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Binderless Jetting: Additive Manufacturing of metal parts via jetting nanoparticles

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Abstract

Binder Jetting AM has been used to fabricate metal parts by first jetting a binder into powder bed; the resulting green part is then thermally post-processed wherein the binder is removed and the metal particles are sintered. In this work, the authors replace conventionally-used polymeric binders with nanoparticle suspensions as a means for binding metal powder bed particles together. After being deposited into the powder particles' interstices, the jetted nanoparticles are sintered at a low temperature via a heated powder bed to provide strength to the printed green part. Regions of the powder bed that do not receive the jetted nanoparticle suspension remain as loose powder as the sintering temperature of the nanoparticles is significantly lower than the larger powder bed particles. The concept of printing metal by jetting a nanoparticle binder made of the same material is demonstrated in the context of copper through printing copper parts with satisfactory green strength.

Key words: Binder Jetting, Nanoparticles, Inkjet Printing, Sintering, Copper

1. Introduction

1.1 Binder Jetting overview

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, followed by post-process sintering of the printed green part. As shown in Figure 1, 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.

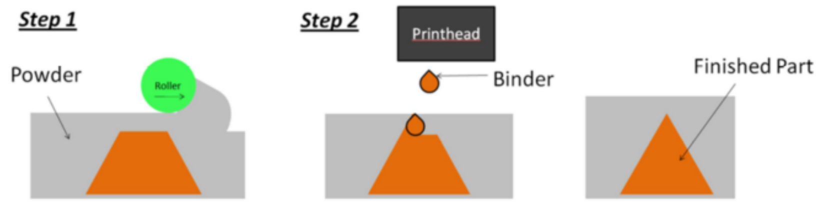

Figure 1. Green part printing process in Binder Jetting

Binder Jetting of metals differs from direct-metal AM technologies in that it separates the geometry formation from the thermal processing. As Binder Jetting of metals functionally separates part creation from powder sintering, the requirement of anchors and/or heat sinks due to the residual stresses imposed by large thermal gradient in direct-metal AM processes is avoided. The ability to fabricate a part in a powder bed without the need for built anchors enables Binder Jetting to create large and geometrically complex parts without the need for the difficult and laborious support/anchor removal in post-processing printed metal parts. In addition, Binder Jetting is an inherently scalable and cost-effective technology, which has been demonstrated in many commercial systems (e.g., Desktop Metal's Single Pass Jetting technology is 100x faster and 20x lower cost than laser-based systems[1]).

1.2 Binder selection

The selection of binder material for Binder Jetting is critical as it determines the success of creating satisfactory green parts and affects the final properties of the sintered parts. Different types of binders have been used in Binder Jetting, including various solvents, colloids, and polymers (Utela et al., 2010). In modern commercial metal Binder Jetting systems, solvent-based binders that contain thermosetting polymers are commonly used to print green parts; thermal curing via an overhead (or integrated) heater removes the solvent and crosslinks the jetted polymer. While polymer binders have demonstrated success with many metal systems, its use in Binder Jetting could add complexity to the manufacturing process and adversely affect the final product performance metrics:

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

1.3 Nanoparticle binder

In this work, the authors experimentally investigate nanoparticle suspensions as an alternative to replace polymer binders. Theories and microscopic observations have shown that many metal nanoparticles manifest size-dependent meting behaviors and lower melting/sintering temperatures compared with the bulk materials (Asoro et al., 2009). For example, copper nanoparticles can sinter and neck within temperature ranges (150-300 °C) that are significantly

[1] https://www.desktopmetal.com/products/production/

reduced from sintering temperature for micron-sized powders (Yu et al., 2011). This unique feature of nanoparticles (sintering temperature reduction), when nanoparticles are jetted as a binder in Binder Jetting, 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.

Experiments are conducted in the context of copper, wherein copper nanoparticles are jetted into the powder bed, and sintered in the powder bed via an overhead heater, providing strength to the green part and acting as a permanent and structural binder in the final printed copper product. The low sintering temperature of copper nanoparticles ensures that only moderate heat is supplied to the powder bed, which ensures that the printed green part can be retrieved from the surrounding loose powder.

