advancing further and further into the foundries due to their possibilities. [3] The drivers here are complexity and freedom of tools. The number of series produced continues to increase.

However, there is currently no additive process that combines the high heat resistance of the investment casting shells with high surface quality. The systems that are processed using powder-based 3-D printing have comparatively coarse grains. [4] This results in a surface that is too rough for many applications.

The aim of the approach presented in this article is to process slurries containing fine ceramic particles via 3-D printing [5]. The 3-D printing step shall be scalable and integrable into the foundry process chain. Process units that differ from conventional 3-D prin-

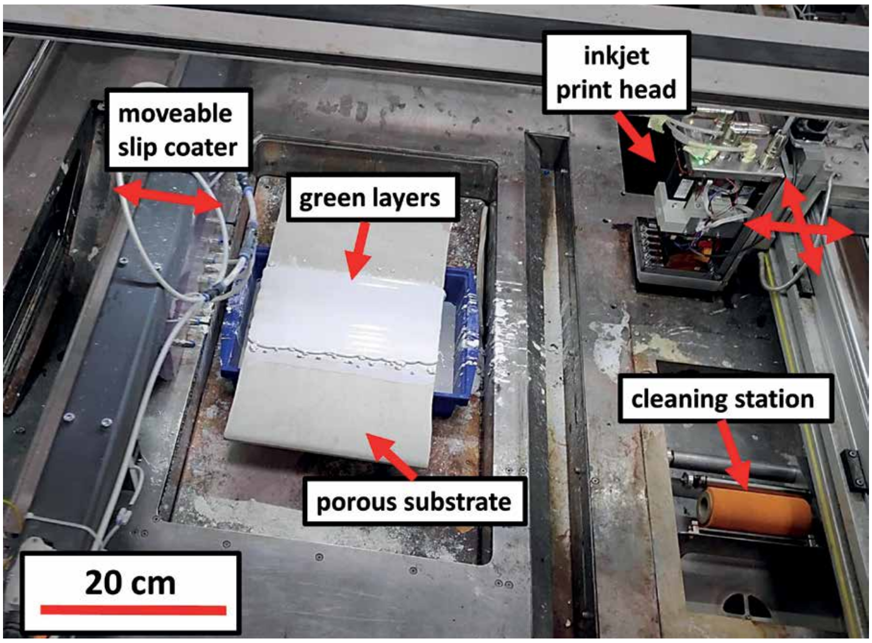

Figure 3: **Building chamber of the prototype slurry-based 3-D printer.**

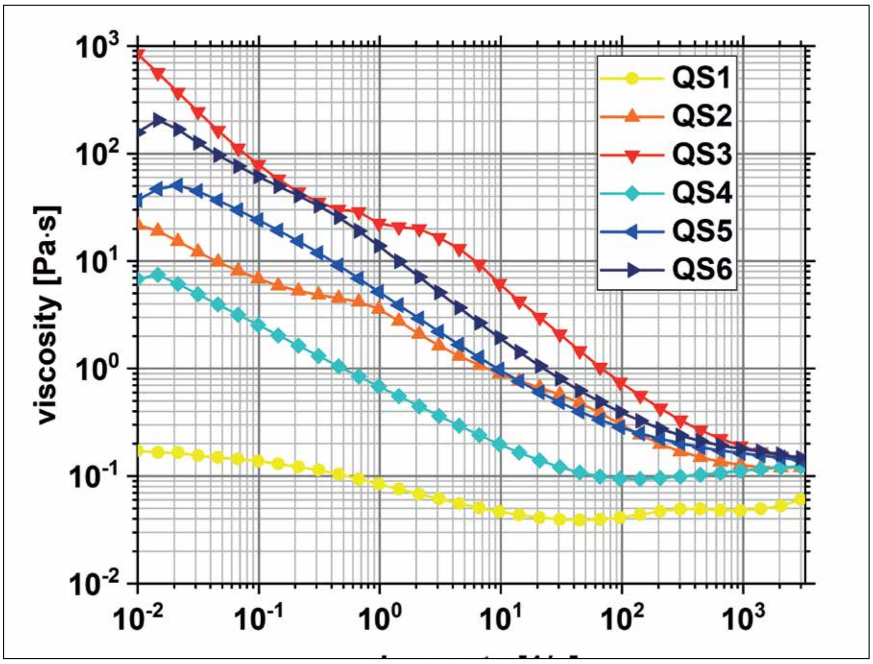

Figure 4: **Flow curves of the quartz slurries presented in Table 1.**

ting and a specially developed material system are used for this purpose.

