Copper Printing by Digital Light Processing

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Abstracts

Digital Light Processing (DLP) is well known to perform polymer and ceramic 3D free-form structures. This paper deals with a high efficiency green material copper powder printing by DLP. Following to the layer-wise DLP process, thermal treatments were performed to burnout the photocurable resins (debinding) and to consolidate the printed copper parts by sintering. C, O, P, S or other light elements coming from resins and photoiniators could be trapped in the copper parts, during the debinding. To fine tune the photocurable resin composition and the conditions of thermal cycle, many printed specimens are required. The DLP printing is the rate-limiting step. For each formulation, a high quantity of copper formulation (several kg) is required, and the printer parameters set up. To save materials and time, a methodology based on a fast gamma rays curing as an alternative to DLP printing is described in this work. Chemical and thermal properties of copper objects cured by gamma rays and by DLP technology are compared.

Introduction

The copper is a green material with high thermal and electrical conductivity, and antibacterial properties [1]. Perfect for building a sustainable world, the copper is used in solar and wind energy, in power electronic and medical. Manufacturing complex parts are required to develop new generation power generators and electrochemical management systems. Digital Light Processing (DLP), a variant technique of Stereolithography (SLA), is a route to create free-form polymer [2–4], ceramic [5–8] and also metallic 3D structures by photocuring a mixture made of powder and photocurable resin. Upon cured formulation, the resin bonds the metallic particles conferring the required strength to obtain green metallic parts. Green parts are then debinded in order to remove organic phase through an appropriate thermal treatment following a sintering stage that confers the final properties of parts [9,10].
Few investigations on parts fabrication from a metal based photopolymer were published on copper [11], aluminum [12] and stainless steel [13,14] components without any data on chemical composition after printing and sintering.
The main technological issues are:

- Achieving high solid loading >45%vol.[15] in the resin to obtain after sintering a dense component,
- Photocuring with a minimum thickness layer of 50 µm
- Determining the binder burnout and densification thermal conditions to give a high density and the expected properties [13],
- The sensitivity of metallic particles to the formation of carbides, nitrides or oxides [13]

To investigate these issues and obtain crack free and pollution free (C, O) parts, debinding protocol (atmosphere, ramp, Temperature, dwell time), several formulations must be performed. Only layers with a thickness between 50 µm to 100 µm are cured by UV LED irradiation. To assess different parameters on the debinding step and test photocurable resins on representative SLA objects, 1 to 3 mm thick parts

should be printed. To print such objects by DLP, 1L filled formulation, either 6 kg of copper formulation should be carry out and machine parameters identified (layer thickness, curing time) for each formulation. Gamma rays irradiation is known to polymerize/cure monomer and oligomer acrylates, polymers used in SLA formulation. This curing approach reduces the materials quantity necessary for the same number of samples and polymerizes several formulations at the same time, with a unique energy dose.
The objective of this paper is to describe a saving time and saving materials methodology to investigate C and O contents based on copper photocurable formulation and thermal cycles:

- Developments of copper formulations and assessment of the reactivity after exposition to UV light
- Irradiation of the copper formulations by gamma rays and investigation of thermal cycle conditions to obtain copper objects, characterization of C and O contents and thermal conductivity
- Printing 3D free-form green copper structures, applying the suitable thermal cycle and characterization of the objects

Materials and methods

Formulation

Four photocurable resins noted F1, F2, F3 and F4 were investigated and described below.
F1 resin is a blend of 1,6-hexanediol diacrylate (SR238 - Sartomer), tetrafunctionnal oligoacrylate (SR355 – Sartomer) and an amine modified polyether acrylate (CN509 – Sartomer). Both photoinitiators (PI), 2-methyl-4'-methylthio-2-morpholinopropiophenone (PI1), known for its high reactivity and the Phenylbis (2,4,6-trimethyl-benzoyl)phosphine oxide (PI2), having a photobleaching behavior are dissolved by magnetic stirring in the monomer and oligomers mixture.
F2 resin, is a modification consists in substituting of SR355 for half by the polyester acrylate (CN371EU).
F3 resin is a mixture of SR238, SR355, ethoxylated bisphenol A dimetacrylate (Diacryl 101 – Sigma Aldrich) and the PI1 and PI2 photoinitators.
F4 resin is equivalent in terms of acrylates to F3. The PI1 & PI2 are replaced by the photoiniator 2-2 Dimethoxy-2- phenyl acetophenone (PI3).
The photocurable resin amounts to 40% vol in the metallic formulation. The PI rate is fixed to 5.4 wt% by photocurable fraction.

