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Slurry-Based Powder Beds for the Selective Laser Sintering of Silicate Ceramics

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Abstract

Selective laser sintering of ceramic powders is a promising technique for the additive manufacturing of complex- and delicate-shaped ceramic parts. Most techniques have in common that the powder to be sintered is spread to a thin layer as a dry powder by means of a roller or shaker system. These layers have a relatively low density. On the other hand, appreciable densities can be reached with the use of ceramic slurries as the starting material. Therefore, the layer-wise slurry deposition (LSD) process has been developed. Layer stacks, i.e. powder beds, built up by employing the LSD technology exhibit a density comparable to ceramic powder compacts processed by means of conventional forming technologies. Writing the layer information with a focused laser beam in these dense ceramic powder compacts enables the manufacture of ceramic bodies with a high density and precision in contour.

Keywords: LSD, powder bed, SLS, additive manufacturing, silicate ceramics

I. Introduction

Additive Manufacturing (AM) describes a class of technologies in which a part is directly generated from a virtual model by adding material to form the part [1]. According to the state of the art, polymeric, metallic or ceramic materials can be processed with these technologies. The philosophy behind AM is that a virtual 3D model and the choice of material are sufficient to define a part. Consequently, it is possible to generate parts with arbitrary geometries without any need to adapt the manufacture process. The material (feedstock) is typically fed into the process as a powder/granulate, paste or suspension, that is the material is in a state optimized for the layer deposition process. In the manufacturing process itself, the material is used to build up the desired object and it is simultaneously transferred into a state possessing its final physical properties, or at least a mechanical strength sufficient to transfer the built object to further processing steps. While in the 1980s and 1990s, basic technologies for AM were developed and flexibility in design was the first priority, nowadays the physical properties of the generated parts are a major concern. Accordingly, the terminology for this class of technologies is gradually shifting from Rapid Prototyping to Additive Manufacturing.

Processing of ceramic materials via AM is rather delicate. Reasons can be found in the extreme physical properties of this class of materials. For a detailed description of the various AM technologies for ceramics, we refer the readers to some recently published reviews [2, 3, 4, 5].

Selective Laser Sintering (SLS) of ceramic powders is a promising technique for the additive manufacturing of complex- and delicate-shaped ceramic parts. Most techniques have in common that the powder to be sintered is spread to a thin layer as a dry powder by means of a roller or shaker system. These layers have a relatively low density. On the other hand, appreciable densities can be reached with the use of ceramic slurries as the starting material. Therefore, the layer-wise slurry deposition process has been developed. This slurry deposition technology combined with laser sintering will be referenced in the following simply as Layerwise Slurry Deposition (LSD) [6]. In previous studies the feasibility of this technology for the manufacture of ceramic parts has been demonstrated [7, 8, 10]. It could be shown that laser-sintered porcelain parts are in a state comparable to a biscuit-fired porcelain body, however, with about half the mechanical strength than a conventional biscuit-fired sample [7]. On the other hand, the mechanical strength has been verified as sufficient for treatments such as glazing and glost firing [8]. In this study, we will highlight most recent achievements with LSD technology and shed some light on the mechanism resulting in the formation of powder beds with high particle packing density.

II. Experimental Methods and Materials

Fig. 1 illustrates the basic concept of the LSD process. A unique feature of the LSD process is the generation of powder layers exhibiting a density comparable to that of a conventional powder compact prepared by means of slip-casting. Most crucial in combination with laser sintering appears the complete drying of deposited layers. Resid-

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ual solvents can result in violent vapor formation during laser processing, which, in turn, can destroy the structure treated by the laser. For water-based slurries, it has been demonstrated that drying can be achieved in less than 10 seconds. Desiccation of a freshly deposited layer is associated with two main mechanisms: First, during and directly after deposition of a layer the solvent is drawn by capillary forces into the supporting powder compact formed by previously deposited layers and, second, rapid evaporation of the solvent. The first mechanism ensures that a freshly deposited layer loses its liquid phase immediately after deposition. Therefore, the temperature of the supporting dry layers can be kept at a temperature significantly exceeding the boiling point of the solvent.

