Production of Sintered Ceramic Patterns Using an Inkjet Printing Process

Wolfgang Voit, Werner Zapka, and Kjell Broström, XaarJet AB, Järfälla, Sweden; Frederic Moscou, Cerlase, Limoges Cedex, France; Sebastien Verilhac, LAMBERTI specialty chemicals, Villefranche, France

Abstract
A fast process for the production of ceramic patterns is presented, utilizing inkjet printing for laying down the pattern digitally. An aqueous ink, containing glycols and surfactants, was printed onto various substrates to act as an adhesive layer for a ceramic mineral powder. The powder was deposited in a dry powder spraying process and formed a uniform layer in contact with the adhesive ink. Excess powder that was not fixed by the ink was blown away by air pressure in the following step, before the pattern was laser sintered. The process was also demonstrated for multi-color ceramic patterns, by applying different colored pigments on successively printed ink patterns. Optimized ink composition and process parameters were investigated, to be able to avoid color changes of the final pattern after laser sintering. A prototype production unit is presented that implements the developed process.

Introduction
The production of sintered ceramic patterns has a wide range of applications for decoration or marking purposes on various substrates, like tableware, glass bottles or ceramic tiles. However, for most of the traditional production techniques for such patterns, where screen-printing techniques are the most common ones, masks have to be produced for each pattern, and problems may arise due to size- or shape variations of the individual parts.

Cerlase has developed a process called '*Celisys*', where a uniform layer of ceramic mineral powder is deposited onto a substrate, and the pattern is sintered by a scanned laser beam before the surplus powder is removed.[1] This process is able to produce ceramic patterns with high resolution and edge definition, but is mainly restricted to monochromatic patterns, and has limitations in the rate of production due to maximum possible laser scanning speeds.

An approach to add more flexibility to this *Celisys*-type process is to utilize the versatility of inkjet printing to produce pattern in a digital fashion. Industrial inkjet printing technologies have emerged in the recent years as deposition technology for a number of functional and decorative applications, such as printing of adhesives,[2] protective coatings or electrical conductive polymers.[3] They allow a fast and easy pattern design, making them suited for short length runs and personalization of the final patterns, while still able to maintain high rates of production.

In this paper an approach to combine existing powder deposition and sintering processes with the advantages of inkjet printing is presented. By laying down a non-pigmented layer that acts as adhesive for the ceramic powder, the pattern is solely defined by the inkjet printing process. This method allows a fast production process, as the pattern can be laser sintered in a full-field fashion. Furthermore, the realization of multi-color pattern is possible, as different colored layers can be produced before the final sintering is performed.

Description of the Process
The process for producing ceramic pattern consists of three major steps: In a first step a water-based adhesive ink is printed onto the substrate in an inkjet printing station, to provide a sticky layer for a ceramic powder. This powder is applied in the next step by a dry powder spraying process. The powder is locked in place where the ink was deposited, and excessive powder that is not fixated will be blown away immediately afterwards with pressurized air. In a final step, the produced ceramic pattern will be sintered by a laser. A schematic for this process is shown in Figure 1. This process can either be performed as a monochromatic process, or for producing multi-color pattern by laying different colored powders down onto the respective ink pattern in subsequent steps and performing a final global laser sintering.

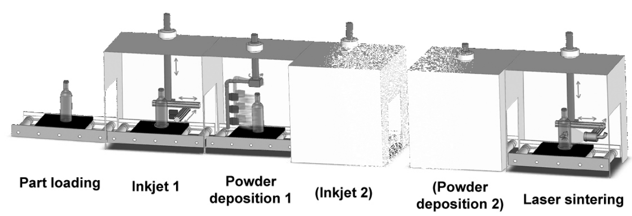

Figure 1. Schematic of the process flow

Inkjet Printing for the Pattern Definition
Piezoelectric drop-on-demand inkjet printheads from *Xaar* were used to print the adhesive inks and so to define the final pattern for the ceramic layers. These printheads work on a shear-mode actuation principle, where an acoustic wave is generated within the actuator channel by a mechanical, non-thermal motion of the walls, creating ink drop ejection through a well-defined nozzle.[4,5]

Figure 2 shows an XJ126-type printhead which was used for this patterning process. It has 126 ink channel in a linear arrangement with a 137µm channel pitch, yielding a natural resolution of 185 dpi (dots per inch). Higher resolutions can be achieved with the printhead inclined against the scanning direction. In the present process most work was performed with the XJ126-200 model, which delivers single drop volumes of typically 80 pl at fire frequencies up to 5.2 kHz.

