

Material Challenges in the Manufacturing of Tailored Structures with Direct Write Technologies

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Abstract

Two different direct write technologies, Direct Write Paste (DWP) and Direct Write Thermal Spray (DWTS), and the general material challenges related to these technologies are described in this paper. These new technologies open new routes to produce highly functional products that can be tailored and customised according to the demands of the applications. The DWP process is based on dispensing paste-like materials through a tip onto a substrate. Depending on the paste material, either 2 or 3 dimensional structures can be printed. The DWTS technique is based on thermal spraying, which is a spray process where the powder material is accelerated in molten form and impinged onto a surface. Products made using DWTS are especially targeted at harsh environment solutions. Results related to development of printable materials and printed products are presented.

Keywords: *Direct write; Dispensing; Additive manufacturing; Thermal spray.*

1. Introduction

Different Direct Write (DW) technologies have been developed to produce high performance solutions with added value in many kinds of applications. The definition of DW technologies refers to additive manufacturing which can deposit two- or three-dimensional functional structures directly onto flat or conformal surfaces in complex shapes, without any tooling or masks. The products can be tailored and customised according to the demands of the applications and in addition the multi-functionality of the products can be increased. DW technologies enable the integration of multiple manufacturing steps and miniaturisation of the components. Manufacturing with new DW technologies faces challenges that can be overcome by developing and tailoring the materials used in manufacturing to produce reliable and low-cost products with high functionality. This study concentrates on general material challenges related to two different DW technologies, namely Direct Write Paste (DWP) and Direct Write Thermal Spray (DWTS).

2. Direct write paste (DWP)

The DWP process is based on dispensing paste-like materials through a tip onto a substrate and it can be used to print antennae, resistors, thermo couples, adhesives, micro-lenses, porous chemical sensors, biological scaffolds and other components and structures. Printing is controlled with a three axis motion system, which utilises CAD approach. The accuracy and repeatability of the XYZ positioning of the dispensing nozzles has a resolution of within a few microns and the system is equipped with a laser scanning system that enables a constant working distance from the surface of the substrate.

The valve technology of the deposition pump generates very precise starts and stops of the printed lines or structures and very fine features starting from 20 μm . The functionality of the printed structure comes from the composition of the paste material and its interaction and bonding with the substrate material. The curing of the paste material also affects the properties of the printed structure. Usually the selection of the curing process (e.g. thermal, UV or laser technology) depends on the used paste material, which might also set some limitations for the possible substrate materials.

The properties of the paste material affect the selection of the nozzle (material, shape, size). The inner diameters of the nozzles are between 12.5 μm and a few millimetres. The printing result also depends on several printing parameters, such as speed, pressure, valve opening and printing height.

2.1 Materials for DWP dispensing

The DWP system allows the use of a large variation of dispensable paste materials with a large viscosity scale (1-1,000,000 cps). The materials available include conductive metals, semiconductor and dielectric polymers, ceramics, piezoelectric, ferrites useful to magnetic elements, gels containing living cells and other material types. The paste materials can be deposited onto almost all kinds of substrate materials including metal, plastic, glass, ceramic, paper and even fabrics.

The common requirement for the paste material to be deposited is that the pastes should exhibit a well-controlled viscoelastic response so that they flow through the deposition nozzle and then set immediately in order for them to retain the deposited features. In addition, they must contain a high colloid volume fraction to minimise shrinkage due to drying and to be able to resist compressive stresses arising from capillary tensions (Lewis 2006).

Most of the commercial screen printing paste materials are suitable for DWP printing, but other paste materials can also be developed and tailored. The general requirements for the paste materials are that particles are not very much agglomerated, especially regarding micro particles, and they should be distributed evenly in the paste material. It is highly desirable for the printed paste materials to maintain a constant and controllable cross-section, or to form a predictable and stable 3-D deposition shape.

