

Binder Jetting Additive Manufacturing with a Particle-free Metal Ink as a Binder Precursor

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Abstract

Metal-Organic-Decomposition (MOD) ink is a particle-free metal ink that can precipitate metal nanoparticles upon heating. This ink-jettable metal nanoparticle ink can be used as a binder precursor to replace commonly used polymer adhesives in the Additive Manufacturing of metals components using binder jetting technology. After being deposited into the powder bed interstices and exposed to a heat, the jetted ink decomposes and form metal nanoparticles that are then fused by sintering to provide bonding strength to the printed parts. Regions of the powder bed that do not receive the jetted nanoparticles remain as loose powder, as the heat supplied to sinter nanoparticles is maintained below the initial sintering temperature of larger powder bed particles. The proof of concept is demonstrated in the context of printing copper by jetting copper MOD ink as a precursor to the binder, with the capability of producing satisfactory geometries when using sufficiently high binder saturation ratio. After sintering, the MOD ink printed parts produce a denser core section but more porous shell in the sintered parts, compared to the polymer binder printed counterparts.

Keywords: MOD ink; nanoparticle; inkjet printing; binder jetting; Additive Manufacturing; copper

1 Introduction

1.1 Binder jetting process

Additive Manufacturing (AM)'s layer-by-layer fabrication approach has enabled key opportunities for high performance structure and material design [1,2]. Among all Additive Manufacturing technologies, binder jetting is a suitable platform to realize material innovations for its wide range material capability and high manufacturing throughput. For example, binder jetting has been used for fabricating high purity copper, a material that is challenging to process using laser-based powder bed fusion technologies due to high thermal conductivity and optical reflectivity [3].

The binder jetting Additive Manufacturing (AM) process can be used to fabricate metal parts by selectively inkjet printing a liquid binding agent into a powder bed (the arrangement and packing of particles inside a contained build piston), followed by post-process sintering of the printed green part. The jetted binder droplets interact with the powder particles to form primitives that stitch together to form a cross-sectional layer. Once a layer is printed and thermally dried/cured, a new layer of powder is recoated on top of the previous layer, which is then printed and stitched to the previous layer by the jetted binder. The layer-by-layer process is repeated to create the complete green part. The unbound loose powder in the bed that surrounds the part supports overhanging structures during the build, and can be removed after printing via compressed air. Once depowdered, the green part is placed in a furnace to burn off the binder and to sinter the powder particles together to obtain final density and strength.

The selection of binder material for binder jetting is critical as it determines the success of creating green parts with satisfactory green strength and affects the final properties of the sintered parts

(e.g., sintered density and sintering shrinkage). Different types of binders have been used in binder jetting, including various solvents, colloids, and polymers based inks [4].

1.2 Polymer binder vs. metal binder

In modern commercial metal binder jetting systems, solvent-based binders that contain thermosetting polymers are commonly used to print green parts [5]. As shown in Figure 1, after jetting binder at each layer, an overhead heater removes the solvent (drying). Once the part is printed, the entire powder bed can be placed in a curing oven to fully set and crosslinks the jetted polymer (curing). While the curing of binder could be integrated into a drying process with longer heating time and higher temperature, it is typically chosen to cure the part separately after printing for economic reasons. The cured polymer binder is then burned at an elevated temperature through polymer pyrolysis when the printed part is sintered.

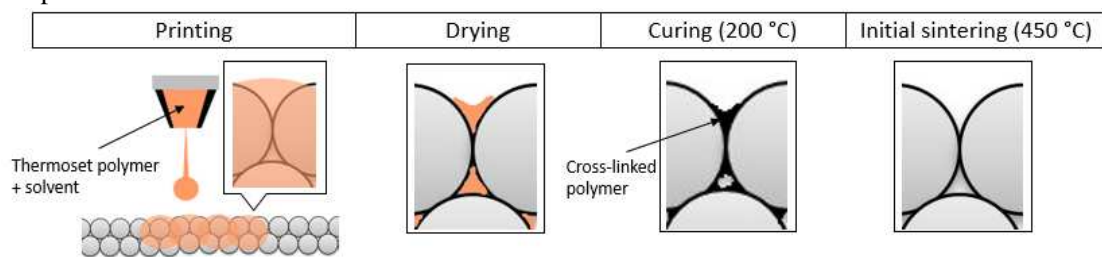


Figure 1. Jetting a thermoset polymer as the binder

While polymer binders have demonstrated a wide success and compatibility with many metal systems, its use in binder jetting can add complexity to the sintering process and adversely affect the final product performance metrics:

- (i) the need to debind polymer binders typically require refined sintering profile and slow heating ramp to facilitate polymer pyrolysis and degassing, and could lead to debinding-related defects;
- (ii) the green part can lose structural integrity (i.e., warping, creep) during sintering if the onset sintering temperature of powders is higher than the binder burn-out temperature;
- (iii) the pyrolysis of polymer binder can leave residual ash, which affects the purity (and thus mechanical, optical, electrical/thermal properties) of the final part.

To circumvent these limitations, the authors propose using metal nanoparticles ink as a binder to replace polymer adhesives. Many metal nanoparticles manifest size-dependent melting behaviors and lower melting/sintering temperatures compared with the bulk materials [6]. For example, copper nanoparticles can sinter and neck within temperature ranges (150-300 °C) that are significantly reduced from sintering temperature for micron-sized powders (around 1000 °C) [7]. When nanoparticles are jetted as a binder in binder jetting, this unique sintering temperature reduction feature of nanoparticles can enable the selective cohesion of the powder bed when heat is supplied at each layer to sinter jetted nanoparticles while not affecting the powder in unprinted regions.

1.3 Review of metal inks used in binder jetting

Metal inks have been explored in prior research for fabricating metal artifacts to enhance material properties. Metal-based binders have existed in the forms of either metal particle suspensions or metal salt solutions, and used as a standalone ingredient or mixed with other adhesives.

1.3.1 Particle suspension metal inks

Particle suspensions can be used together with polymer binders to enhance material properties [8–10]. For example, silver nanoparticles were dispersed into suspensions and used together with a water-based organic binder to print micron-sized silver powders, which achieved higher sintered density (88.9%), reduced shrinkage and warpage compared to just using the polymer binder.

Jetted particulate suspensions can be also used without the presence of other adhesives. Yoo *et al.* jetted carbonyl iron (1.7 μm) suspended into water to stainless steel powders (60 μm) followed by firing the entire powder bed in forming gas at 600–700 $^{\circ}\text{C}$, under which temperature the interstitial carbonyl iron particles sintered without sintering the base powder, generating weak but retrievable printed parts [11]. Similarly, Hadjiloucas *et al.* used silver suspensions as the binder for printing molybdenum powders [12]. The printed interstitial silver particles melted and bonded the base powder particles after heating at 1000 $^{\circ}\text{C}$; at this temperature, the base powder remained loose and ensured part retrieval from the powder bed.

In prior work, the authors have successfully used nanoparticles as a binder to print micron-sized powders in a single material system (e.g. copper) [13]. A copper nanoparticle suspension was jetted into copper powder as a binder without polymer binders. Green parts with satisfactory integrity (flexural strength of 1.1 MPa) were produced by sintering the jetted nanoparticles after subjecting the printed powder bed to heating (200–250 $^{\circ}\text{C}$). The printing process schematic for nanoparticle binders is depicted in Figure 2. Compared to the sacrificial polymer binder in Figure 1, the nanoparticle binder is permanent as it remains after sintering and becomes part of the final product.