For the build-up of 3D structures, the process steps layer deposition, drying, and laser sintering are repeated. Typical layer thicknesses are in the order of 100 µm. The width of the layer stack is defined by the width of the doctor blade used, the length is controlled by the movement of the blade parallel to the supporting surface and is therefore quite flexible. Within the boundaries of the supporting platform's surface area, the blade's width and trajectory of movement determine the area of material deposition. This feature is sometimes helpful when only small amounts of material are available and, the total volume of the powder bed must be reduced at a reasonable ratio between width, length and height of the processing volume. The height is simply the sum of all layers deposited.

The layer-spreading process works with a doctor blade, the function of which is twofold: First, feeding the ceramic slurry and spreading the slurry into a layer with uniform thickness. The slurry is fed from a reservoir by a rotary positive-displacement pump, type Nemo from Netzsch, Selb, Germany, through a gap of 500 µm in the oblong, hollow doctor blade. The slurry is spread simply by moving the blade at a constant distance parallel to the supporting platform's surface. Before the spreading process starts, a pool of slurry is deposited onto an additional platform, the starting platform. This platform is oriented in plane with the substrate platform, but can be adapted in height to the actual layer position. The starting platform is required for supporting the pool of slurry without absorbing the slurry's solvent and changing its rheological properties, and is cleaned after each layer deposition event so as to provide a defined surface for the start of the spreading process. From the starting platform the pool of slurry is spread into a thin layer, the thickness of which is defined by the interstice between the doctor blade and the platform's surface. The setup is illustrated in Fig. 2.

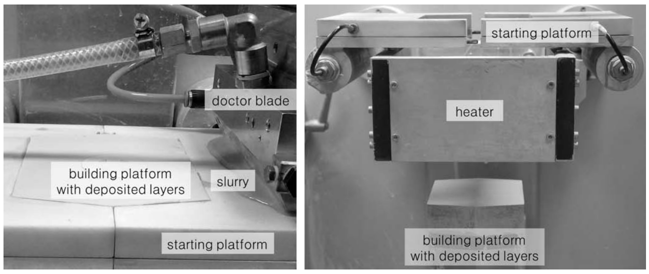

Fig. 2: Left: doctor blade just before layer spreading, right, overview of setup with the building platform in idle position.

According to this setup, material feeding is not controlled by exactly supplying the amount of slurry required for deposition of a layer, but a pool of slurry is spread over the surface. After the first layer has been deposited, previously deposited layers act as a support for the current deposition process. After drying, the layer information is scribed into the topmost layer by a laser (YLR-100-AC, Ytterbium fiber lasers 100 W cw. at 1070 nm wavelength, IPG Lasers GmbH, Burbach, Germany). The layer deposition process itself combines features of tape casting and slip casting. As illustrated in Fig. 1, the slurry is spread as a thin layer comparable to tape casting, while within this layer a cast is formed comparable to slip casting.