2.2 DWP experiments and results

The DWP technique is suitable for printing lines or droplets onto flat or 3D surfaces, but building 3D structures by printing is also possible. In this study, different kinds of paste materials were developed and 3D scaffold structures were printed. In addition, the effects of different commercial conductive paste materials and sintering temperatures on the conductivity of printed lines were examined.

2.2.1 Printed scaffolds

New advanced printing technologies open novel routes to building two- or three-dimensional structures and scaffolds for polymeric, ceramic and cementitious materials. In tissue engineering, one of the strong emerging technologies, scaffolds are used to construct artificial organs *in vitro* before implanting them *in vivo*. These 3D scaffolds mimic nature's organic components in directing the migration and orientation of the cells in the construct. The same concept of printing 3D scaffolds was used in this work.

Biodegradable polymer pastes were prepared by dissolving poly-caprolactone (PCL) in chloroform. Pastes were sonicated in a water bath and de-aerated before dispensing. Highly volatile solvents like chloroform have the advantage that directly after printing, the solvent on the surface evaporates, leaving a solid polymer skin. This means that the flow of the paste is minimised and the printed structures well retain the printed dimensions. Scaffolds with a constant pore size and gradient architecture were printed at a relatively low printing speed to ensure the evaporation of the solvent of the PCL paste before printing the next layer on the top of the previous one (Figure 1). Scaffolds were ready directly after the printing and natural evaporation of the solvents. PCL paste was quite easy to print, mainly because there were no particles in the paste matrix.

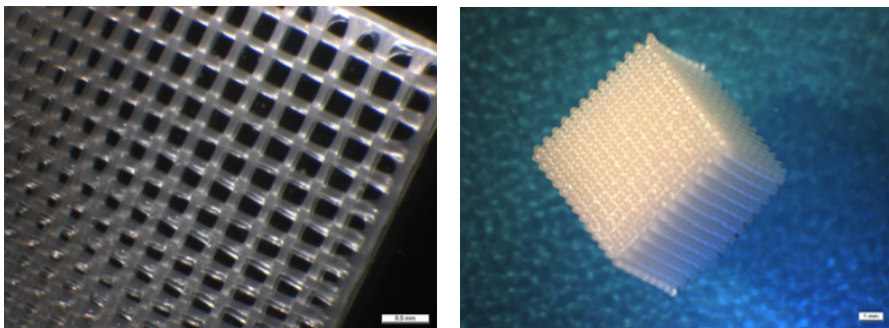


Figure 1. PCL scaffolds (side length ~ 5 mm). Gradient structure (left) and 180 layers high with conformal pore size (right).

Titanium dioxide (TiO_2) pastes were prepared by modifying a formulation for titanium hydride (Ahn et al. 2010). In brief, TiO_2 powder was mixed with a mix-

ture of dichloromethane (DCM), 2-butoxyethanol and dibutyl phthalate and sonicated in a water bath. A polymer solution (poly-acrylate block-polymer in DCM) was then added and the suspension was homogenised and concentrated using a sonicating probe. The printing of ceramic scaffolds was more demanding than polymeric ones because the paste clogged little by little into the printing tip. However, it was possible to produce scaffolds with a few tens of layers (Figure 2). The next step will be the sintering of the ceramic scaffolds to generate solid structures. This will be a two-fold objective: first the polymer is pyrolysed and a pure TiO_2 structure is generated. At higher temperatures ($\sim 1000^\circ\text{C}$) the individual ceramic particles are merged into a continuous ceramic structure.