Commercial spherical copper powder supplied by Ecka were used as filler in the photocurable formulation. The copper powder consists in a monomodal distribution below 45 µm with 22 µm as a mean diameter. The powder has a purity > 99.9 % and contains 0.02 wt % of phosphorus.

Curing routes

Curing by DLP printer

The curing reactivity of the copper formulation is determined by measuring the cured thickness versus the exposure time to UV light at 365 nm and an irradiance of 88 mW/cm². The copper formulation is spread on a glass substrate. The emitting UV device prints a square pattern onto the spread layer. Its thickness is measured with a digital micrometer.

Cu printing is conducted on the F1 photocurable copper formulation using a Digital Light Processing equipment (ProMaker V6000 - Prodways). The operating principle is described in Figure 1.

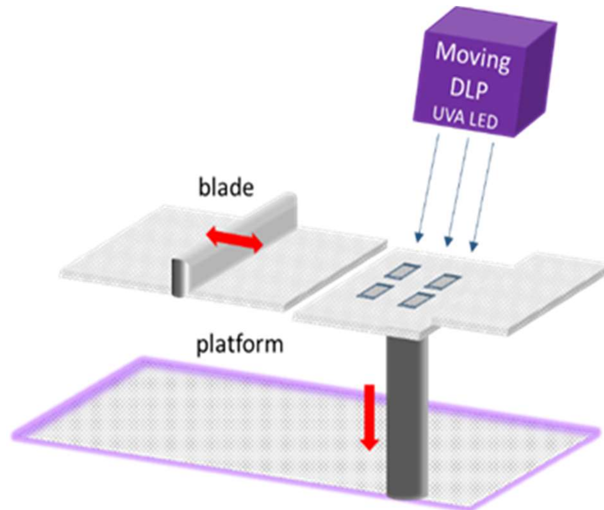

Figure 1. DLP operating equipment

To print a 3D free-form object, a numerical file is prepared and loaded onto the machine. Parts are virtually sliced into layers by the machine during the build job. A feeder system delivers a volume of paste onto the platform, which is spread in thin layers (25 to 100 µm). The UV light (Wavelength 365nm – Power 88 mW/cm²) head projects a pattern of the layer slice of the part to be built onto the platform covered with the paste. Upon photocross-linking, the platform moves down of a height corresponding to the previously cured layer thickness. A new layer of paste is spread on top of the previous one, and the process is carried on until the 3D part is built by stacking of cured layers.

Curing by Gamma-rays

For a fast curing out of the printer, the copper formulation is poured in tubes and cured by gamma rays radiation at a unique dose of 30 kGy. The green copper samples are then sliced in cylinders with 5 mm height and 13 mm diameter.

Thermal debinding and sintering

Final carbon and oxygen rates, and therefore, the purity and the properties of final products are closely correlated to the composition of photocurable resins, and the debinding stage (gas nature and flow). To optimize the debinding parameters according to copper formulations, the thermal process were performed from room to debinding temperature, using different debinding temperatures up to 800°C, with various dwell time (4h, 7h and 10h) and different atmospheres (vacuum, argon, hydrogen and air). For hydrogen, various partial pressure (50 mbar, 400 mbar and 600 mbar) were studied as well. Finally, the Cu samples are naturally cooled to room temperature.

Then, from the optimal debinding thermal treatment, the printed parts were sintered, in hydrogen atmosphere at three temperature dwells 980°C, 1030°C and 1050°C and a constant heating rate of 3°C/min. The hydrogen atmosphere reduces the oxygen in the copper powder and makes the copper densification easier.

Results and discussion

Photocuring by UV light

The first step of the methodology is to assess the interaction of the UV light exposition and the copper photocurable formulation, knowing that a minimum cured thickness required is 50 µm. The four photocurable resins filled with 60% vol of copper powder have (Figure 2) a high reactivity with cured thickness above 50 µm. The high filled formulations are suitable with DLP manufacturing process and high-density copper structures.

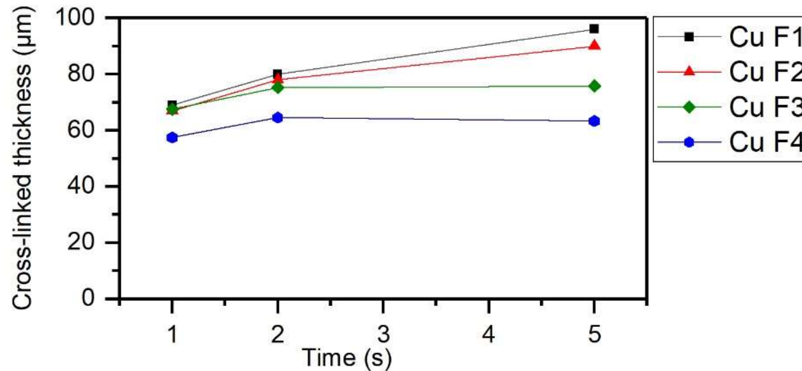

Figure 2. Reactivity - Photocured resins filled with 60% vol of copper
UV irradiance 88 mW/cm²

Curing under gamma-rays irradiation

C and O contents

The four Copper formulations were cured by gamma rays irradiation. The organic resins are then burnout and the parts sintered in H_2 (partial pressure 400 mbar) at 980°C during 4h. The density of samples were measured after sintering, with the Archimedes immersion method in anhydrous ethanol. Internal Gas Analysis (IGA) were performed to measure carbon and oxygen elements on sintered copper parts.