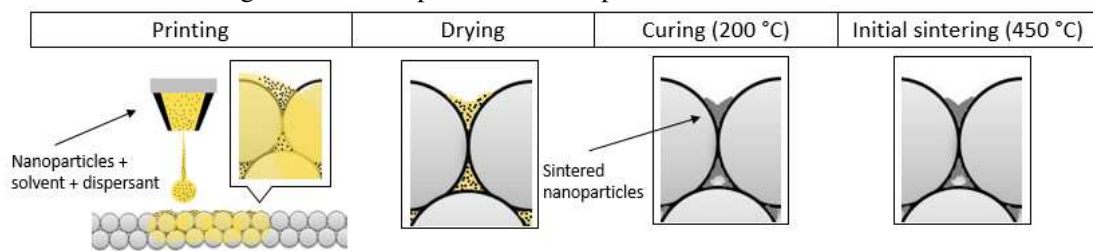


Figure 2. Jetting a nanoparticle suspension as the binder

Despite the vast success of using particle suspensions demonstrated in the literature, the overall effectiveness of using particle suspension as a metal binder is limited by (i) the difficulty to disperse particles and requirement of capping materials in the suspension, and (ii) possible ink sedimentation and printhead nozzle clogging during inkjet printing.

1.3.2 Metal salt inks

Due to the challenges in inkjet printing particle suspensions, researchers have looked to use metal salt as an alternative metal ink. Metal salts dissolved in solvents can be jetted, and then precipitate metal solids through decomposition or reduction upon heating. Various inorganic metal salt solutions have existed for the use as a precursor ink in conductive pattern printing (e.g., copper nitrate hydroxide [14] and copper sulfate [15]). Compared to particle suspension binders, metal salt ink is particle-free and therefore is more suitable for inkjet printing applications, such as (i) reducing the risk of clogging inkjet printhead, (ii) preventing ink sedimentation and increasing ink shelf life, and (iii) alleviating surface oxidation in metal nanoparticles during storage.

Metal salt has been used with or without polymer binder for printing metals in binder jetting. Liu *et al.* used metal salts as precursor inks to strengthen printed metal parts [16]. Copper or nickel acetate saturated solutions were deposited into stainless steel powders, after firing at a temperature below the powder sintering temperature (450 $^{\circ}\text{C}$), metals formed and sintered to the metal powder particles and to

one another in the powder interstices. Yoo *et al.* used silver nitrate as a binder for steel powders [11]. Silver nitrate reduced to an adherent silver film in the powder neck region and produced pellets with satisfactory strength after firing in forming gas at 400 °C, at which temperature the steel powder did not sinter. Hadjiloucas *et al.* used copper and silver salt solutions as binders for molybdenum powders [12]. The molybdenum powder allows an ultra-high temperature (>1000 °C) to cure the metal salt binder without sintering the powder bed. The printed parts were heated above the melting temperature of the elemental metals, where the metal salts decomposed, melted and formed a necking between powder particles.

While metal salt inks circumvent the dispersion and jettability issues in jetting particle suspensions, its use as a binding agent in binder jetting is limited in that (i) the metal content is limited by the metal salt solubility in saturated solutions, and (ii) the metal salt decomposition or reduction typically requires ultra-high temperature and reducing atmosphere. For example, copper acetate water solution is difficult to be used as a binder for printing copper, as the metal content cannot exceed 2.3 wt% due to solubility limits, and the required ink metallization temperature (300 °C in air [17]) exceeds the initial sintering temperature of micron-sized copper powders.

1.3.3 Metal-Organic-Decomposition (MOD) inks

Metal-Organic-Decomposition (MOD) ink is a metal ink that has been widely used for printed electronics [18,19]. MOD ink contains an organometallic compound formed by introducing ligands (complexing agents) to metal salts. Compared to metal salt inks, the introduction of complexing agents (e.g., amines) can (i) lower the required metallization temperature, (ii) control the precipitated particle size, or (iii) improve solubility of the metal-organic compounds in solvents. This makes MOD ink more suitable for printing metal patterns as a precursor ink on flexible polymer substrates that cannot withstand high curing temperature [20–22].

This unique feature of MOD ink also creates an opportunity for its use as a precursor to the nanoparticle binder for binder jetting of metals. After applying a moderate heat to the jetted ink without fusing the surrounding powder, the MOD ink is capable of depositing nanoparticles with controlled growth, which can be sintered to form a bond for the powder. MOD ink is similar to nanosuspension in a way that nanoparticles are deposited to the powder necking and interstices after drying (Figure 3). However, unlike nanoparticle suspension, MOD ink is particle-free during printing, and therefore has a potential to alleviate the challenges encountered in particle inks (e.g. nozzle clog, sedimentation, etc.)

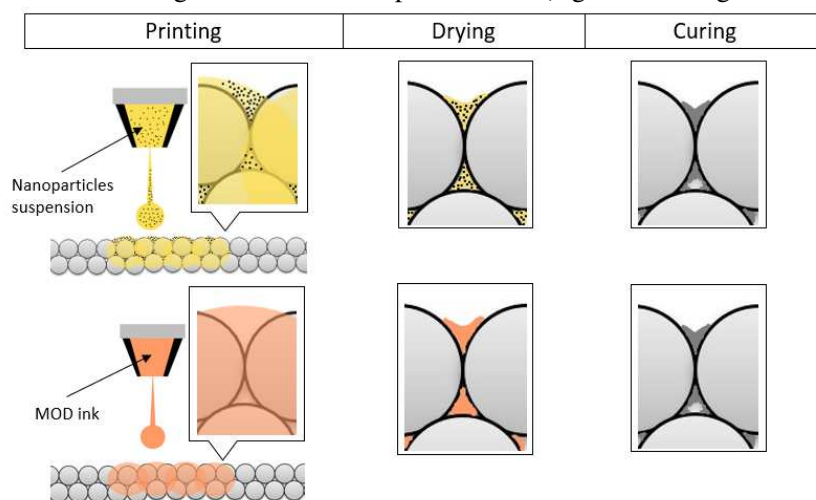


Figure 3. Comparison between jetting a nanoparticle suspension (with particles) and MOD ink (particle-free) as the binder

1.4 Roadmap

The goals of this article is to (i) demonstrate the concept of using Metal-Organic-Decomposition (MOD) ink as a particle-free metal binder in binder jetting, and (ii) experimentally explore of its effects on the printed part properties. The use of MOD ink is validated in the context of binder jetting of copper, based on an established manufacturing process for copper from prior work [3,23].

Section 2 provides the details on the material system, printing process, and experimental procedures; Section 3 discusses the experimental outcomes from using copper MOD inks in binder jetting of copper.

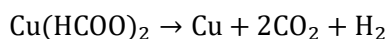
2 Experimental methods

To experimentally validate the use of MOD ink as a nanoparticle binder, green parts were printed on a binder jetting platform using copper powder and synthesized copper MOD inks and then sintered. To study the MOD binder's impact on green and sintered part properties, binder saturation ratio and green part curing temperatures were varied to study their effects on the green part structural integrity and sintered part density. Parts were also printed with similar conditions using conventional polymer binders to establish a datum for comparison.

2.1 Ink formulation and synthesis

The formulation and synthesis of copper MOD inks is well established in the electronic printing industry. Among copper carboxylates (e.g., copper glycolate [22], oxalate [24], lactate and oleate [25]) that can decompose to form copper when annealed at elevated temperatures, short carbon chain copper carboxylates (e.g., copper formate and acetate) are typically used in order to increase the metal content of the inks. Amines are the commonly used complexing agents for copper MOD inks (e.g. isopropanolamine [26], cyclohexylamine [27], and aminediols [28], etc.). In order to generate copper nanoparticles, octylamine can be used to control particle growth, and 2-amino- 2-methyl-1-propanol (AMP) can be used to improve solubility in organic solvents and lower decomposition temperature [21]. In a similar study, copper formate and AMP combination was deemed as most ideal to print conductive patterns compared with other studied ligands [20].