3-D printing is based on a layer-by-layer breakdown of a molded body into essentially undercut-free layers. A vertically movable construction platform is used for this, which delivers the individual layers with high precision. In the first step, a layer of particulate material is applied to this building platform. In this project, unlike conventional 3-D printing, a ceramic slip is applied, levelled and then dried. This layer is then selectively coated with a binder. The last step is to lower the building platform by one layer thickness. These steps are repeated until a layer stack has been created in which the desired components are embedded.

In a second step, this stack of layers is returned to its liquid state in a water bath. The printed binding agent ensures that the component itself is not dissolved in the water bath.

The component obtained in this way is now in the green state. This is followed by a thermal treatment in the furnace, in which the binder is first burned out and then the ceramic is sintered at higher temperatures. After this process, the ceramic component is many times stronger than in the green state. At the same time, shrinkage occurs because the sintering closes the pore space from the building process.

The aim of the method presented here is to generate high green densities in the powder bed, so that the sintering shrinkage of the components and thus the component distortion can be controlled more easily. In addition, it is possible to use the water-based process for environmentally friendly manufacturing, compared to similar state-of-the-art processes.

Experimental procedure

Slurry preparation

As a raw material powder, quartz powder (Sikron SF500, 4 µm, Quarzwerke GmbH, DE) has been used. Aqueous slurries have been prepared by dispersing varying amounts (38.1 - 43.8 vol.-%) of the above mentioned powder in deionized water on a roller for 12 h, using 12 mm alumina beads and 0.5 wt.-% Dolapix CE64 (Zschimmer & Schwarz, DE) respecting the solid content as a dispersant. To prevent the rapid sedimentation of the quartz particles, 0.10 -1.56 wt.-% (referred to the water content) of a viscosity modulating agent (VMA) was added (see below). In order to prevent foaming and microbial contamination, 0.05 wt.-% of a defoamer (LP-C 22787, BYK, DE) and

Table 1: **Solid content and VMA contents of the slurries used.**

Slurry	Solid content in vol.-%	VMA content in wt.-%	VMA type
QS1	43,8	0,31	sheet silicate
QS2	43,8	0,94	
QS3	43,8	1,56	sheet silicate
QS4	42,5	0,1	polysaccharide
QS5	40,7	0,23	polysaccharide
QS6	38,1	0,42	polysaccharide

0.1 wt.-% of a preservative (Preventol® P301, Lanxess, DE) were added.

The slurry rheology has been characterized via rotational measurements using a cylinder setup in a rheometer (Physica MCR301, Anton Paar, DE). The stability of the slurries has been characterized via Turbiscan LAB (Formulaction, FR), in which an ampoule filled with a liquid is sequentially scanned with a laser, and the transmission and backscattering signal is detected.

Analysis of sintering behavior

With the slurries, cylindrical green samples (10 mm diameter, 10 mm height) have been prepared via slip casting in a plaster mold. The in-situ analysis of the sintering behavior of the samples has been conducted using thermooptical measurement (TOM) devices at Fraunhofer-Center HTL as seen in Figure 1. [6]

Mechanical strength

Via slip-casting, rectangular bars (50 x 7.5 x 4.0 mm³) have been prepared. The samples have been casted, dried at room temperature for at least 48 h and then sintered in a furnace at 1200 °C and 1300 °C for 1 h and 5 h. Density of the samples has been measured via the Archimedes method. The three-point bending strength has been determined in a universal testing machine (Inspect table 100 kN, Hegewald & Peschke GmbH) with a support spacing of 40 mm.

Slurry-based 3-D printer test setup

At Fraunhofer IGCV, a test setup for implementing the 3-D printing process was built, which has all the essential functions for the process (Figure 2). A construction platform is supported by a high-precision axis for raising and lowering, which, via a spindle and a stepper motor control, achieves a repeat accuracy and resolution better than 1 µm. The construction platform itself is connected to this axis via a load cell. This enables the monitoring of the various process steps.