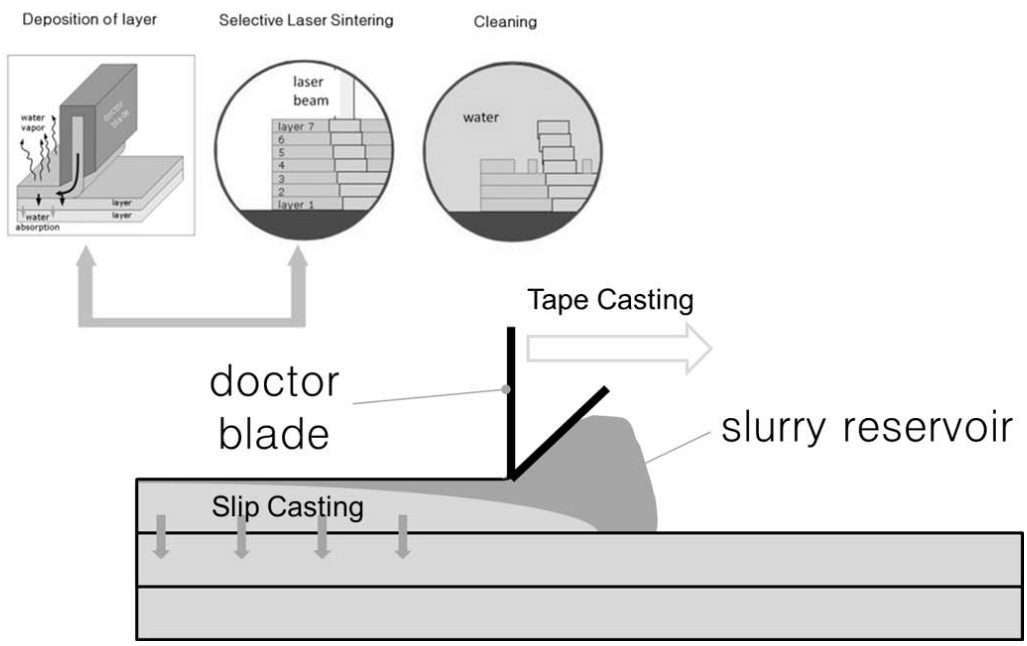

Fig. 1: Schematic of the rapid prototyping process using layer-wise slurry deposition.

Parts were generated by using a conventional porcelain slurry in a fully automatic rapid prototyping machine (LSD 100, Tools and Technologies GmbH, Schönwald, Germany) in which all the LSD-based process steps are integrated. In the machine a 100 x 100 mm platform with a kinematic resolution of 1 µm/step for vertical motion (lower the part for each layer) is used as a support for the layers in the multi-layer deposition process. A galvano-scanner (Hurryscan, Scanlab AG, Germany) is utilized for moving the laser spot on the dried ceramic layers. The focused laser beam has a spot size of approx. 50 µm. The scanner is controlled by software in which the geometry model is sliced into many layers and each layer is hatched in the respective cross-section according to the preset parameters (Sam3D, SCAPS, Munich, Germany). Repeating the deposition and laser sintering process builds up the final component. Finally, the entire powder bed, that is the compact block of densely packed powder particles embedding the laser-sintered structure, is placed into water to remove any powder not consolidated by the laser.

In the case of processes using loose powders, the laser-sintered body is easily released from the powder bed, but not in the LSD process. After the deposition of all layers required for building up the desired geometry, the laser-sintered body is embedded in a powder compact, see also Fig. 3. The powder compact must be dissolved in a solvent. In the case of water-based slurries, water can act as a solvent for the powder compact. For this task, the powder compact with embedded laser-sintered body is placed in a pool of water. Dissolution of the powder compact is the most critical process step within the LSD process chain, because swelling of the powder compact by solvent ingress precedes its dissolution. Fortunately this swelling does not affect the entire volume of the compact simultaneously. Swelling and dissolution start from the surface of the green body in direct contact with the solvent. The laser-sintered body acts as barrier for the solvent, thus, preventing the powder bed from swelling. Even though the sintered body is not completely dense it acts as an effective diffusion barrier for the solvent.

In practice, for the release of the sintered body it is helpful to support local removal of material by means of spray rinsing. The intensity of the spray influences the surface quality of the sintered body. While no or a mild spray leaves material on the body's surface, smoothening surface artifacts, an intense spray leaves only the sintered material with the body and artifacts, such as steps from the individual layers, coming to the fore. Sonication is also helpful for the removal of residual material.