Based on the reviewed literature, in this study the authors choose copper(II) formate as the precursor and 2-amino- 2-methyl-1-propanol (AMP) and octalamin as the ligand, in order to make the ink dissolvable in organic solvents and achieve (i) high copper loading, (ii) low decomposition temperature, and (iii) minimal organic residual. Copper nanoparticles are generated through the decomposition of copper formate which follows [21]:



To synthesize the copper organometallic compound, 42 g of AMP and 64 g of octalamin as complexing agents was added to 90 g of methyl alcohol and magnetically stirred for 30 min. Then, 112 g of copper(II) formate tetrahydrate powder was added to the mixture so that the molar ratio of copper(II) formate to the complexing agents was 1:2. This solution was stirred for 60 minutes to ensure complete formation of the copper organometallic complex, and dried in a vacuum oven for 8 hours to remove the solvent.

2.2 Ink rheology and metallization

The final MOD ink was prepared by diluting the organometallic compound with 2-methoxyethanol. An ink rheology that is suitable for inkjet printing was obtained by varying the concentrations of the organometallic compound. 2-methoxyethanol is the main solvent for ExOne's

solvent-based polymer binder, and it is used in the MOD inks for a more predictable printing process. The viscosity and surface tension of copper MOD ink was measured by a TA Instrument hybrid rheometer and sessile drop tensiometer.

In order to verify the metallization of synthesized MOD ink and observe the precipitated nanoparticles, silicon wafer substrates were coated with MOD ink films and heated with various temperatures that are typically used for curing printed green parts, and characterized by SEM. The metal content of copper MOD inks was measured by Thermogravimetric Analysis (TGA) to quantify the nanoparticle weight percentage in the MOD binder that is used towards constructing the final sintered parts.

2.3 Printing process and green part properties

The green parts were printed on an ExOne R2 3D printer. A high purity (>99%) gas atomized copper powder with 17 μm median particle size was used for printing. A standard, ExOne solvent-based polymeric binder was used to print parts as a control group in this study. The printing parameters used to print the green parts were: 10 mm/s powder spreading speed, 1.3 feed-to-build powder recoating ratio, and 80 μm layer thickness.

Interlayer drying during printing and post-print curing is typically required for polymeric binder to dry the solvent crosslink polymers. When printing polymer binder, the powder bed temperature controller was maintained at 80 $^{\circ}\text{C}$ and the overhead heater was set at 200 $^{\circ}\text{C}$ with a scanning speed of 1 mm/s for each printed layer. When printing MOD inks, the suitable drying and curing temperature was determined by studying the particle formation in the ink metallization process. An infrared thermometer was used to monitor the actual powder bed temperature during printing. After printing, the green parts printed by both binders were cured in a controlled atmosphere oven. Curing temperature was varied to study its effect on the green part strength.

The binder saturation ratio for each binder (copper MOD ink and polymeric binder) was determined by the measured powder bed density and recorded binder drop volume. The measured drop volume for copper MOD ink and polymeric binder was 50 pL and 96 pL, respectively.

Several 18 \times 6 \times 3 mm test coupons were printed to evaluate print quality, strength and density of the printed green parts. In the binder jetting metal printing process, sufficient green strength of the printed parts is required part removal and depowdering via compressed air. Therefore, several parts were printed for each binder saturation, and the green strength was evaluated by assessing part damage after depowdering using compressed air.

2.4 Sintering and sintered part properties

The printed, cured, and depowdered green parts were then sintered in a pure hydrogen atmosphere for copper oxide reduction, with an isotherm at 450 $^{\circ}\text{C}$ for 30 min to facilitate debinding of polymeric binders [3]. While no polymer pyrolysis is needed for MOD ink printed parts, the debinding isotherm was still incorporated into the heating schedule to ensure parts printed with different binders receive same heat treatment for comparing sintered properties. With a heating ramp of 5 $^{\circ}\text{C}/\text{min}$, printed samples were heated to different peak temperatures (1025-1075 $^{\circ}\text{C}$) and maintained for 2 hours.

Three parts were printed for each binder and binder saturation ratio to evaluate sintered part properties at each sintering condition. Sintered density and porosity was measured by Archimedes immersion method [29] and metallographic methods. The sintered part surface morphology and composition was characterized by a LEO (Zeiss) 1550 field-emission SEM.

3 Results and discussion

3.1 Ink rheology

Figure 4 shows the measured viscosity of MOD inks with different concentrations of organometallic compound in solvent (50 wt% and 75 wt%). While being near Newtonian fluid, the MOD ink's viscosity clearly depends on the weight percent of organometallics in the solvent.

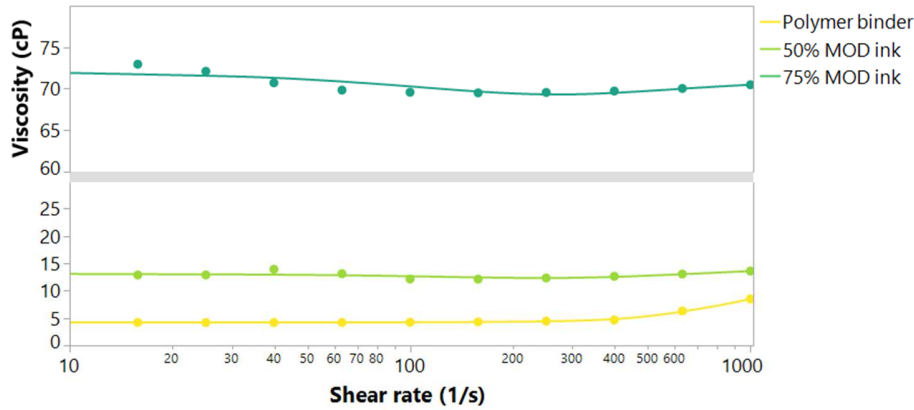


Figure 4. Viscosity of the copper MOD ink in the solvent with different concentrations, compared to the polymeric binder

In inkjet printing, jettability is dictated by the Ohnesorge number (Oh), a function of an ink's viscosity (μ), density (ρ), surface tension (γ), and nozzle diameter (Equation 1). Specifically, if the inverse of the Oh of an ink has a value between 1 and 10, then the ink is likely to be successfully jetted on most commercial Drop-on-Demand (DOD) platforms [30].

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\mu}{\sqrt{\rho\gamma D}} \quad (\text{Equation 1})$$

Table 1 summarizes the rheology information and calculated Ohnesorge number for the MOD ink and polymer binder, showing only 50% MOD ink is predicted to be able to inkjet through a 55 μm printhead nozzle. The surface tension of 50 wt% MOD compound dispersed in the solvent was measured by the pendant drop in Figure 5.

Table 1. Summary of binder rheology and jettability

Binder type	Viscosity (cps)	Surface tension (mN/m)	Density (g/ml)	Nozzle diameter (μm)	1/ Oh
50 wt% MOD ink	12	29.4	0.90	55	3.2
Polymer binder	4.5	31.2	0.99	55	9.2

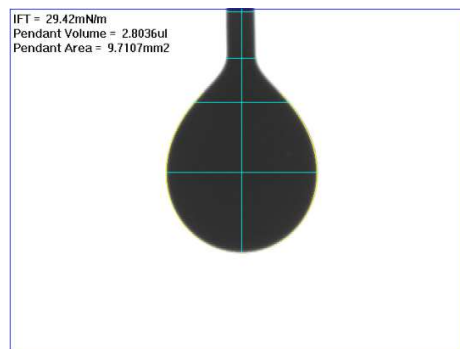


Figure 5. Pendant drop of 50% MOD ink, with a calculated surface tension of 29.42 mN/m

3.2 Ink metallization

Metallization of MOD ink is confirmed with electronic microscopy, where copper particles have formed upon heating the copper MOD ink at 250 °C (Figure 6). In both reducing and inert atmosphere, the precipitated particles from ink metallization is a mixture of larger particles (over 100 nm) and nanoparticles (less than 100 nm). When heated in air atmosphere, large micron-sized particles formed instead, with more oxidation on particle surface.