The slip coater is supported by a long spindle axis for the movement in horizontal direction. The spindle axis is also controlled by a stepper motor and enables homogeneous feed speeds. The coater itself is de- signed as a two-part construction. Between the two parts, there is a fluidic channel structure that distributes the slip evenly to individual slot nozzles of approx. 5 mm width. The fluid system is connected to the reservoir by a hose. The slip is stored in this and can be subjected to excess pressure for metering. Likewise, the outflow from the nozzles can be safely stopped with negative pressure.

An infrared heat lamp is also attached to the spindle axis to dry the layer. The infrared system has a fan that cools the lamp and also speeds up the drying process. Additional drying nozzles allow drying to be further intensified.

The inkjet print head is mounted between the slip coater and the infrared system. It is connected to another reservoir that contains the binder. The mounting position of the binder reservoir allows the setting of a back pressure on the print head that is required for reliable function. The print head operates with a commercial phenolic resin binder. For its processing, the print head is temperature-controlled by an electric heating cartridge.

Prototype slurry-based 3-D printer

At the Voxeljet labs, a printer prototype has been set up in order to upscale the slurry-based 3-D-printing process for industrial production of 3-D-printed slurry-based casting cores. It is based on a frame- work already used for a binder jetting process. The building chamber of the prototype printer is shown in Figure 3. In this configuration, the slip coater for the application of the slurry is moveable along an axis with a traverse, while the porous substrate is placed on a building plate, which can be lowered stepwise after each layer.

On the backside of the slip coater traverse, a heating lamp is installed for drying the slurry layers. An inkjet print head for the application of the binder is mounted on another traverse and can be moved in two directions. Furthermore, a cleaning station for the cleaning of the print head is available. Based on this, a building envelope with a base area of up to 850 x 450 mm² is accessible.

Results and discussion

Rheological behavior and stability

In order to provide for the processability via slurry- based binder jetting, the slurries solid content, viscosity and stability are essential. Table 1 shows the composition of several slurries investigated concerning rheological behavior and stability. As VMA, a sheet silicate (Luvogel W2N, Lehvoss Group) and a synthetical polysaccharide were used.

The flow curves of the respective slurries are shown in Figure 4. It can be seen that with increasing amount of VMA, the viscosity and the degree of structural viscosity increase. A high viscosity at zero stress and a high yield stress counteract the sedimentation of the quartz particles, which is important for a high shelf life and an efficient redispersibility in case of a longer storage period. Nevertheless, the viscosity at higher shear rates must be kept low in order to make the slurries processable during pumping and depositing. This is to be achieved by a high degree of structural viscosity, which is derived from the negative slope of the flow curves (compare Figure 4).

It can be seen that with increasing amount of VMA and with increasing slurry viscosity, sedimentation becomes slower. In the case of the slurries QS3 and QS6, no considerable sedimentation over the course of 24 h could be detected. In contrary, an increase of the backscattering signal on the top of the ampoule can be seen, which is attributed to the drying of the slurry above the slurry meniscus on the ampoule wall. Figure 5 shows the slurries after an additional sedimentation of 144 h. It can be seen that slurry QS6 shows no signs of sedimentation, despite having a lower mean viscosity than QS3. Furthermore, slip cast green cylinder samples produced with QS6 exhibited a higher green packing density (1.45 g/cm³ or 54.4 %) than in case of QS3 (1.37 g/cm³ or 51.2 %). Therefore, the slurry QS6 was chosen as the basic slurry material for the following steps.

Sintering behavior

Figure 6 shows the results of the analysis of the sintering behavior of samples prepared with slurry QS6 and a modified slurry QS6, in which 5 wt.-% of the solid content was replaced by kaolin as a sintering additive (Kremer Pigmente GmbH, Germany; mean particle size 2 µm). Depicted is the relative width of the cylinder samples (standardized to unity at the be- ginning) versus the temperature. The arrows indicate the course of the lines during the thermal cycle. The heating rate was 2 K/min., the cooling rate was 5 K/min. The dwelling times at 1300 °C were set to be 5 h, the dwelling time at 1200 °C was 1 h.

