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Original Article

3D printing of porcelain by layerwise slurry deposition

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ABSTRACT

The Layerwise Slurry Deposition is a technology for the deposition of highly packed powder layers. A powder bed is achieved by depositing and drying layers of a ceramic suspension by means of a doctor blade. This deposition technique was combined with the binder jetting technology to develop a novel Additive Manufacturing technology, named LSD-print. The LSD-print was applied to a porcelain ceramic. It is shown that it was possible to produce parts with high definition, good surface finish and at the same time having physical and mechanical properties close to those of traditionally processed porcelain, e.g. by slip casting.

This technology shows high future potential for being integrated alongside traditional production of porcelain, as it is easily scalable to large areas while maintaining a good definition. Both the Layerwise Slurry Deposition method and the binder jetting technologies are readily scalable to areas as large as $> 1\,m^2$.

1. Introduction

Stoneware and porcelain products have been used for centuries as high quality ceramics for tableware, sanitaryware, tiles and art, as well as several technical applications [1].

Desired characteristics of these products are good chemical durability, mechanical properties and water impermeability (absence of open porosity). Porcelain objects are typically produced by pressing or slip casting. Both technologies are well suitable for the large production volumes required by the traditional ceramic industry.

There still is a number of applications which require a high flexibility in production, such as prototyping, customized or small series, pieces of art etc. Intricate shapes are also often difficult or even impossible to produce by slip casting or pressing. For such applications, Additive Manufacturing (AM) provides innovative shaping possibilities, which have a high potential for being integrated alongside traditional production.

Addressing this need, there are several AM technologies already on the market which can produce ceramic parts [2,3]. The simplest of these technologies applied to silicate ceramics based on the extrusion and selective deposition of clay-based paste. (WASP clay extruder, Wasp, Italy; 3D Potter Bot, USA; LUTUM 3D Clay printer, VormVrij | 3D, The Netherlands).

This process is favorable for coiled geometries, but it has limitations for more complex geometries, besides generating clearly stepped surfaces.

Recently, some results on Vat photopolymerization of porcelain have been described. (Porcelite by Theton 3D, NE, USA) In this process, layers of a photocurable resin mixed with ceramic powder are spread and selectively hardened by a laser or a light projector. The parts obtained after the process are debound to decompose the resin, fired and glazed. Despite being able to deliver complex geometries with an excellent surface finish, due to the large amount of resin used (Volume fraction higher than 40%) this technology is not very well suited to produce thick-walled parts.

An additional technology is powder based 3D printing (binder jetting), which is already used commercially for porcelain as well. This process is favorable for its high volume throughput, the possibility of producing large parts and shape flexibility. 3D printing service companies, such as I-Materialise (Belgium), produce porcelain parts by binder jetting into a powder bed, firing and glazing. An alternative, utilized for example by Shapeways (USA), is to produce plastic molds by AM, which are then used to slip cast a porcelain slurry. The advantage of this last procedure is that it achieves parts with a material which is similar to traditional slip casting; on the other hand, it imposes some geometrical limitations because of the use of a mold, and it adds an additional step to the process chain.

Little scientific literature is available on AM of silicate ceramics, mainly dedicated to powder based 3D printing for art or dental applications [4,5]. These results showcase typical aspects of this technology applied to ceramic materials. Parts with intricate shape and good surface finish after glazing could be produced, but the high porosity of the powder bed led to a porosity after firing significantly higher than for standardly manufactured objects.

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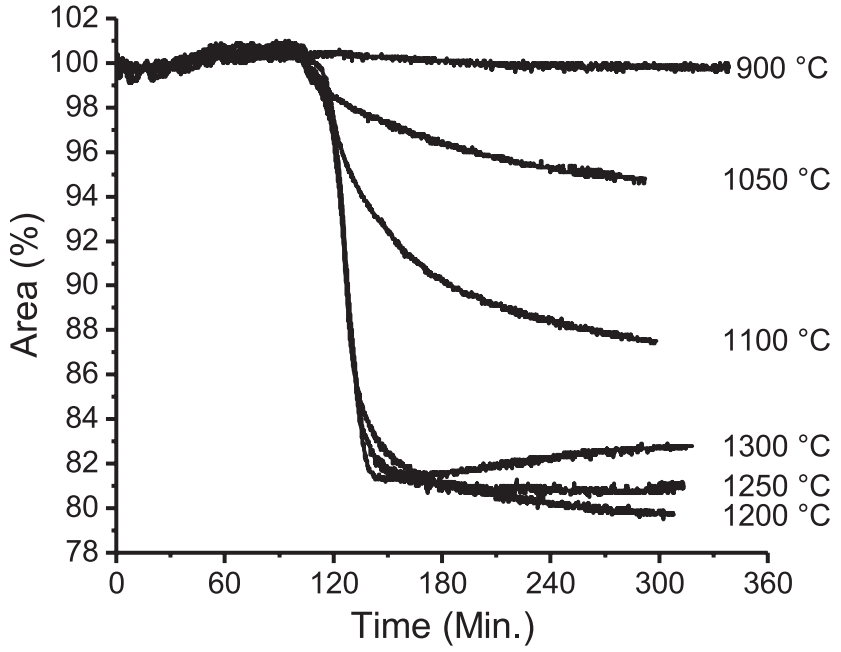