The successful use of MOD ink as a nanoparticle binder relies on the controlled particle growth and development of oxidation when the ink is metallized. As a result, the heating of jetted MOD inks in air with elevated temperature and prolonged time should be avoided.

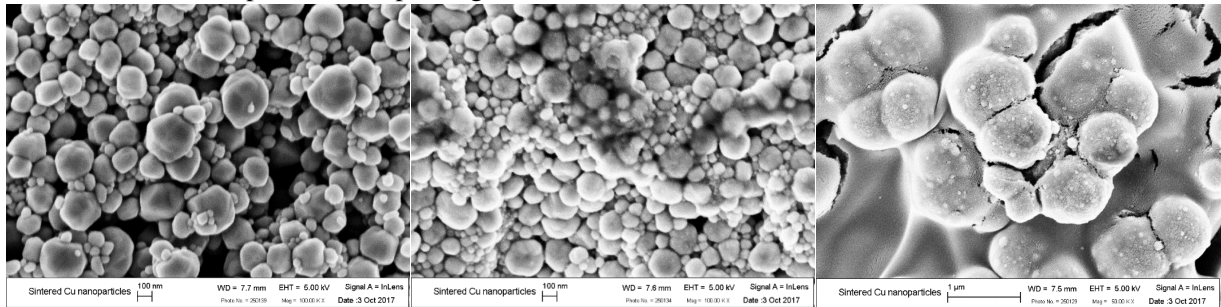


Figure 6. SEM images of copper MOD ink, heated at 250 °C for 3 hours in hydrogen (left, 100kx), nitrogen (middle, 100kx), and air (right, 50kx), with copper weight percent measured by EDS of 98.2%, 93.9% and 77.4%

TGA was used to study the ink metallization kinetics and the metal loading of the synthesized MOD ink. As revealed in Figure 7, the copper MOD ink was heated at 5 °C/min in nitrogen, and finished decomposition by reaching to the final composition at 150 °C, in a time span of approximately 25 minutes. In this MOD ink, 7.4% of the total binder content turned to copper particles that can be utilized towards building the final sintered parts; verses in polymer binder, approximately 9% percent polymer was left after solvent removal but later pyrolyzed, leaving 0.7% carbon residual that becomes impurities.

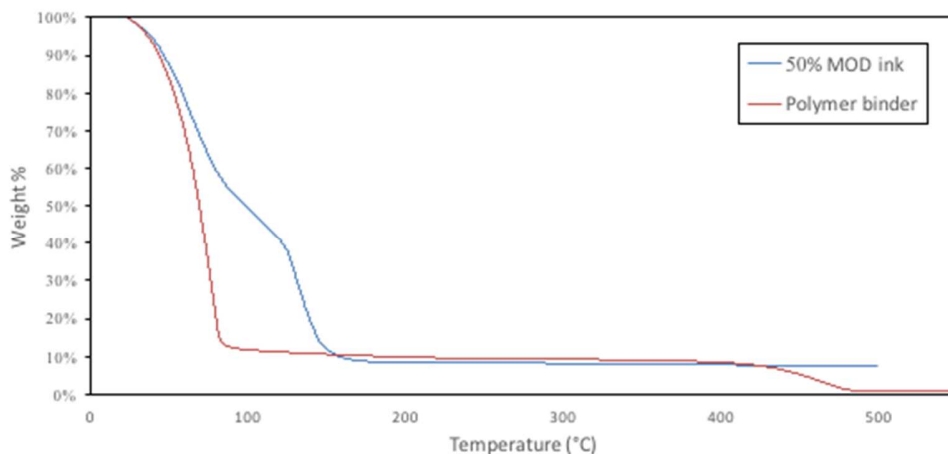


Figure 7. Thermogravimetric analysis of copper MOD in (50 wt% compound in solvent) and polymer binder

3.3 Green part properties

The ink metallization process studied in Section 3.2 provides a guidance for the development of appropriate drying and curing conditions for printing MOD inks. To ensure the successful printing MOD

ink as a nanoparticle binder, the jetted ink needs to metallize and precipitate particles in an inert or reducing atmosphere. As a result, the heating conditions for drying and curing MOD were set in a way that (i) solvent can be dried with limited ink metallization when heating printed layers in the air, and (ii) nanoparticles can be completely precipitated from the ink and then sintered when curing the printed parts in controlled atmosphere.

An overhead heater (set at 200 °C) with scanning speed of 5 mm/s was used to dry the jetted MOD inks. When the heater scanned over the copper powder bed, the powder directly under the heater reached to a temperature of 160 °C for a few seconds, and then rapidly drops down to a temperature below 100 °C after the heater moves away. While the peak powder temperature has reached the ink decomposition temperature (Figure 7), the fast scanning speed did not allow sufficient time for ink metallization, thus preventing the unwanted particle growth and oxidation when heating MOD ink in the air (Figure 6).

Figure 8 shows the interparticulate bonding within the green parts from drying jetted MOD inks (without any post-print curing). The drying condition did not allow a completed ink metallization; as a result, the jetted ink mainly remained as not decomposed organometallics. Despite no nanoparticle sintering is evident at this stage (after drying without post-print curing), the gelled MOD ink was able to provide enough bonding strength to ensure printed part removal from the powder bed (Figure 9).

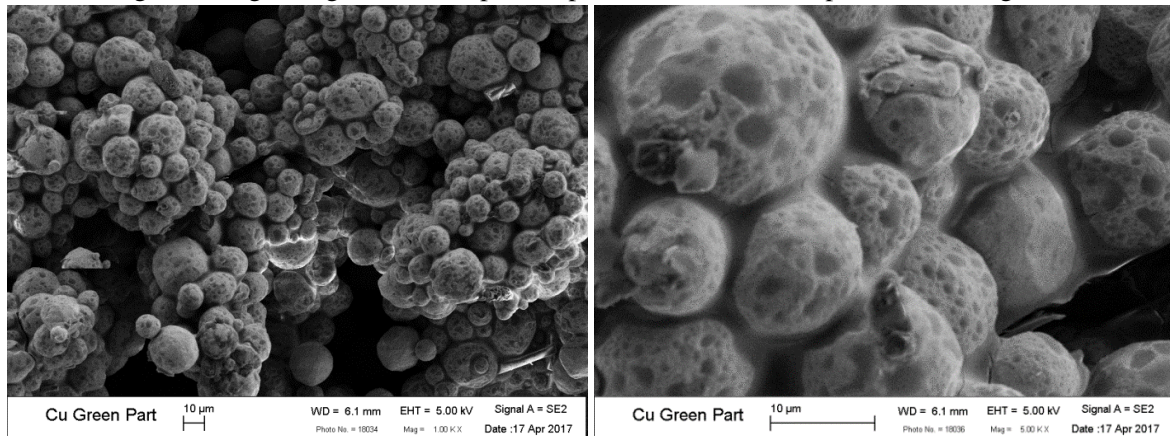


Figure 8. SEM images of the green parts printed with MOD ink (150% binder saturation, without post-print curing): 1kx (left) and 5kx (right) magnification rate

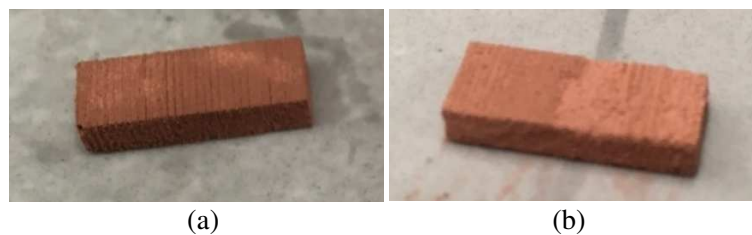


Figure 9. MOD printed part (18×6×3 mm) with (a) 150% saturation ratio and (b) 75% saturation ratio, after retrieving from the powder bed without post-print curing

After retrieval from the powder bed, the MOD ink printed parts were cured in a controlled-atmosphere oven to complete the decomposition of MOD ink and formation of nanoparticles. The curing temperature was varied from 200 to 250 °C, in order to (i) ensure the sintering of precipitated nanoparticles, and (ii) study the effects of curing temperature on green part integrity. A reducing

atmosphere was used facilitate nanoparticle sintering by reducing surface oxidation. After curing, sintered nanoparticles can be found at the necking of powder particles (Figure 10).