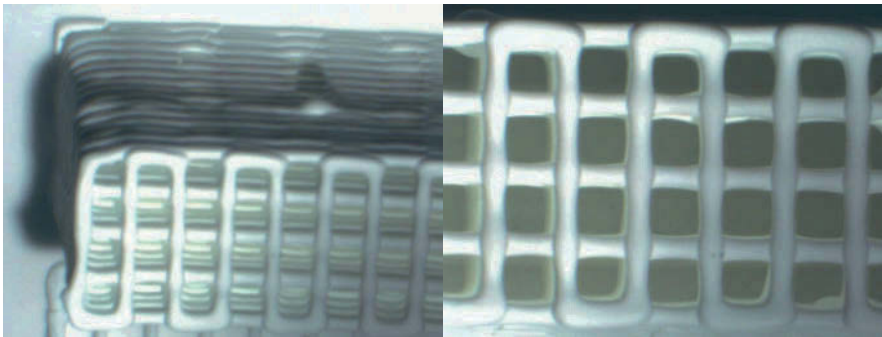


Figure 2. TiO_2 scaffolds. Pore size $\sim 1\text{ mm} \times 1\text{ mm}$.

Mineral hydration materials can also be used for printable 3D structures. Mineral hydration is an inorganic chemical reaction where water is added to the mineral crystal structure through the dissolution – precipitation process (Bullard et al. 2011). The reaction product is called a hydrate. Ordinary Portland Cement (OPC) hydration is a well-known mineral hydration material used in the construction industry. The main component of OPC, impure tricalciumsilicate, reacts with water producing calcium-silicate-hydrates. Calcium phosphate cement (CPC) is another mineral hydration material which can be used for repairing bones, for example (Liu and Shen 1997). The final product of CPC hydration is hydroxyapatite.

Mineral hydration materials are self-hardening, so there is no need for additional hardening treatment as ceramics, for example need sintering. The hardening process of mineral hydration material is also auto-acceleratory. At the beginning of hydration reaction, the reaction rate is low. When hydration proceeds, the reaction rate increases. This type of behaviour causes a relatively long dormant period at the beginning, where hydrating paste is printable. Because of hydration's auto-acceleratory nature, hardened structures can be attained within 24 hours. The reaction rate of hydration reaction can be easily manipulated with appropriate admixtures (Thomas et al. 2009).

Mineral hydration materials also exhibit limited hardening shrinkage. At the beginning, mineral powder and water have an almost equal volume to that in the final hardened structure. A small amount of hardening shrinkage enables accurate 3D structures.

The biggest problems in mineral hydration materials were encountered in actual printing. Mineral hydration pastes have a natural tendency to segregate. In 3D

structures, mineral hydration pastes must have a certain yield stress, but the paste must remain printable. It was found that minimising particle size, optimal dispersion and increased viscosity of liquid phase enabled printable 3D structures with mineral hydration pastes.

With OPC paste optimised according to presented principles, preliminary 3D structures were printed. These structures had a 30MPa compression strength and a total porosity of 30%.

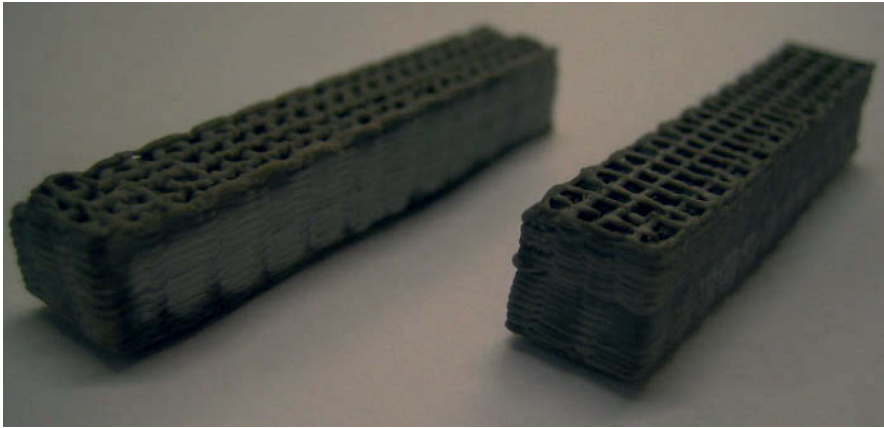


Figure 3. Printed OPC paste 3D structures (pore size ~2mm x 2mm).