At the beginning, rapid thermal expansion occurs, until the quartz inversion point is reached at about 570 °C, where phase transition of the alpha to beta modification takes place. From there, thermal expansion continues to a smaller extent until the on- set of the sintering at about 1100 °C, where compaction of the cylinder occurs, until the dwelling temperatures are reached. During a dwelling time of 5 h at 1300 °C (red and blue line), the samples begin to inflate due to the formation of cristobalite. However, the inflation of the sample with kaolin as a sintering additive is significantly lower due to a superimposition with shrinkage related to sintering. In case of QS6 with kaolin, at a dwelling at 1200 °C for 1 h (black line), a small amount of sintering shrinkage (about 0,7 %) occurs.

Upon cooling, the samples shrink again due to thermal contraction. Altogether, the QS6 sample sintered at 1300 °C for 5 h expanded by approx. 0.7 %, the QS6 sample with kaolin expanded by approx. 0.3 % when sintered at 1300 °C for 5 h, while it contracted by about 0.2 % after sintering at 1200 °C. When comparing these values, it can be envisioned that by finding an appropriate composition and sintering profile, a shrinkage-free sintering can be achieved, which may lead to a high shape accuracy of the sintered casting cores.

Density and mechanical characterization

The density values achieved with the QS6 slurry with and without kaolin are shown in Table 2. It can be seen that at 1300 °C, density first increases due to sintering shrinkage (at 1 h), but then decreases again with increasing dwelling time (5 h).When using kaolin as a sintering additive, sintered density increases considerably. Sintering at 1200 °C shows only a slight increase in density, when kaolin is used; in case of pure QS6, the density remains basically the same, which also corresponds to the observations made above.

In Figure 7, the results of the three-point bending test of test bars sintered at different temperatures and dwelling times are depicted. It can be seen that, despite the observations made in the chapter “sintering behabiour”, the bending strength is increased considerably when sintered at 1300 °C. At 1200 °C, no positive impact of kaolin on the mechanical strength can be observed. At 1300 °C however, the bending strength of samples with 5 wt.-% kaolin is almost 70 % higher than with- out kaolin addition, despite having a larger standard deviation. This also indicates an increased sintering activity upon addition of kaolin.