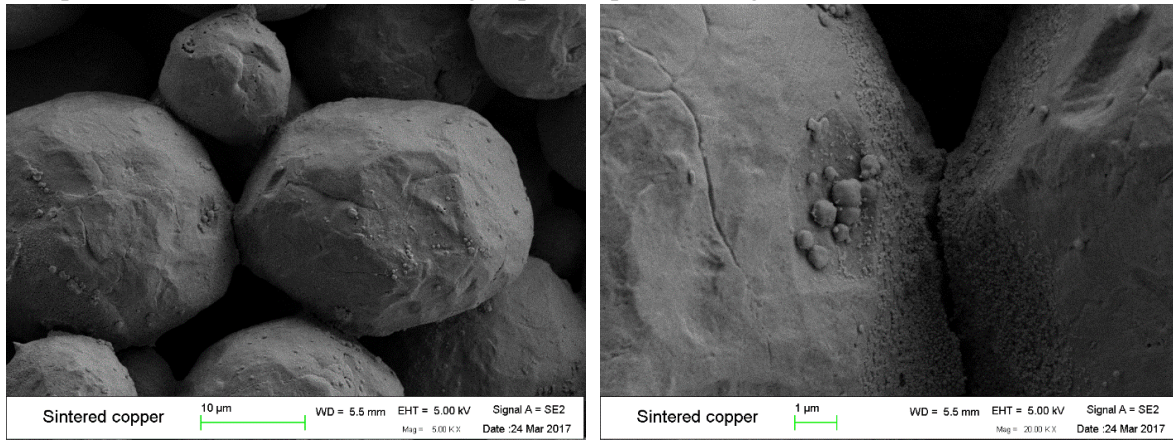






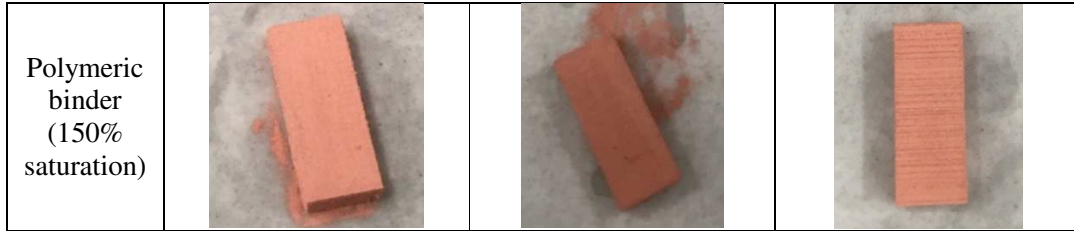


Figure 10. SEM images of the powder particle bonding formed by sintered copper nanoparticles (150% saturation): 5kx (left) and 20kx (right) magnification rate

To evaluate the integrity of printed green part after depowdering, the cured green parts were subjected to a compressed air stream at the surface (Table 2). Compared to curing at 200 °C, curing with 250 °C produced better green strength, especially in 150% saturation ratio printed parts. While satisfactory printed part strength can be achieved with sufficient binder saturation and curing condition, it is noted that, overall, the MOD binder printed green part is less strong than the polymer binder counterparts.

Table 2. Before and after depowdering comparison of the green parts cured at different temperatures for 1 hour in hydrogen

	<i>Cured parts before depowdering</i>	<i>200 °C cured parts after depowder with 20 psi compressed air</i>	<i>250 °C cured parts after depowder with 40 psi compressed air</i>
MOD ink (75% saturation)			
MOD ink (150% saturation)			



The green density of MOD ink and polymer binder printed parts was measured prior to post-print curing (Figure 11). When printed with same saturation ratio (150%), MOD ink printed parts have a similar green density with polymeric binder printed parts, corresponding to the binder residual percentage measured by TGA in Figure 7 (approximately 7% and 9% for MOD ink and polymer binder).

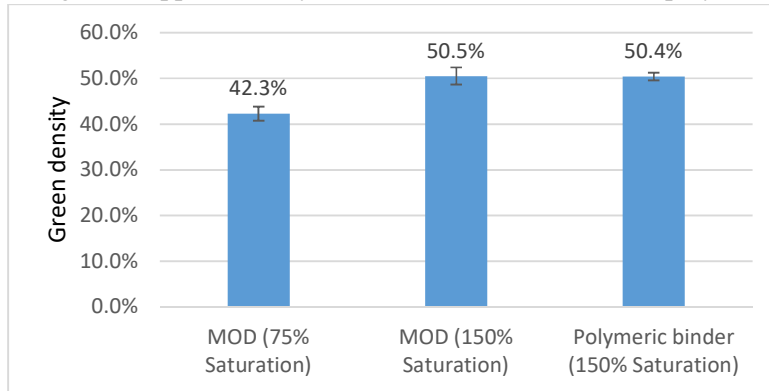


Figure 11. Green density of MOD ink printed and polymeric binder printed parts

3.4 Sintered part properties

3.4.1 Sintered density and shrinkage

The polished cross-sections of sintered MOD ink printed parts have shown a unique pore distribution, where large pores are concentrated near surface and the core section is relatively pore-free (Figure 12). For further porosity distribution analysis, Figure 12 was converted to black and white images as a binary representation of the microscopic images, where dark regions represent occurrence of the porosity. In Figure 13, the distribution of large and small pore distribution is studied separately for MOD ink and polymer binder printed parts. A pixel number of 10 is used to differentiate small and large pores. A map of pore occurrence intensity is created for large and small pores.