Section 2 provides a critical analysis of the prior art, and establishes the rationale for this approach. Experimental methods for (i) validating the use of nanoparticle binder in the Binder Jetting of a single material system and (ii) exploring of the effects of jetted copper nanoparticles on green and sintered part properties are presented in Section 3. Subsequent results are presented in Section 4.

2. Literature review

Adding fine particulates or nanoparticles into the polymeric binders used for Binder Jetting have been investigated for different contexts and purposes, including local control of composition (Godlinski and Morvan, 2005; Techapiesancharoenkij et al., 2004), sintering densification enhancement (Bailey et al., 2016; Elliott et al., 2016), strengthening green parts (Bai et al., 2013), and reducing sintering shape distortion (Bai et al., 2009; Crane, 2005). In general, these approaches were shown to improve material properties, but were still using an existing polymeric binder and relying on the curing of the polymer to provide green strength.

The concept of using metal and ceramic particle slurries or colloids as a binder in Binder Jetting has been explored in prior work. Yoo et al. used jetted particulate suspensions as binders in steel powders in order to reduce the shrinkage by eliminating the need to sinter steel powders (Yoo, 1995). Carbonyl iron (1.7 μm) was suspended into water and inkjet printed to stainless steel powders (60 μm) followed by firing the entire powder bed in forming gas at 600-700 °C, under which temperature the interstitial carbonyl iron particles sintered without sintering the base powder. The printed part was "fairly weak" according to the authors, but was shown to be successfully retrieved from the powder bed and depowered. Hadjiloucas et al. used silver suspensions as the binder for printing molybdenum powders (Hadjiloucas, 1997). The printed interstitial silver particles melted and bonded the base powder particles after heating at 1000 °C, at which the base powder remained loose and ensured part retrieval from the powder bed. Techapiesancharoenkij et al. printed iron and nickel oxide slurries into Fe-30Ni base powders for printing bimetallic bars (Techapiesancharoenkij et al., 2004). After heat treatment at 400 °C in a reducing atmosphere, the printed bars can be retrieved from unbound powders.

While the feasibility of using metal or ceramic particle suspensions as binder has been demonstrated in the literature, the success of printing and material system selection is contingent upon the large sintering temperature gap between the base powder material and the binder material. As a result, dissimilar material systems composed of refractory powders and low-melting-point-material binders have been used with the requirement of sintering the powder bed in a controlled atmosphere furnace after printing. The feasibility of using a metal binder of the same material as powder in a single material system has not been demonstrated.

3. Experimental methods

The experiments were conducted to (i) determine the process parameters and establish the manufacturing process for fabricating copper parts via jetting copper nanosuspension as a binder, and (ii) explore the nanoparticle binder's effect on green strength and green/sintered densities. To achieve this goal, the drying and sintering condition for printing copper nanosuspensions was first determined; then, the nanosuspension was printed as a binder for copper powders with different binder saturation ratios. Green part strength/density and sintered density were measured for both nanoparticle and polymer binder printed parts with different binder saturation ratios.

The overall copper part manufacturing process chain followed an established procedure in authors' prior work (Bai et al., 2017; Bai and Williams, 2015). The material system and manufacturing process used for evaluating copper nanoparticle as binders is discussed in Section 3.1-3.3, with the characterization methods for printed copper green and sintered parts provided in Section 3.4.

3.1 Material system

A gas atomized copper powder with median particle size of 17 µm and packing density of 52% was chosen as the base powder material. A commercially available copper nanoparticle suspension with a solid loading of 20-26 w.t.% and average particle size under 100 nm was used (Gwent Electronic Materials Ltd.). This product is designed for the electronics printing industry and has a proven rheology (30mN/m surface tension and 13 cps viscosity) that is suitable for inkjetting by commercial piezoelectric printhead.

ExOne's solvent-based polymer binder was selected to print parts as control group for the experiments.