Fig. 1. Isothermal densification curves at temperatures between 900 °C and 1300 °C.

In this publication, we present results on a novel AM technology applied to porcelain ceramic, the Layer-wise Slurry Deposition (LSD). LSD is conceptually similar to power bed 3D printing, but uses a ceramic slip as feedstock instead of a dry powder.

By using a ceramic slurry as feedstock, improved material properties can be achieved. Green bodies can be formed with a particle packing density of up to 60%, even when using a fraction of fine particles.

The LSD process therefore brings together advantages of slip casting (good powder packing) and advantages of powder bed 3D printing. Additionally, the LSD process makes use of ceramic slurries which are similar to ceramic slips used in the industry for slip casting. This makes the process ready to be integrated with the existing know-how and technologies of the traditional silicate ceramic industry.

The current work presents results on the LSD-print of porcelain complex parts, having density, microstructure and mechanical properties comparable to slip casted samples.

2. Materials and methods

The LSD-print technology combines the deposition of ceramic slurry layers by means of a doctor blade, followed by drying, with binder jetting of 2D cross-sections of a part.

The equipment used is a custom setup, a detailed description of which can be found elsewhere [6].

The porcelain slurry used in the process was characterized by means of particle size distribution (Mastersizer 2000, Malvern, UK). A sample of powder was obtained after drying the slurry and its theoretical density was measured by gas pycnometer (Pycnomatic ATC, Thermo Fisher Scientific, USA); phase quantification was performed by Rietveld refinement of an XRD measurement (D8 Advance, Bruker AXS, Germany).

The measured composition in mass fraction was: 13.1% quartz, 44.7% Kaolinite, 20.3% Albite, 16.2% Orthoclase and 6.8% Muscovite.

LSD-printed samples at the end of the process were removed from the powder bed by washing in deionized water. The parts were let drying in air for one day and then heat treated at 500 °C, decomposing the binder system, followed by sintering at temperatures ranging from 900 °C to 1400 °C. The heating rate was 2 °C/min until 500 °C and 10 °C/min until reaching the maximum temperature.

Isothermal densification curves at temperatures between 900 °C and 1400 °C with same heating rate were obtained by hot stage microscopy (Hesse-Instruments, Osterode am Harz, Germany).

Green and sintered samples were characterized by density measurement and by observation of their macro- and microstructure. The density was measured geometrically for the green samples and by Archimedes' method (according to ISO 3233-1:2013) in distilled water for sintered samples. The samples were observed by optical microscopy (Keyence, Osaka, Japan) and by SEM (Vega W-Rem; Tescan, Brno, Czeck Republic).

The biaxial mechanical strength was tested by the ball-on-three balls method [7] on tablets with a diameter of 10 mm and 2 mm thickness, using stainless steel balls with a diameter of 7 mm. A set of 30 samples was tested for samples printed in XY, XZ and YZ plane. XY indicates the layer plane, X being the deposition direction, Y perpendicular to X in the layers plane and Z the direction in which the layers are stacked, that is, normal to the XY plane.

Uniaxially pressed samples and slip casted samples were used as reference for comparison. 30 tablet shaped samples were uniaxial compacted at 60 MPa. 30 tablet shaped samples were slip casted in gypsum molds.

The pressed samples, slip casted samples and LSD-printed samples were tested with the same equipment by ball-on-three-balls method on a static universal testing device (Zwick Roell Z005 5 kN, Ulm, Germany).

The measured values were elaborated by Weibull statistic and compared.

3. Results

The experimental work consisted of a preliminary optimization of the firing conditions for the porcelain material, and of the following LSD-print and characterization of printed samples.

3.1. Optimization of the firing conditions for porcelain samples

Fig. 1 shows densification curves with heat ramp of 10 K/min for all samples and an isothermal dwell of 5 h at temperatures between 900 °C and 1300 °C.

The samples started to shrink at the same time for all probes, corresponding to a temperature of ca. 1000 °C, indicating onset of sintering