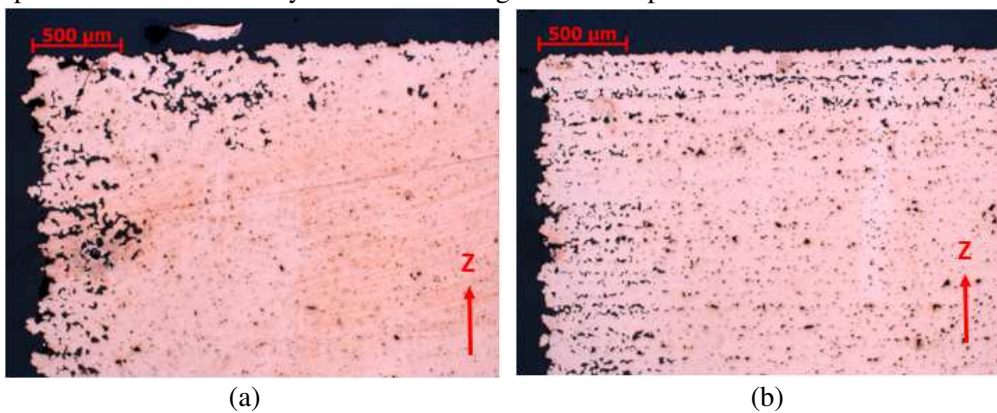


Figure 12. Optical microscopic images of the sectioned and polished sintered parts, printed by (a) MOD ink and (b) polymeric binder, using 150% binder saturation ratio

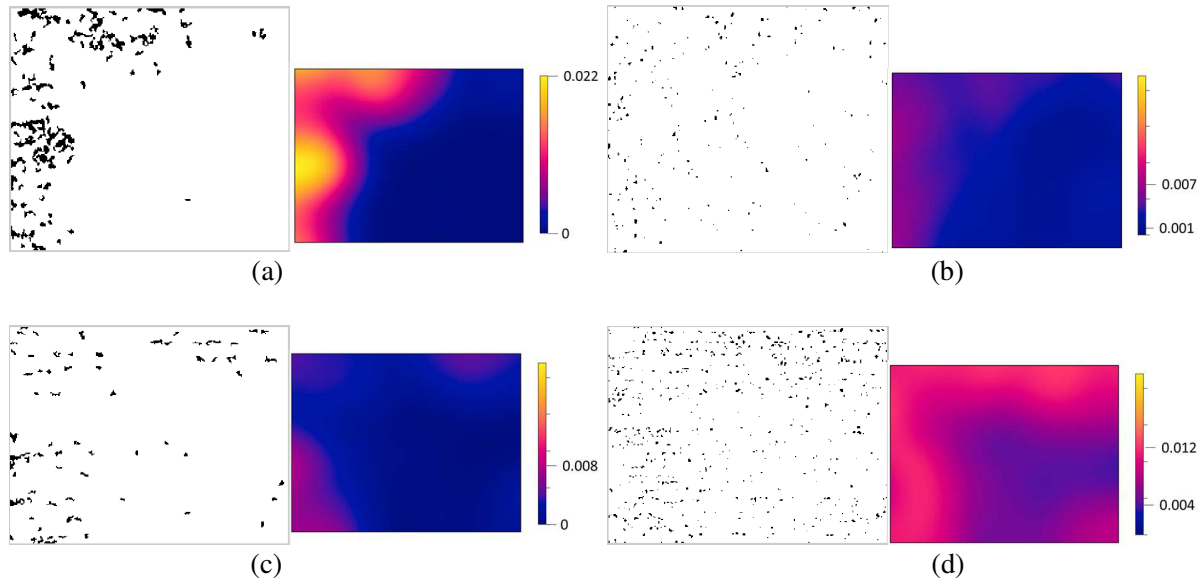


Figure 13. Porosity distribution analysis by separating large and small pores from Figure 12: (a) large pores in MOD ink parts, (b) small pores in MOD ink parts, (c) large pores in polymer binder parts, and (d) small pores in polymer binder parts

In binder jetting printed parts, small pores typically represent the inherent inter-particle spacing, while large pores are more likely caused by factors including powder packing irregularities and powder loss due to missed binder jets. As seen in Figure 13, both MOD ink and polymer binder printed parts have a porous shell composed of large pores and inner section with small pores. However, the porosity in MOD ink printed parts is mainly contributed by the large pores, while small pores are more dominant in polymer binder printed parts (Figure 14 and 15). When only the core section is compared, the MOD ink printed parts have significantly less porosity, as a result of the densifying effects from depositing extra metal contents to the powder bed. However, the overall porosity in MOD ink printed parts is raised by the porous shell, which is attributed to the loss of powder during depowdering due to insufficient green part strength.

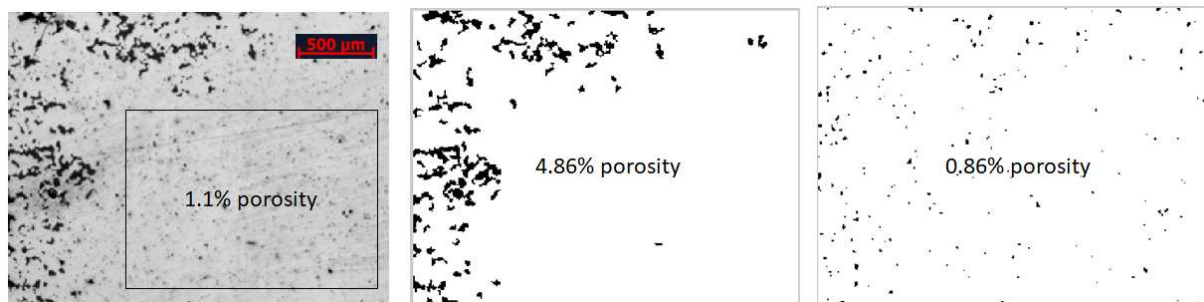


Figure 14. Porosity measurement (by optical pixel counting) for MOD ink printed part (Figure 12): core section only (1.1%), large pores (4.86%), and small pores (0.86%)

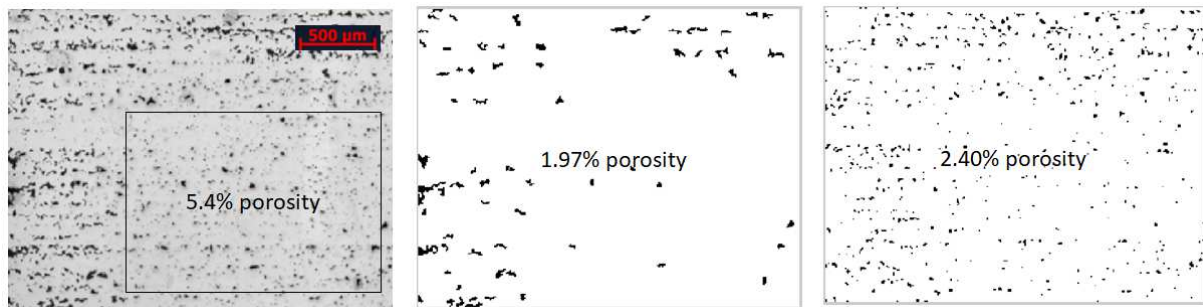


Figure 15. Porosity measurement (by optical pixel counting) for polymer binder printed part (Figure 12): core section only (5.4%), large pores (1.97%), and small pores (2.40%)

This unique pore distribution of MOD ink printed parts is also reflected in the measured sintered density by Archimedes' method with oil impregnation (Figure 16). When a porous sintered part is oil impregnated which seals surface pores, the envelope density of sintered part is measured which reflects the actual part density of both core and shell section. While the overall sintered density of MOD ink printed parts is lower than that of polymer binder printed parts (Figure 16), the core section in MOD ink printed parts is denser (Figure 14 and 15).