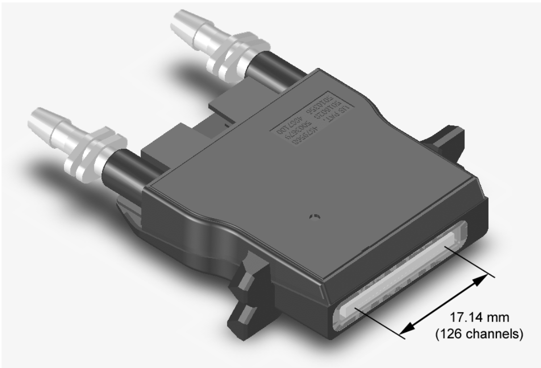

Figure 2. The XJ126 printhead model with 126 channels in a linear arrangement

Powder Application and Removal of Excessive Powder

A mineral powder mixture, consisting of mineral pigments, frit, and further elements to improve fluidization or laser light absorption, has been applied onto the inkjet printed adhesive pattern by dry powder spraying. The system utilized for this process uses a modified '*Venturi'* pumping system (*Wagner*) that pumps the mineral powder from a container that has an air fluidization bed in the bottom and provides additional air to it, before the powder was sprayed through a nozzle onto the substrate. This process enabled the distribution the powder mixture in a homogeneous layer over the whole substrate surface, where the thickness of the powder layer was controllable by the deposition parameters.

In places where the adhesive ink was printed onto the substrate, the adhesive layer was saturated by the mineral powder and the powder was locked in place. Unbound powder on unprinted areas was blown away by high pressure air exposure in a successive step immediately after the powder spraying step. The removed excessive powder was then collected and re-used.

Laser Sintering of Structured Patterns

A final laser sintering process was performed to sinter the patterned ceramic powder on the substrate. It was found that best results could be obtained by using infrared lasers in the short wavelength regime (around 1000 nm), as at this wavelength most laser energy was absorbed by the powder, which was sintered and transmitted enough energy to the substrate to fuse the ceramic layer to it. At longer infrared wavelength (10 micron) more of the laser energy is absorbed by the substrate, and the substrate would be engraved by the laser beam.

For the present process, two different kinds of laser systems have been used: An Ytterbium laser with an output power from 10W to 50W (at 1072nm), with fibre excitation and a mono mode spot (50 microns). The laser spot can be scanned in various speeds across the substrate by a scan head, to facilitate large field sintering.

As the speed of operation is strongly limited for the Ytterbium laser by the small laser spot size and the speed of the scan head, a diode laser system that has the capability to deliver larger spot sizes at high output power has been employed. The kind of diode lasers used for this work from *Laserline* delivered a laser spot that can be shaped from a square to a line shaped geometry, at an energy from 350W up to 6000W at 980 nm. The typical line profile of this laser can be seen in Figure 3, were the line could have a maximum length of 63mm and width of 4,2 mm. For full field sintering the substrate was moved across the laser beam to sinter the patterned area.

Both laser systems were found to sinter the ceramic pattern and fuse it to the substrate, with the diode laser having the advantage of being able to run at sintering speeds suitable for high rates of production.

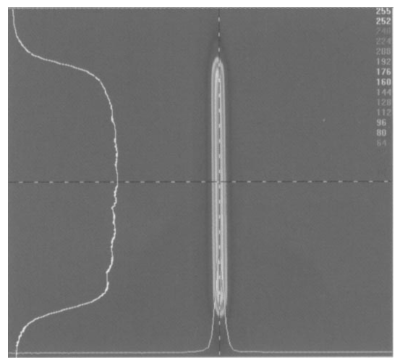

Figure 3. Profile of the diode laser output power

Process Details and Experimental Results

One of the key objectives of the present work was to identify and compose a suitable fluid that acts as an adhesive to fix the mineral powder to the substrate. Important parameters there were suitable viscosity and surface tension for inkjet printing, and ability of the fluid to wet the substrate and bind sufficient powder. Furthermore it was important that the fluid didn't contain any substances that could carbonize during the final laser-sintering step, and consequently could produce color changes of the ceramic pattern.