2.2.2 Conductive lines

The aim of the conductivity measurements was to compare the properties of three silver-based commercial conductive paste materials (DuPont 5028, ANP DGP, Spraylat XCSD-006N) and to study the effect of the curing temperature on the conductivity values. Generally, all three paste materials were suitable for DWP dispensing and the profiles of the printed lines were controllable. Alumina (Al_2O_3) plates were used as substrate materials.

Several parallel lines with each silver paste material were dispensed on the alumina plates. The samples were cured at three different temperatures: 120°C, 300°C and 750°C. The direct current (DC) conductivity was measured using the 4-point probe method. The cross-sections of the cured lines were determined with a 2D-profilometry.

The results of the DC conductivity measured from 2-4 parallel lines are presented in Figure 4. The conductivity of printed lines is presented as a percentage of the conductivity of the bulk copper. The curing temperature had an effect on the conductivity, since the higher the temperature was, the better the conductivity was. There were also significant differences between different paste materials. The conductivity of XCSD-006N paste was highest after curing at 120°C. When curing at 300°C, ANP DGP nano silver had the highest conductivity values, but conductivity of XCSD-006N dropped significantly. However, at 750°C very good conductivity (>75%) was reached with both 5028 and XCSD-006N. Nano silver paste reached 45% DC conductivity of bulk copper at 750°C.

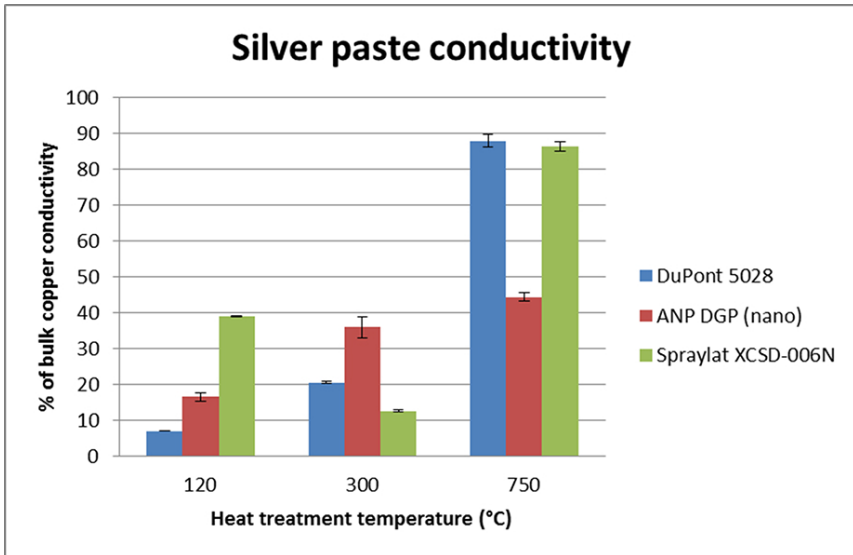


Figure 4. DC conductivity average values and standard deviations of three silver pastes after three different heat treatment temperatures.

The material structures of the printed lines were also changed with the higher curing temperatures. The polymeric binder materials were sintered away from the paste and only metallic components were left after sintering at high temperatures (Figure 5). This might have an effect on the functionality of the paste materials in certain applications.

	120°C	300°C	750°C
ANP DGP			
Spraylat XCSD-006N			

Figure 5. Microscopic images of conductive lines (width ~200µm) printed with two different pastes materials and cured at 120°C, 300°C and 750°C.

3. Direct write thermal spray (DWTS)

The DWTS technique is based on thermal spraying, which is a spray process where powder material is accelerated in molten form and impinged onto a surface. A dense and strongly adhered deposit of material is formed by rapid solidification on the substrate surface (Sampath et al. 2002). In DWTS, the material is injected in the powder into a thermal plasma flame, which imparts thermal and kinetic energy to the particles. The deposit is built up by successive impingements of droplets, which are flattened, solidified platelets, or splats. The microstructure and mechanical properties of the deposits are dependent on the process parameters.