The final density is about 90% of the theoretical value of the DHP (deoxidized high phosphorus) copper (8.94 g/cm^3) after a debinding cycle in air at 400°C - 4h and a sintering step. For other debinding conditions in Ar, H_2, vacuum and at 0.06 % and 5 % O_2 in Argon up to 800°C, the density decreases to 70%. The decrease is mainly due to the presence of carbon in the Copper The carbon comes from the partial degradation of the organic fraction and inhibits the copper sintering.

As confirmed on the Figure 3, the debinding amosphere is a crucial factor on the carbon and oxygen rates. A neutral, reducing or slighly oxidizing atmospheres leads to a carbon rate about 20 times higher (0.36 wt%) than in air, whatever the partial pressure, dwell temperature and dwell time. In air, the carbon rate is equivalent to the raw copper powder (0.019 wt %). In this condition, the oxygen rate is however 3 times higher (0.085 wt%) than the raw copper powder.
To reduce the oxygen rate in the final part, the sintering conditions in hydrogen atmosphere could be optimized. For example, in sintering cylinders at 1050°C, the oxygen content is reduced to 0.067 wt% and the density increases to 94 %.

Table 1 summarizes the C and O contents of the four copper formulations after a debinding in air at 400°C and a sintering in hydrogen at 980°C.

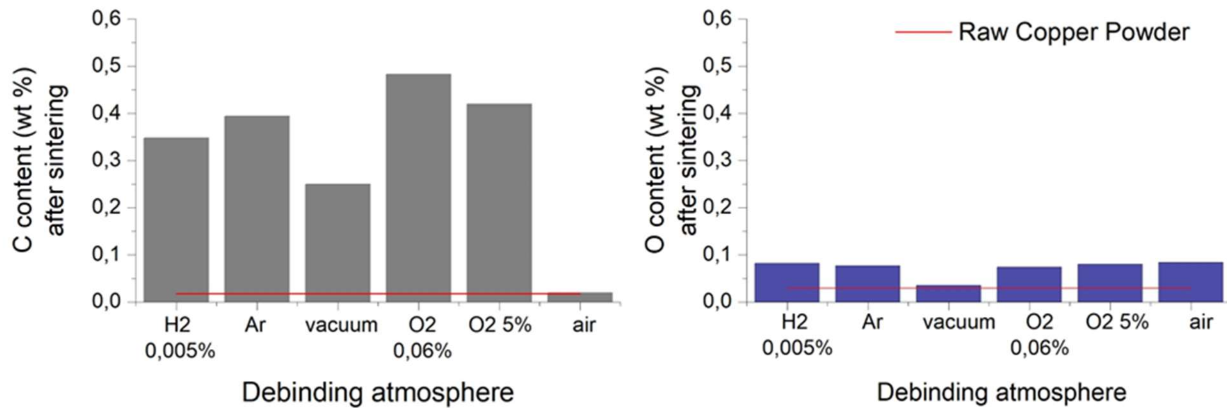

Figure 3. C and O content (wt %) versus debinding atmospheres of Cu F1 formulation -on left after sintering at 980°C during in H_2 (Cu F1-s) – on right

	Raw copper Powder		Cu F1-s		Cu F2-s		Cu F3-s		Cu F4-s	
	C (wt %)	O (wt%)	C (wt %)	O (wt%)	C (wt %)	O (wt%)	C (wt %)	O (wt%)	C (wt %)	O (wt%)
	0.018	0.028								
Photocurable copper formulation debinded in Ar			0.394	0.077						
Photocurable copper formulation debinded in Air			0.019	0.084	0.022	0.063	0.018	0.054	0.013	0.077

Table 1. C and O contents (wt %) of the raw copper powder and the Cu F1 to F4 formulation cured under γ-rays irradiation, debinded in air or argon 600 mbar at 400°C -4h ramp 1°C/min, sintered at 980°C - 4h ramp 3°C/min in hydrogen 400 mbar (Cu F1-s to Cu F4-s)

Thermal conductivity

The thermal conductivity is calculated by using the following equation (1)

$$\lambda = Cp * \rho * \alpha \quad (1)$$

where λ [W/m.K] is the thermal conductivity, Cp [J/g.K] is the heat capacity, ρ [g/cm^3] is the material density and α [mm²/s] is the diffusivity.
The thermal conductivity were compared to copper pressed powder cylinder sintered during the run of the debinded Cu F1 to F4 samples.