Aqueous solutions of either monopropylene glycol (MPG) or diethylene glycol (DEG) were identified as possible candidates for the fluidic adhesive. Different solutions with varying glycol concentration were mixed and characterized, to find the concentration for a suitable viscosity for binary Xaar printheads, which is in the order of 10 mPa·s. Figure 4 shows such a chart for the viscosity versus MPG concentration in an aqueous solutions. From these measurements a 70wt% (weight percent) MPG solution with a viscosity of 10.4 mPa·s, and a 75wt% DEG solution with a viscosity of 11.3 mPa·s were chosen for the further work.

The physical properties for these two aqueous glycol solutions are summarized in Table 1. The equilibrium surface tensions of both solutions was higher than typically required for *Xaar* printheads to be able to run in a reliable fashion (28-35 mN/m). Furthermore it is favorable to have a range in surface tension available to be able to adapt the printing process for different surface energies of the substrate. This could be achieved by adding suitable surfactants to the glycol solutions. *'Surfactant 1'* (polyglucoside based) reduced the surface tension to 31,8 mN/m in a concentration of 0,5wt% in the 70wt% MPG solution (as shown in Table 1). Further addition of *Surfactant 1* resulted in further decrease of the surface tension, yielding a value of 27,9 mN/m for 2wt% concentration. Another surfactant, based on copolymers of propylene and ethylene glycol (*'Surfactant 2'*), reduced the surface tension to 33,8 mN/m for a 0,5wt% concentration in the MPG solution. However, higher amounts of *Surfactant 2* did not result in further decrease in surface tension.

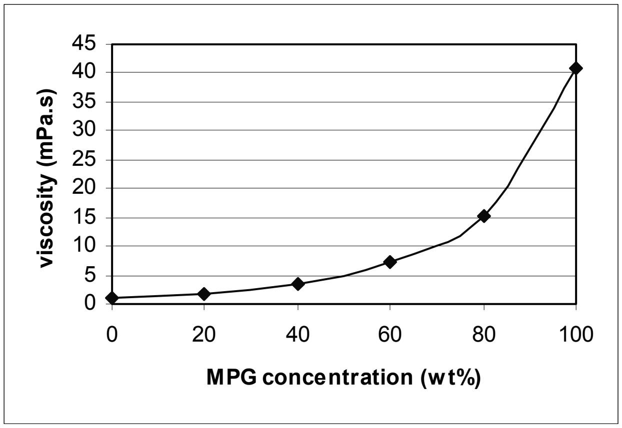

Figure 4. Viscosity dependence on the MPG concentration in an aqueous solution

Table 1.: Properties for Different Adhesive Ink

Adhesive ink	DEG 75% in H_2O	MPG 70% in H_2O	MPG 70% + 0,5% *Surfactant 1*
Viscosity @ 200 1/s	11,3 mPa.s	10,4 mPa.s	10,4 mPa.s
Density (measured)	1,088 g/ml	1,04 g/ml	1,04 g/ml
Surface tension	48,1 mN/m	40,3 mN/m	31,8 mN/m

The performance of XJ126-200 inkjet printheads with the different glycol-based adhesive inks was studied in a microscope rig with stroboscopic illumination. It was found that reliable drop formation up to maximum printing frequencies of 5,2 kHz was possible with both the MPG ink and the DEG ink with 0,5% of either *Surfactant 1* or *Surfactant 2*. To achieve best performance, the driving waveform for the printhead was slightly modified. The printhead supplied drop volumes of about 90 pl up to the maximum frequencies when firing with all channels. Without the addition of surfactants, instabilities and loss of ink channels occurred at frequencies above 4 kHz in case of the MPG ink and above 1 kHz in case of the DEG ink.