The three-point bending strengths were in a range from 1.9 to about 18

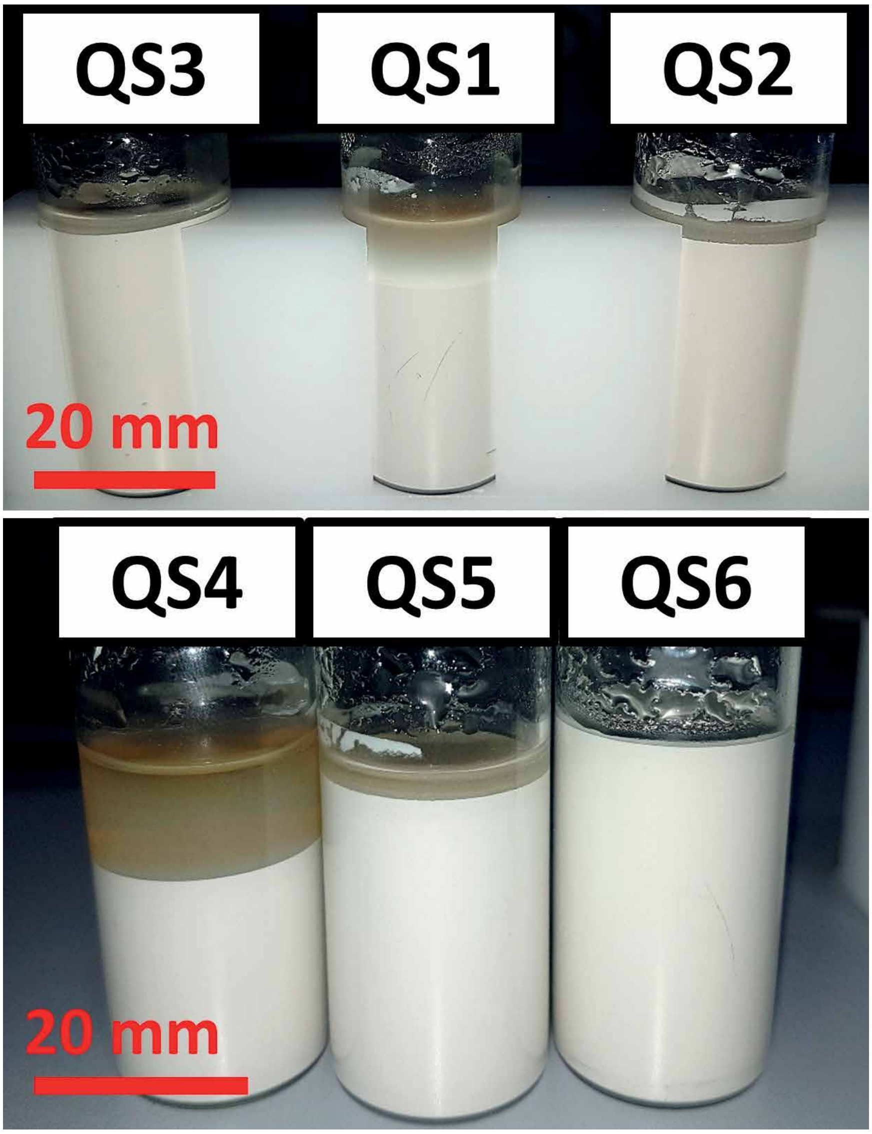

Figure 5: **Sedimentation front of the different quartz slurries after 7 days.**

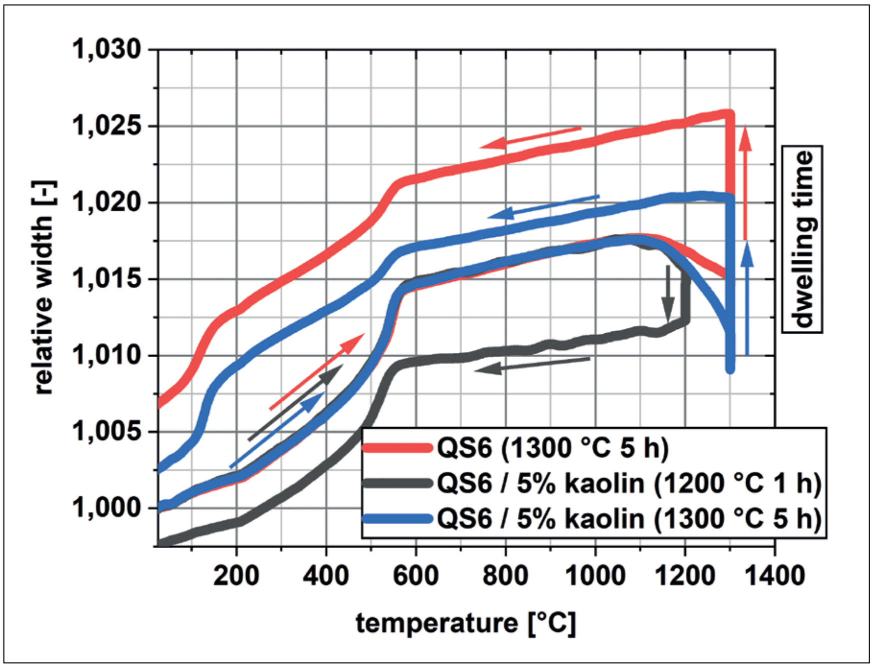

Figure 6: **Results of the in-situ analysis of the thermal treatment cycle of the QS6 slurry with and without kaolin as a sintering aid. The arrows indicate the course of the lines during the heating cycle.**

MPa. It is worth noting that maximizing mechanical strength is not the intended in this project, as the manufactured sintered casting cores are to be mechanically removable from the cast component after the casting process. However, a mechanical strength of at least 10 MPa is considered necessary for applications in investment casting.