3.2 Nanoparticle binder drying condition

Finding an appropriate drying condition is critical to ensure the success of printing a new binder. The polymer binder printed parts were dried following the standard procedure (a ceramic overhead heater set to 200 °C scans the printed layer at a speed of 5mm/s following the jetting pass). As a result of this drying pass, the temperature of the powder bed surface reached to 170 °C when the heater is directly placed above (measured by an infrared thermometer).

The drying condition (powder bed temperature and drying time) for nanosuspension was determined through experimentation based on the thermogravimetric analysis (TGA) performed on a TA Instruments platform.

3.3 Manufacturing process

Copper green parts were printed with copper nanosuspension or polymer binder on an ExOne R2 3D printer. Powder was spread with 5mm/s with a feed-to-build ratio of 1.2:1. A standard 100 µm layer thickness was applied to the printing of both binders.

The drop volume for each ink was measured before and after printing to ensure accurate binder saturation ratio. While the drop volume measured for the standard polymer binder at a standard jetting waveform is consitent (101 pL), the drop volume measured for copper nanosuspension was inconsistent and varied in a range (65-75 pL). The binder saturation ratio for the nanosuspension is therefore selected by assuming a drop volume of 70 pL. A summary of measured drop volume and adopted binder saturation ratio is provided in Table 1.

Table 1. Measured drop volume and adopted binder saturation ratio

	Measured drop volume	*Binder saturation ratio*
Polymer binder	101 pL	100%
Copper nanosuspension	70 pL	70% & 140%

The green parts printed by polymer binder or nanosuspension were retrieved from the powder bed immediately after the printing finished. The polymer printed parts were subjected to an additional post-process curing process (200 °C for 1 hour) to fully set the polymer binder, as prescribed by the standard procedure. Post-process curing was skipped for nanosuspension printed parts. The depowdered green parts were then sintered in a hydrogen furnace with pure hydrogen atmosphere, following an established sintering profile which features 5 °C/min heating to a 2-hour isotherm at 1075 °C.

3.4 Green and sintered part characterization

Green part strength was evaluated by identifying the peak load at specimen rupture in a 3-point bending test (MTS platform;1kN load cell), using ASTM B312 standard as a reference. In order to reduce the material and time consumption in making the specimen, the green strength specimen geometry was scaled down to 60% of the original size specified in the standard. In addition, a constant displacement rate (0.1 mm/s) was used instead of controlled loading rate due to the instrument used.

A series of 18mm×6mm×3mm test coupons were printed for evaluating green and sintered densities. Green part density was calculated from the measured part mass and dimensions. The sintered density was measured by oil impregnation and immersion method using Archimedes principle following ASTM Standard 962. A LEO (Zeiss) 1550 field-emission SEM was used to evaluate printed green parts. Three green strength specimens and three density coupons were printed and tested for each binder and saturation ratio.

4. Results

4.1 Nanoparticle binder drying condition

Figure 2 shows a failed printing with the nanosuspension ink when using the polymer binder's standard layer drying condition (Section 3.2). In this failure, the recoating of an insufficiently dried layer printed by the copper nanosuspension has created an uneven powder bed surface and damaged the previous layer. Therefore, a sufficient drying and setting of the jetted binder is required to enable the printed layer with enough integrity that can withstand the compressive force imposed by the powder-spreading roller.

Figure 2. Powder bed defects occurred on top of the printed layer after recoating, caused by insufficient binder drying

As shown in Figure 3, the complete drying of the copper nanosuspension requires higher temperature (200 °C) and longer time (10 minutes) than that of the polymeric binder when a 20 °C/min heating ramp was used for TGA. Through a series of experimental printing trials, it was determined that directly placing the overhead heater above the powder bed for 2 minutes maintains the powder bed surface temperature at 260 °C, which is capable of sufficiently drying the printed layer without incurring recoating defects. This drying condition also ensures leaving the copper powder bed unsintered and free-flowing, which enables printed green part retrieval (Figure 4b).