To investigate the capability of all components used for the adhesive inks with the laser sintering process, all substances have been laser treated either as single components or in appropriate mixtures. These tests showed that no carbonized residues remained for all components after treatment with the laser.

To test the whole process sequence, a ceramic mineral powder was applied onto test pattern, which was inkjet printed with the glycol solutions, and finally laser sintered. In Figure 5 the optical image of such a tests structure is shown. In this case the pattern was produced on a glass substrate with a white mineral powder applied onto the inkjet printed 70% MPG solution with surfactant. These powders consisted of typically more than 50% frit, the colored pigment (10 to 50%), 1 to 3% absorbents for the laser sintering, and 1 to 3% fluidizers (silica gel). The sintering was performed with the scanned Ytterbium laser at 10W laser power and a scan speed of 100mm/sec. The sintering process of this white powder mixture did result in a densely sintered layer without any color changes, thus a successful deposition process could be demonstrated.

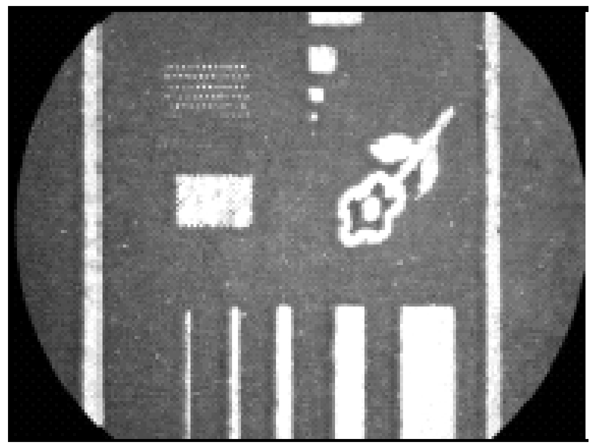

Figure 5. Laser sintered test pattern consisting of white mineral powder; no color change was observed

From the opaqueness of the ceramic pattern a layer thickness of about 40 micron could be estimated. It was sufficient to print the adhesive ink in a single-pass printing mode to bind enough ceramic particles required for this kind of final layer thickness. Furthermore is was found that in the time between powder deposition and laser sintering an certain amount of the adhesive ink was evaporated, which reduced further the risk of carbonization during laser sintering.

Based on the first printing, deposition and laser sintering results, a prototype station for a production process was designed and built. Figure 6 shows an image of this equipment, where sample transport, printing unit and powder deposition part can be seen. The laser sintering process was at this point implemented as a separate station.

For optimized process parameters, it could be expected to be able to produce one sample with this prototype station within a few seconds.

As a demonstrator object, glass cups were decorated in monochromatic color with this unit, as shown in Figure 7. This was achieved by spraying a blue mineral powder onto a MPG based adhesive ink, following a laser sintering process with the diode laser system in a subsequent step.

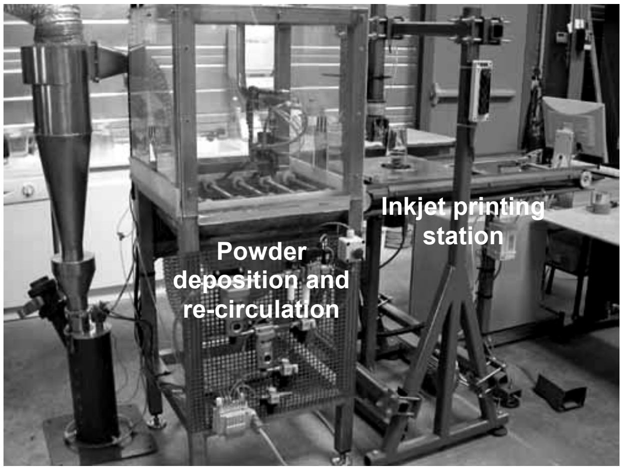

Figure 6. Prototype production unit for the adhesive printing and powder spraying process steps