DWTS uses a miniature spray gun and an aperture assembly to create fine feature spray depositions (United States Patent, US 6,576,861 B2, 2003). The technique has the ability to spray in a computer-aided patterning way both dielectric and conductive materials directly to the component surface to form conductors, sensors, antenna structures and electromagnetic surfaces, for example. The typical line widths and feature sizes achievable routinely with DWTS are 300 μm ; smaller dimensions have also been demonstrated (Sampath 2010). The DWTS deposition process is controlled by a six-axis articulated robot that enables deposition of patterns and features onto non-conformal 3D surfaces.

3.1 Materials for DWTS

By controlling the spray process, a wide range powder of materials can be deposited with DWTS, covering metals, ceramics, polymers, semiconductors and their combinations. The requirement for the powders is that the particle size is very fine, normally between 10-30 μm , to ensure through melting and enable finely detailed structures to be sprayed. These kinds of powders can be manufactured by high pressure inert gas atomisation (metals) and spray drying with high speed rotary nozzle. The DWTS materials undergo a melting and solidification process during deposition and can be used in an as-deposited state without post-treatments. Several dielectric materials can be sprayed for electrical insulation with differing dielectric properties. Typical dielectrics, such as Al_2O_3 and MgAl_2O_4 , can also be used as protective coatings on layered structures. Typical metals used for electrical components are e.g. copper for conductors and e.g. NiCr and Ni-5%Al for sensor materials (Sampath 2010).

There are several challenges for material development as well as for manufacturing technology that is used to fabricate the desired material. In order to successfully embed the electric circuits on or into the structures, certain prerequisites needs to be met. For example, the electronic structures need to be electrically insulated from the conductive materials of the component. In a similar way, it is viable to cover the electronic structure with a protective layer. The insulating dielectrics need to have high resistivity, high permittivity (close to bulk value) and low dielectric losses. When the electronic structures are fabricated on mechanical components, the insulating layers must also have sufficient mechanical strength. The material properties of the electronic structures need to meet the functional re-

quirements. Conductor material, for example, needs to have high conductivity to e.g. minimize power losses. For wireless communication the radio-frequency (RF) conductivity also has to be sufficiently high to meet the functionality requirements. The functionality requirements are mainly set by the desired application and the manufacturing process and therefore the multi-material structures need to meet the desired lifetime expectations.

The material development and the manufacturing technique are closely related to each other. In order to achieve good material properties, both of them need to be developed and tuned.

3.2 DWTS experiments and results

In thermal spraying, metallic materials are melted or heated and some oxidation will take place during the flight onto substrate and on the substrate. There is a strong need to find a solution to produce metal wiring from cheaper materials, such as copper, without oxidation. In this study, the approach was to compare commercially available copper for DWTS and further develop these powders to achieve better conductivity values. Conductive lines were sprayed with DWTS using three different commercial copper powder materials (Table 1, Figure 6). The DC conductivity of the lines was measured, and it was noted that several parameters influenced the printed structure made using DWTS. One of those is the number of sprayed layers, as thermal spray coatings are normally made by several passes over the surface area. The cross-sections of the printed structures were dependent on the number of sprayed layers, and the powder-feeding parameters also influenced the coating. From the powder side the powder type, morphology and size distribution had the greatest influence on the spray parameters and are thus powder-dependent variables.

Table 1. DWTS sprayed copper materials.