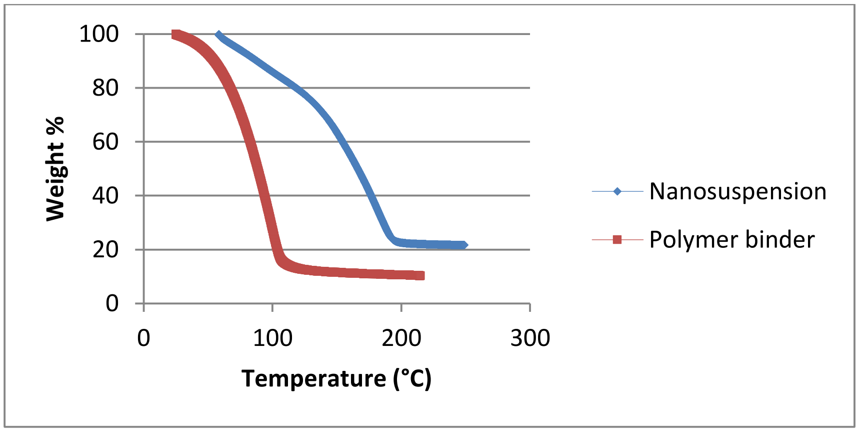

Figure 3. Thermogravimetric analysis (TGA) of the copper nanosuspension and polymer binder

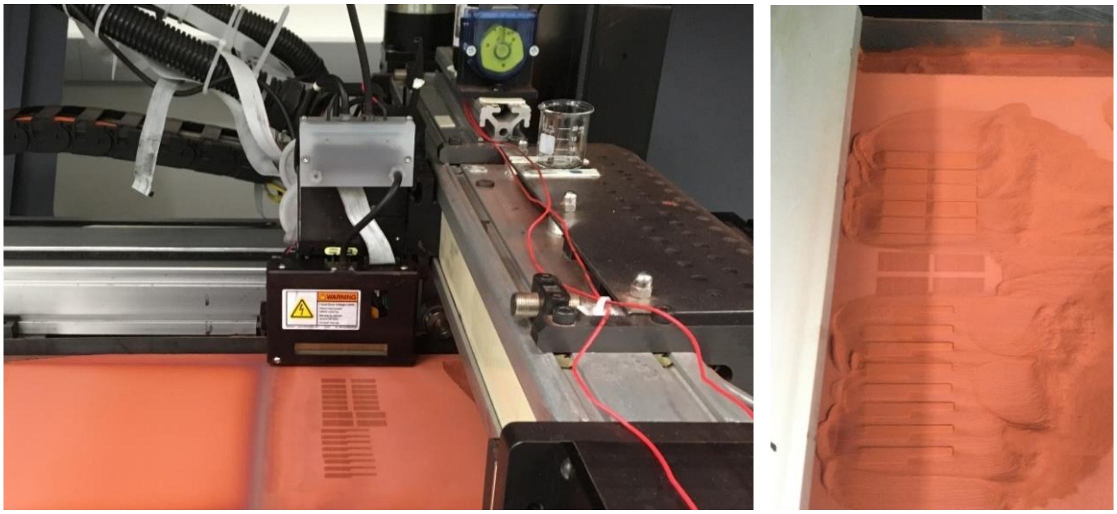

Figure 4. (a) printed layer by copper nanosuspension and (b) printed green parts surrounded by brushed-off loose powder prior to retrieving from the powder bed

4.2 Nanoparticle bonding

The source of the interparticular bonding in printed green parts is revealed in Figure 5-7. In polymer binder printed parts (Figure 5), cured polymers existed between copper particles, whereas in copper nanosuspension printed parts the powder particles are connected by the same material-copper (Figure 6).