III. Results and Discussion

Fig. 3 shows two photos taken before and during the release of two espresso cups made by means of the LSD process using commercial porcelain slurry. The cups are formed by 132 layers with a thickness of 200 µm each. The powder bed generated by the LSD technology has a density comparable to powder compacts formed by means of conventional slip casting. No obvious texturing originating from the layer deposition process is observed. However, the powder bed generated by LSD using porcelain or fine fire clay slurries shows an anisotropic sintering: in the plane of the deposited layers approximately 10 % relative shrinkage and perpendicular to this plane approximately 18 % for porcelain, and in the plane approximately 6 % and perpendicular 8 % for fine fire clay. The properties of the powder bed regarding density and mechanical strength are comparable to those of powder compacts formed with conventional slip casting. This gives rise to a unique feature of the LSD process, that is layers can be stacked without any supporting structure. Supporting structures, typically required for fixation of laser-sintered bodies in a loose powder bed, are not required irrespective of the complexity of the part to be built.

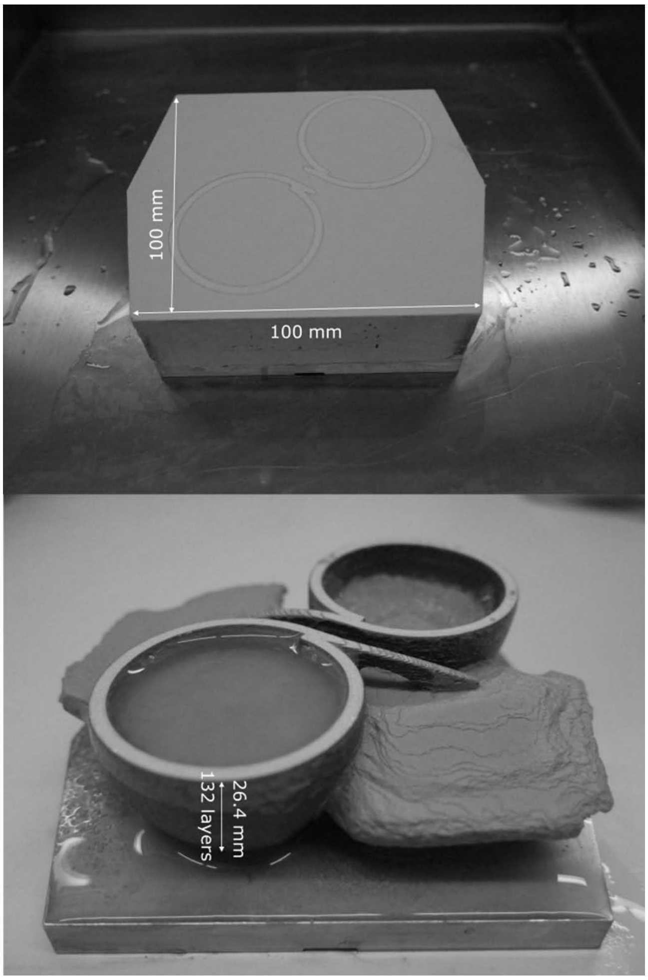

Fig. 3: Release of two espresso cups made of porcelain by employing the LSD technology. Upper picture: powder bed formed by 132 layers of 200 µm thickness with two cups laser-sintered, lower picture, partially released cups.

In conventional slip casting, the slip or slurry is brought into contact with a sucking porous body, the casting mould. When a liquid wets a porous body, capillary forces can draw the liquid phase of the suspension into the porous mould. The particles start to form a powder compact, the cast, at the mould's surface. The cast formation kinetics obeys a square-root-of-time law by depositing individual particles from the suspension to the surface of the mould. In case of the LSD process the mould is formed by the already deposited and dried layers. Slip casting results in the formation of powder compacts with densities exceeding 60 % theoretical density. Furthermore, owing to the free settling of the powder particles from the suspension, no obvious interface is formed between the layers in the LSD process.

The formation of a cast starts as soon as the slurry is in contact with the previously deposited and dry layers. Upon layer deposition, the slurry reservoir in front of the doctor blade is first in contact with the dry layers. Hence, the speed of the doctor blade relative to the dry layers must be high enough to prevent collision of the doctor blade with the freshly formed cast. In the case that the speed of the doctor blade is not sufficiently high, the cast will grow within the slurry reservoir up to a thickness exceeding the layer thickness, that is the interstice between blade and surface of previously deposited layers. In that case the cast will collide with the doctor blade and previously deposited layers will be disrupted on the building platform. On the other hand, when the speed of the doctor blade is too high, the layer deposition is not uniform. Sheer stresses within the slurry will result in inhomogeneous deposition. For commercial silicate ceramic slurries a speed of the doctor blade of 50 mm/s has been proved to be useful. For technical ceramics the cast grows significantly faster and the speed of the doctor blade is increased up to 100 mm/s or higher.