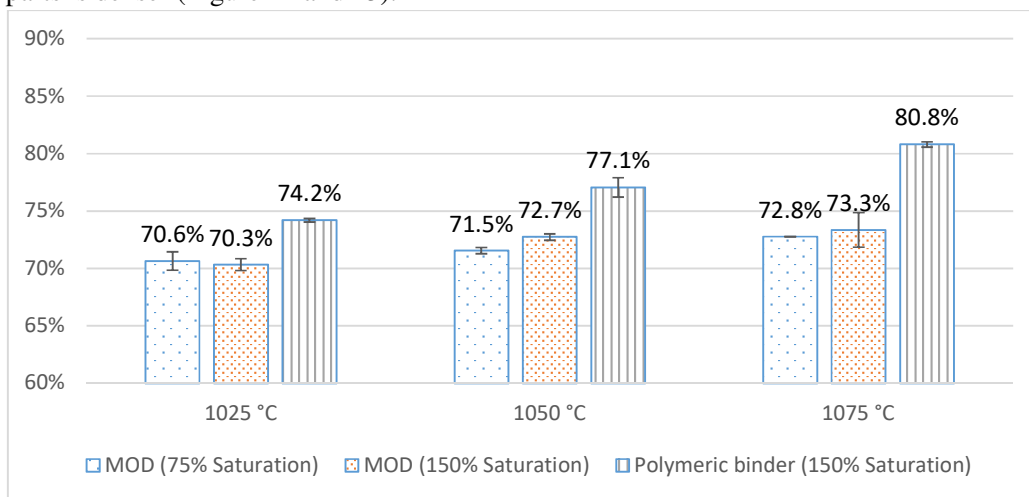


Figure 16. Sintered density measured with oil impregnation

Figure 17 compares part shrinkage at three different sintering temperatures for MOD ink and polymer binder printed parts. In MOD ink printed parts, the result reveals that higher amount of nanoparticles in 150% binder saturated parts reduced the overall shrinkage compared to the lower saturation parts. This can be attributed to the improved green density in 150% saturated MOD ink parts (Figure 11).

It is also noticed that the shrinkage and densification in sintered MOD ink printed parts is less dependent on the peak sintering temperature, compared to the polymer printed parts (Figure 16 and 17).

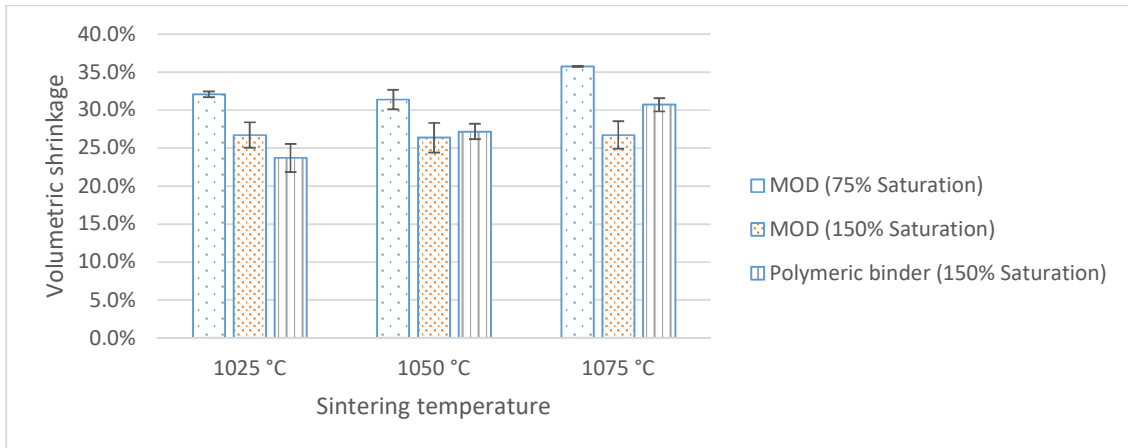


Figure 17. Volumetric shrinkage of the sintered part

Density (or porosity) in sintered artifacts made in binder jetting is influenced by many factors. Previous study in binder jetting of copper has shown that sintered density can be affected by printing and sintering conditions [3], powder particle size [31], and post-processing [32]. The results discussed in this work also show that sintered density and pore distribution can be affected by the binder compositions and green part structural integrity and strength.

3.4.2 Surface morphology

The use of copper MOD ink also produces a different part surface morphology than traditional polymeric binders. In polymer binder printed parts, a trench-like surface composed of a network of closely packed powder granules is formed as a result of polymeric binder penetrating and rearranging powder particles (Figure 18a). In comparison, the printing of MOD inks produces a relatively more flat and uniform surface (Figure 18b). This is because of the smaller Oh number of MOD ink (Table 1) represents less kinetic energy and surface tension in the binder to overcome its viscosity when penetrating powder and rearranging particles. The insufficiently saturated MOD ink part (Figure 18c) suffered from low green part strength and powder loss, thus shows more occurrence of surface damage.

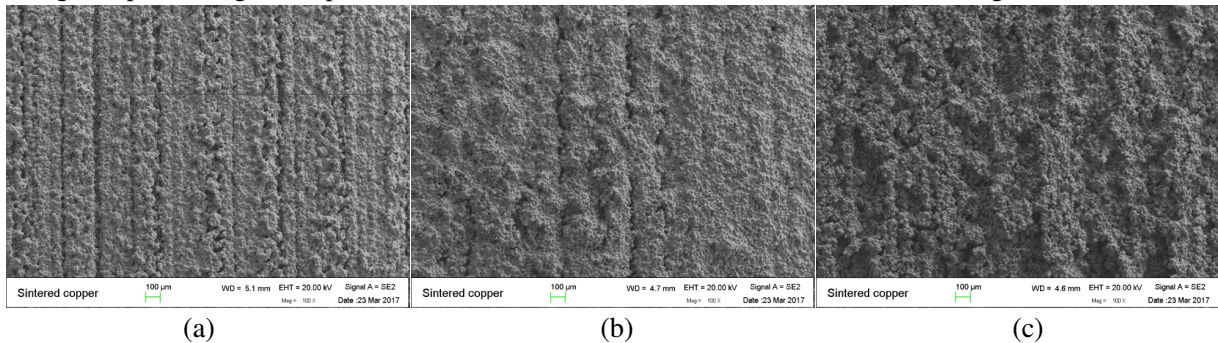


Figure 18. SEM images (100x magnification) of sintered part surface (sintered at 1075 °C), for surface morphology comparison between parts printed by (a) polymeric binder, (b) 150% saturation MOD ink, and (c) 75% saturation MOD ink

4 Conclusion

This work demonstrates that Metal-Organic-Decomposition (MOD) ink can be used as a precursor to the nanoparticle binder for binder jetting of metals, by initiating binding between metal powders through sintering the precipitated nanoparticles from jetted ink. As a particle free ink, MOD ink is more cost-effective, and more suitable for inkjet printing as it can potentially alleviate the sedimentation, particle oxidation, and nozzle clog issues found in particle suspensions.

This concept is validated through experimentation in the context of binder jetting of copper. Copper organometallic complex was synthesized with a shown capability of producing copper nanoparticles upon heating (Figure 6). A metal content of 7.4 wt% of was achieved (Figure 7) as a result of mixing the synthesized organometallic complex with a solvent to maintain ink jetability (Figure 4).

Using a similar print setting in printing polymeric binders, the inkjet printed MOD ink was dried between layers by an overhead heater to remove the solvent; the printed parts went through post-printing curing in a reducing atmosphere to fully precipitate and sinter nanoparticles from the jetted and dried organometallic complex, providing a bonding strength to the powder. While the green part produced from MOD ink is less strong compared to the conventionally printed polymeric binder counterparts (Table 2), it can maintain a structural integrity after depowdering with compressed air (using 150% binder saturation ratio).

The sintered copper parts printed by copper MOD ink have generated a dense core section that has less porosity than polymer binder parts (Figure 12). However, a porous outer shell composed of large pores is formed around the dense core in MOD ink printed parts, which has led to lower sintered density compared to the polymer binder counterparts (Figure 16). The porous shell is mainly caused by the powder loss due to weak powder bonding at surface in MOD ink printed parts.

In conclusion, copper MOD ink has been successfully used as a binding agent to print copper parts. Future work may focus on improving material properties thorough developing a higher metal loading ink, as well as expanding the presented concept into more materials.