Powder	Composition	Structure	Particle size (μm)	Oxide content (w%)
Cu	Cu	spherical	8–15	0,51
Cu(H)	Cu (High purity)	spherical	7–21	0,18
Cu(H2)	Cu heat treated in H2	spherical, contain agglomerates	9–36	0,36

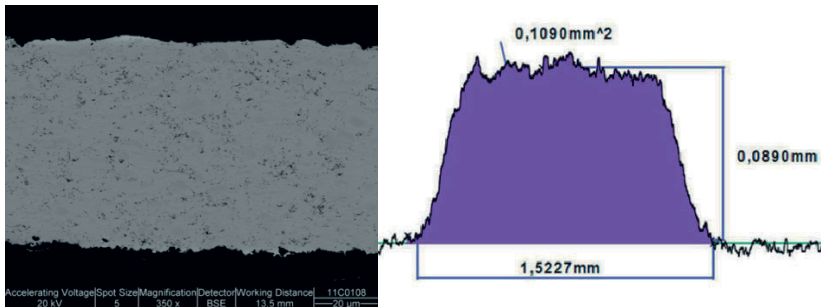


Figure 6. SEM microstructure of typical DWTS sprayed Cu conductor (left) and a typical Cu line profile cross section (right). Note the magnification x50 and y500.

The conductivity of sprayed structures is presented as a percentage (%) IACS (International Annealed Copper Standard) of bulk copper conductivity (Figure 7). In general, the increment of the cross-section area from 0,020 to 0,060 mm² increased the conductivity of all materials. Above 0,060 mm² the effect of the cross-section on the conductivity was not significant. The conductivity of high purity copper with the smallest particle size and oxygen content was highest, while the normal copper reached the lowest values. As summarised, both the powder material and its oxygen content had an effect on the conductivity.

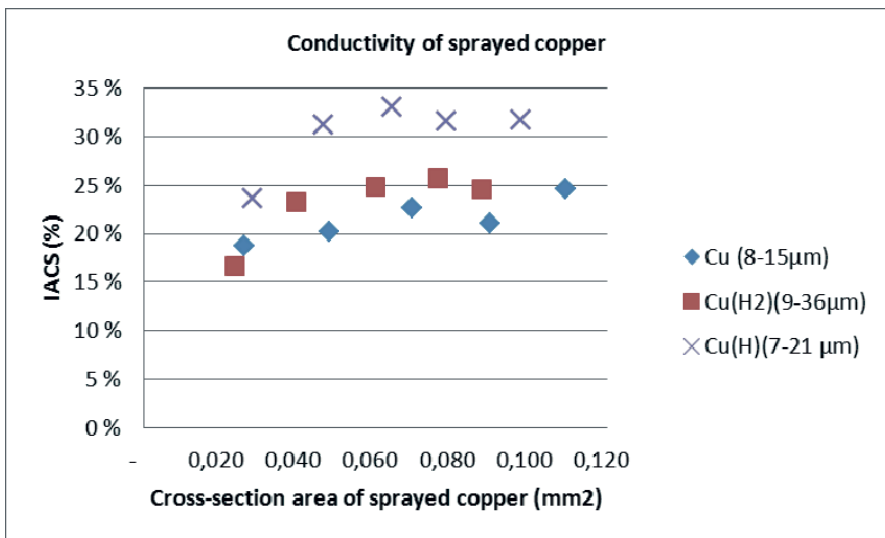


Figure 7. The effect of the cross-section area of the sprayed material on conductivity (IACS value). Maximum standard deviation (STD) is 1,97 % for the IASC values and 5,76 % for the cross-section values.

4. Conclusions

Material challenges related to DWP and DWTS technologies differentiate from each other. DWP technology is based on dispensing paste-like materials and DWTS technology is based on thermal spraying, which is a spray process where powder material is accelerated in molten form and impinged onto a surface. Different kinds of paste materials were developed and 3D fine structures were printed with DWP. In addition, the printing of commercial conductive pastes was tested and significant differences between the conductivity values of different paste materials were detected. The sintering temperature also had a remarkable effect on the conductivity. Three different commercial copper materials were sprayed with DWTS and the conductivity of the printed structures was determined. The amount of sprayed layers and the composition of the powder material had a significant effect on conductivity values.

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