For the generation of complex ceramic parts the feasibility of the LSD process has been demonstrated. On the other hand, it has been found that the properties of samples generated by the LSD process are not comparable to those of conventionally fired samples. Reasons can be found in the harsh treatment of the powder bed by the laser. In the laser focus, the laser generates a hot spot on the surface of the powder bed based on the dissipation of radiation energy into heat. From this hot spot the heat is transferred via heat conduction through the material. Hence, the surface-near region reaches the highest temperatures and densification of the powder by sintering and formation of a liquid phase is highest. Deeper regions do not receive that much energy and, thus, exhibit partially sintered powder [8]. This inhomogeneous annealing of each individual layer results in the formation of a glassy phase containing larger bubbles (up to 30 μm) at the surface of each layer. Nonetheless, the laser-sintered body exhibits a phase composition and a density comparable to a biscuit-fired porcelain body [7], that is 65 % theoretical density (TD). The laser-sintered body can be glazed and glost-fired. Fig. 4 shows the cup from Fig. 3 biscuit-fired (900 °C, dwell 1 h, ramp 5 °°C/min), the same cup glazed (1080 °C, dwell 1 h, ramp 5 °C/min), and a glazed and glost-fired porcelain cup (1280 °C, dwell 1 h, ramp 5 °C/min) made from 500 layers with a thickness of 100 μm each. The bubbles induced by excessive laser heating of the layers surface reduce the sinter activity of the laser-sintered body. Therefore the density of fired bodies does not exceed 80 % theoretical density. The shrinkage during sintering in all three dimensions is about 5 % relative and, thus, in contrast to the powder bed that has not received laser treatment significantly smaller but uniform.

3D printing of dry-deposited silicate ceramic powders can also lead to beautiful results [11]. A critical point, however, is the binder burnout associated with the firing. Organic binders burn out before sintering and, thus, before consolidation of the printed structure. Hence, the printed structure becomes very fragile during firing and printing of an additional structure, acting as a support during firing, is required for its stabilization. Furthermore, the phase composition of the powders must be adapted to the specific needs of firing powder compacts with low particle packing density. Finally, residual porosity after biscuit firing is filled with glaze, requiring multiple glazing and firing. The LSD technology has the striking advantage that the laser-sintered parts are already in a biscuit-fired state and thus provide sufficient mechanical strength and density for post-treatment, such as glazing and glost-firing. Moreover, filigree structures are more easily replicated with this technology.

Fig. 4: Lower left, biscuit-fired cup, upper left, glazed and glost-fired cup from Fig. 3, right, glazed and glost-fired cup. All cups shown are made of porcelain with the application of the LSD technology.

Future work will concentrate on technical ceramics and the optimization of laser parameters to obtain more homogeneous sintering and higher densification of the ceramic powders in the laser sintering process. The current setup uses a 100 Watt cw. fiber laser system. On the other hand, pulsed laser systems have the advantage that very high intensities can be delivered at short time intervals, in the range of ns., and far from the thermodynamic equilibrium appreciable densifications of dry-deposited powders are achieved [11]. Similar strategies might be useful in combination with the slurry deposition technology.

IV. Conclusions

The laser sintering of ceramic powders deposited as thin layers by means of the slurry deposition (LSD) technology was used for the additive manufacture of complex ceramic parts. Contrary to technologies based on the deposition of dry powders, LSD improves the green densities of the powder bed, which in turn positively affects the densification of the powder in the laser sintering process. However, a better understanding of the light-material interaction is required in order to improve the heat distribution within the powder bed and to improve the microstructure of the parts produced.

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