Figure 8. 2-color pattern produced on a plate

Figure 7. Decorative monochromatic pattern on glass

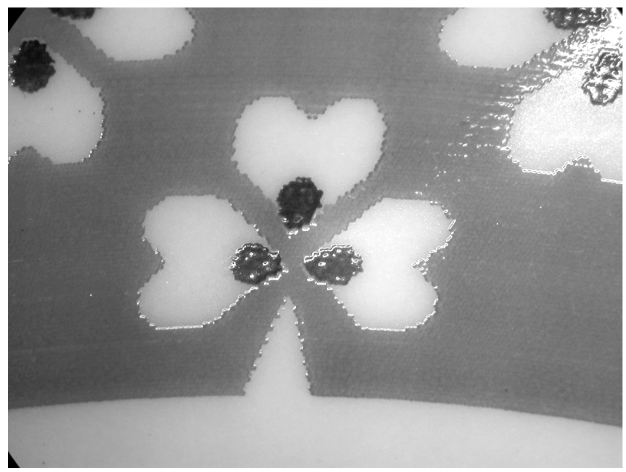

Figure 9. Magnification of the decorative pattern shown in Figure 8

As a further example for this process, the printing of multicolor pattern for the decoration of tableware was demonstrated. A plate that was decorated with a 2-color print is shown in Figure 8. For the first color only the adhesive ink was printed in the prototype station, and a brown mineral powder was deposited manually, as the unit is currently only capable of printing one color automatically at a time. Afterwards the plate, which was still mounted on its fixture, was inserted again, and the second color, a black powder, was deposited fully automatically. Finally the plate was fired in a traditional way instead of the laser sintering. However, deposited multi-color patterns could as well sintered by the laser sintering process, and for other samples we have demonstrated 3-color deposited and laser sintered patterns.

Figure 9 shows the produced pattern of the plate from Figure 8 in larger magnification. It can be seen in the image that good structure accuracy and edge definition can be achieved, even for samples like plates where larger printing distances are required due to dimension variations of the plates.

Conclusions

A process for the deposition of ceramic patterns has been developed, where the pattern structure is defined by a digital inkjet printing process. The ceramic mineral powder that was applied onto the adhesive ink formed layers with high uniformity and edge definition after laser sintering or traditional firing. The process has been demonstrated for the decoration of glasses or tableware, where both monochromatic as well as multi-color patterns have been produced. By finding suitable adhesive inks, powder compositions and process parameters, it was possible to avoid color changes of the sintered ceramic patterns. The results of these investigations have been implemented in a prototype production station, which is able to process various substrate types.

Acknowledgements

This work was funded as 'Celisys Color' project by the French funding agency ANVAR and the Swedish Agency for Innovation Systems (VINNOVA) under the EU Eureka label. The authors would also like to thank Jean-Pierre Roy from Wagner, France, for participation and supply of parts for the powder spraying system.

References

1. *Cerlase* patent EP1040017, B1 - WO9929519.
2. W. Voit, K. V. Rao and W. Zapka, Direct-write process for UV-curable epoxy materials by inkjet technology, Mat. Res. Soc. Symp. Proc. Vol. 758, pg. LL3.5.1- LL3.5.7 (2003).
3. W. Voit, H. Sjöblom, L. Wang, J. Birgerson, A. Fogden and W. Zapka, Inkjet Printing of Well-Adapted PEDOT-PSS Dispersions, Proc. IS&T's NIP 20, pg. 226-231, (2004).
4. G. Beurer and J. Kretschmer, Function and performance of a shear mode piezo printhead, Proc. IS&T's NIP 13, pg. 621-625 (1197).
5. H. J. Manning and R. A. Harvey, Xaar Greyscale Technology, Proc. IS&T's NIP 15, pg. 35-39, (1999).

Author Biography

Wolfgang Voit is member of the Technology Department at Xaar. He has worked for the past 8 years on both inkjet printhead technology as well as on developing new applications of inkjet printing. He received his diploma from the University of Applied Sciences in Regensburg, Germany, in 1996. Wolfgang Voit is presently finalizing his PhD thesis on inkjet printing of magnetic and functional devices at KTH (Royal Institute of Technology), Stockholm..