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6 Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

7 Reference

- [1] Bourell, D. L., Leu, M. C., and Rosen, D. W., 2009, *Roadmap for Additive Manufacturing: Identifying the Future of Freeform Processing*.
- [2] Gao, W., Zhang, Y., Ramanujan, D., Ramani, K., Chen, Y., Williams, C. B., Wang, C. C. L., Shin, Y. C., Zhang, S., and Zavattieri, P. D., 2015, "The Status, Challenges, and Future of Additive

- Manufacturing in Engineering,” *Comput. Des.*, **69**, pp. 65–89.
- [3] Bai, Y., and Williams, C. B., 2015, “An Exploration of Binder Jetting of Copper,” *Rapid Prototyp. J.*, **21**(2), pp. 177–185.
- [4] Utela, B. R., Storti, D., Anderson, R. L., and Ganter, M., 2010, “Development Process for Custom Three-Dimensional Printing (3DP) Material Systems,” *J. Manuf. Sci. Eng.*, **132**(1), p. 11008.
- [5] Jianxin, L., and Kuhn, H. A., 2006, “Materials Development for ProMetal,” *Mater. Sci. Technol.*, **66**(3), pp. 911–917.
- [6] Asoro, M., Damiano, J., and Ferreira, P., 2009, “Size Effects on the Melting Temperature of Silver Nanoparticles: In-Situ TEM Observations,” *Microsc. Microanal.*, **15**(S2), p. 706.
- [7] Yu, E.-K., Piao, L., and Kim, S.-H., 2011, “Sintering Behavior of Copper Nanoparticles,” *Bull. Korean Chem. Soc.*, **32**(11), pp. 4099–4102.
- [8] Bai, J. G., Creehan, K. D., and Kuhn, H. a, 2007, “Inkjet Printable Nanosilver Suspensions for Enhanced Sintering Quality in Rapid Manufacturing,” *Nanotechnology*, **18**(18).
- [9] Godlinski, D., Petzoldt, F., and Morvan, S., 2004, “Tailored Functional Gradients by 3D-Printing Using Metal Powder and Nano-Particulate Inks,” *Euro PM2004*.
- [10] Bailey, A., Merriman, A., Elliott, A., and Basti, M., 2016, “Preliminary Testing of Nanoparticle Effectiveness in Binder Jetting Applications,” *27th Annu. Int. Solid Free. Fabr. Symp.*, pp. 1069–1077.
- [11] Yoo, H. J., 1995, “Reactive Binders for Metal Parts Produced by Three Dimensional Printing.”
- [12] Hadjiloucas, C., 1997, “Low Shrinkage Metal Skeletons by Three Dimensional Printing,” Massachusetts Institute of Technology.
- [13] Bai, Y., and Williams, C. B., 2017, “Binderless Jetting: Additive Manufacturing of Metal Parts via Jetting Nanoparticles,” *Solid Freeform Fabrication Proceedings*.
- [14] Draper, G. L., Dharmadasa, R., Staats, M. E., Lavery, B. W., and Druffel, T., 2015, “Fabrication of Elemental Copper by Intense Pulsed Light Processing of a Copper Nitrate Hydroxide Ink,” *ACS Appl. Mater. Interfaces*, **7**(30), pp. 16478–85.
- [15] Petukhov, D. I., Kirikova, M. N., Bessonov, A. a., and Bailey, M. J. a., 2014, “Nickel and Copper Conductive Patterns Fabricated by Reactive Inkjet Printing Combined with Electroless Plating,” *Mater. Lett.*, **132**, pp. 302–306.
- [16] Liu, J., 2009, “In Situ Created Metal Nanoparticle Strengthening of Metal Powder Articles.”
- [17] Lin, Z., Han, D., and Li, S., 2012, “Study on Thermal Decomposition of copper(II) Acetate Monohydrate in Air,” *J. Therm. Anal. Calorim.*, **107**(2), pp. 471–475.
- [18] Perelaer, J., Smith, P. J., Mager, D., Soltman, D., Volkman, S. K., Subramanian, V., Korvink, J. G., and Schubert, U. S., 2010, “Printed Electronics: The Challenges Involved in Printing Devices, Interconnects, and Contacts Based on Inorganic Materials,” *J. Mater. Chem.*, **20**(39), p. 8446.
- [19] Kamyshny, A., 2011, “Metal-Based Inkjet Inks for Printed Electronics,” *Open Appl. Phys. J.*, **4**(1), pp. 19–36.
- [20] Farraj, Y., Grouchko, M., and Magdassi, S., 2015, “Self-Reduction of a Copper Complex MOD Ink for Inkjet Printing Conductive Patterns on Plastics,” *Chem. Commun.*, **51**(9), pp. 1587–1590.
- [21] Shin, D. H., Woo, S., Yem, H., Cha, M., Cho, S., Kang, M., Jeong, S., Kim, Y., Kang, K., and Piao, Y., 2014, “A Self-Reducible and Alcohol-Soluble Copper-Based Metal-Organic Decomposition Ink for Printed Electronics,” *ACS Appl. Mater. Interfaces*, **6**(5), pp. 3312–3319.
- [22] Yang, W., Liu, C., Zhang, Z., Liu, Y., and Nie, S., 2014, “Copper Inks Formed Using Short Carbon Chain Organic Cu-Precursors,” *RSC Adv.*, **4**(104), pp. 60144–60147.
- [23] Bai, Y., Wagner, G., and Williams, C. B., 2017, “Effect of Particle Size Distribution on Powder Packing and Sintering in Binder Jetting Additive Manufacturing of Metals,” *J. Manuf. Sci. Eng.*, **139**.
- [24] Salavati-Niasari, M., Davar, F., and Mir, N., 2008, “Synthesis and Characterization of Metallic Copper Nanoparticles via Thermal Decomposition,” *Polyhedron*, **27**(17), pp. 3514–3518.
- [25] Deng, D., Qi, T., Cheng, Y., Jin, Y., and Xiao, F., 2014, “Copper Carboxylate with Different Carbon Chain Lengths as Metal-Organic Decomposition Ink,” *J. Mater. Sci. Mater. Electron.*,

- 25**(1), pp. 390–397.
- [26] Li, Y., Qi, T., Cheng, Y., and Xiao, F., 2015, “A New Copper Ink with Low Sintering Temperature for Flexible Substrates,” *2015 16th International Conference on Electronic Packaging Technology*.
- [27] Yang, W. dong, Wang, C. hai, Arrighi, V., Liu, C. yan, and Watson, D., 2015, “Microstructure and Electrical Property of Copper Films on a Flexible Substrate Formed by an Organic Ink with 9.6% of Cu Content,” *J. Mater. Sci. Mater. Electron.*, **26**(11), pp. 8973–8982.
- [28] Yabuki, A., Tachibana, Y., and Fathona, I. W., 2014, “Synthesis of Copper Conductive Film by Low-Temperature Thermal Decomposition of Copper-Aminediol Complexes under an Air Atmosphere,” *Mater. Chem. Phys.*, **148**(1–2), pp. 299–304.
- [29] ASTM Standard B962-08, *Standard Test Methods for Density of Compacted or Sintered Powder Metallurgy (PM) Products Using Archimedes’ Principle*.
- [30] Derby, B., 2010, “Inkjet Printing of Functional and Structural Materials: Fluid Property Requirements, Feature Stability, and Resolution,” *Annu. Rev. Mater. Res.*, **40**(1), pp. 395–414.
- [31] Bai, Y., Wagner, G., and Williams, C. B., 2017, “Effect of Particle Size Distribution on Powder Packing and Sintering in Binder Jetting Additive Manufacturing of Metals,” *J. Manuf. Sci. Eng. Trans. ASME*, **139**(8).
- [32] Kumar, A., Bai, Y., Eklund, A., and Williams, C. B., 2017, “Effects of Hot Isostatic Pressing on Copper Parts Fabricated via Binder Jetting,” *Procedia Manuf.*, **10**, pp. 935–944.