Figure 4 relates to the thermal conductivity measured on the pressed and sintered raw copper powder used as a reference and on the Cu F1 to F4 sintered (s) samples. The thermal conductivity is measured after a sintering at 980°C, 1030°C and 1050°C in hydrogen. The thermal conductivity of the raw copper powder is about 250 and 270 W/m.K, value significantly lower than the pure copper at 393 W/m.K[16] (electronic copper Cu-OFE pure at 99.99% with 0.0005% of O) . The lower value could be explained by the presence of phosphorus (0.025 wt %), which decreases drastically the thermal conductivity.

Cu F1-s to F3-s samples have a lower thermal conductivity, derived from the integrity of the cylinders and from the addition of phosphorus based on PI (0.035 wt%) in the final object.
The formulation F4 leads to a thermal conductivity similar to the reference. The parts do not exhibit cracks and have a composition in light elements (C, O & P) similar to the raw powder. The oxygen content is higher, as previously commented, and has a minor contribution on the thermal conductivity.

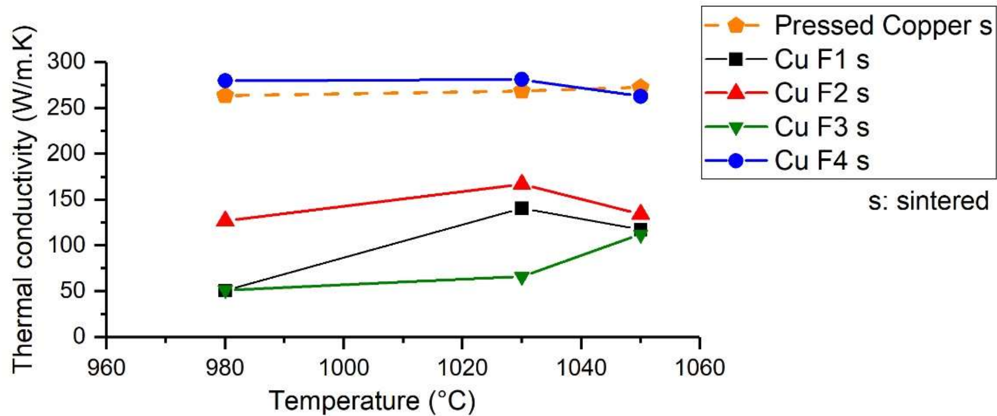

Figure 4. Thermal conductivity based on the Cu F1 to F4 formulation – cured under γ-rays irradiation, debinded in air at 400°C - 4h ramp 1°C/min, sintered at 980°C, 1030°C et 1050°C - 4h ramp 3°C/min in hydrogen 400 mbar (Cu F1-s to Cu F4-s)

Complex shape parts printed by DLP

Cylinder copper parts for diffusivity measurement (12.6 mm diameter on 3 mm height) and gears (X=Y=21.4 mm Z=2.8 mm) were printed by DLP process from the Cu F1 formulation. Cu F1 formulation shows the highest reactivity to photocure (Figure 2) and a low thermal conductivity (Figure 4). Printed parts were debinded in air and sintered in hydrogen according to the previous results.
The carbon and oxygen contents measured on complex parts are respectively 0.017 wt% and 0.022 wt%, values close to those of the raw copper powder. The contamination in light elements depends on the geometry of parts specially the thickness. As the wall thickness of gear are thinner than the cylinders cured by gamma rays irradiation, the efficiency of copper reduction in hydrogen is improved.
The thermal conductivity of the printed parts were measured between 100 and 110 W/m.K after a sintering at 1030°C, for 140 W/m.K for a gamma rays part. The thermal conductivity of printed structures is lower than the value measured on gamma rays cured cylinders. Since the formulation and the thermal conditions are the same, the difference of thermal conductivity seems mainly due to the layer by layer shaping.
Further investigations should be done on Cu F4 formulation.

Figure 5. SLA copper structures
Green copper part (Cu F1), debinded part and sintered part (left to right)

Conclusion

As shown in this paper, the methodology based on a curing approach by gamma rays irradiation of copper photocurable formulations is suitable to investigate the influence of the formulation composition and thermal treatment conditions, on C and O contents.

Such methodology appears to be promising to investigate other metals and ceramics printing by DLP followed by a thermal cycle.

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