Preparation of powder beds via printer test setup and prototype printer

At the 3-D printer test setup at the Fraunhofer IGCV, parameters for the homogeneous and defect-free recoating of dried solid powder beds have been developed. Parameters such as slip coater geometry, layer thickness, recoating speed, drying configuration and substrate type have been varied. An example for applied slurry layers is shown in **Figure 8.**

Conclusion

In the ongoing project, quartz slurries for the application in slurry-based binder jetting have been developed. The slurries are sedimentation-stable and processable via a slip recoater in order to get homogeneous powder beds. The sintering of slip-cast samples was connected to a slight volume expansion at 1300 °C due to cristobalite crystallization while being connected to a small sintering shrinkage at 1200 °C. The addition of kaolin improved the sinter ability of the samples at 1300 °C, which could be seen in an enhanced shrinkage and mechanical stability.

It is concluded that by appropriate sintering parameters and the corresponding kaolin content, casting cores with zero net sintering shrinkage can be produced. This prevents distortion and stress formation during sintering and allows for maximum geometrical accuracy.

The mechanical properties are adjustable via sintering temperature and slurry composition and range from about 2 MPa to 18 MPa. This gives a certain scope for the CAD design of the casting cores which are to be mechanically removable.

A 3-D printer test setup has been constructed, and printing parameters have been developed for the production of homogeneous solid powder beds, consisting of 50 µm layers. Likewise, a prototype 3-D printer was constructed, which is able to produce homogeneous powder beds at a larger scale.

Table 2: Sintered density values of slip-cast QS6-samples without and with 5 wt.-% kaolin. The green densities were 1,37 g/cm³ and 1,41 g/cm³, respectively.

sample unit	QS6 g/cm³	QS6, 5 wt.-% kaolin g/cm³
1200 °C, 1 h	1,38	1,43
1200 °C, 5 h	1,37	1,44
1300 °C, 1 h	1,44	
1300 °C, 5 h	1,36	1,54

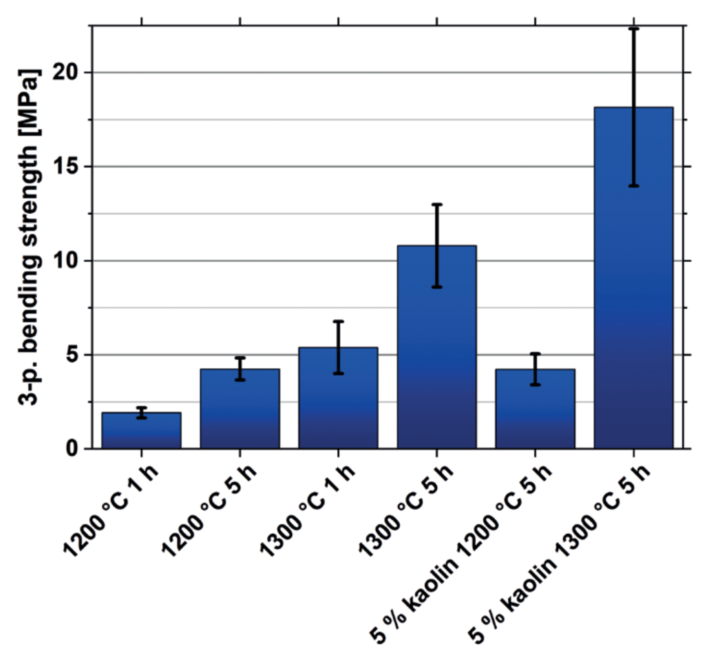

Figure 7: Three-point bending strength and standard deviation with 14-18 samples, each fabricated from slurry QS6, sintered at different temperatures and dwelling times.

Figure 8: Slurry layers applied at the prototype printer at Voxeljet (300 x 180 x 10 mm³).

The next step will be the production of green parts via the application of binder through inkjet print heads. Debinding parameters will be elaborated, and the mechanical and microstructural properties will be analyzed. Furthermore, casting trials with produced parts will be conducted at NRU.

Joachim Vogt and Marina Stepanyan (Fraunhofer-Center HTL, Bayreuth) Patricia Erhard, Daniel Günther (Fraunhofer IGCV, Garching) Sebastian Schmalzl (Voxeljet AG, Friedberg) and Sven Gläser (NRU GmbH, Neukirchen, all Germany)

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