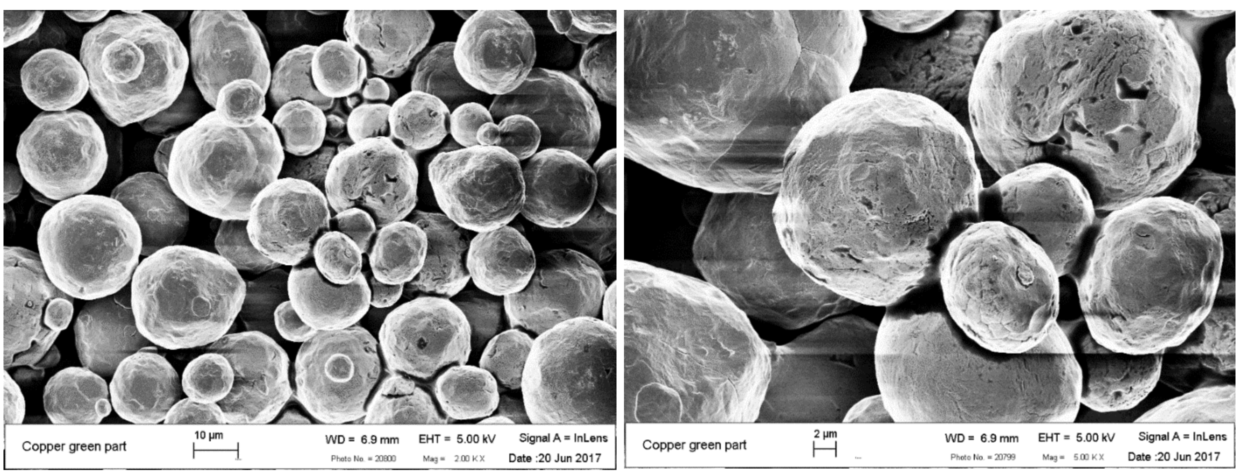

Figure 5. The surface of the green parts printed by polymer binder (100% saturation), characterized by SEM at magnification of 2kx (left) and 5kx (right)

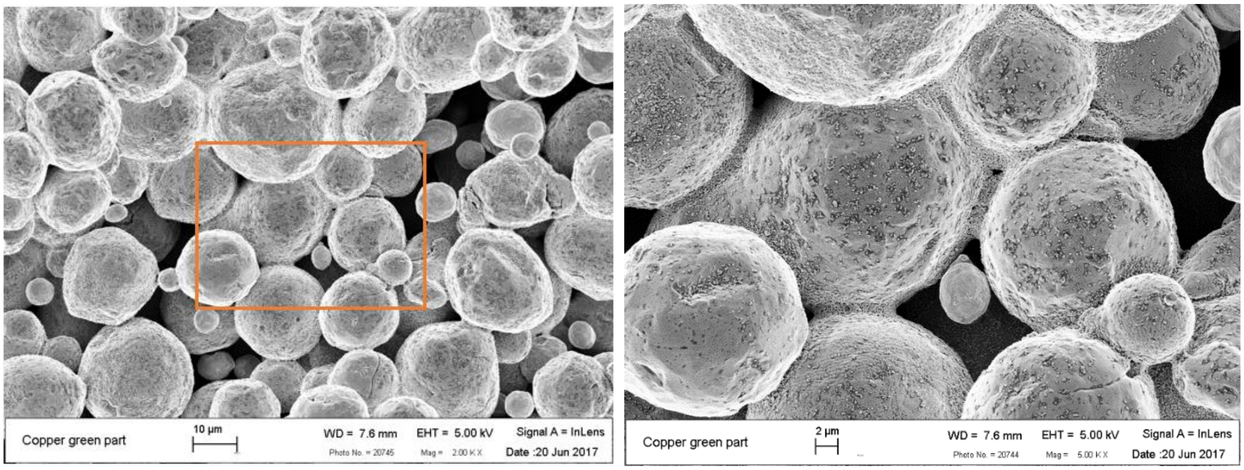

Figure 6. The surface of the green parts printed by nanosuspension (70% saturation), characterized by SEM at magnification of 2kx (left) and 5kx (right)

A further magnified imaging of the necking region reveals a network of copper nanoparticles that have sintered at the operating temperature (260 °C) to provide interparticular bonding to the copper powders (Figure 7). It is also clear that the elevated operating temperature did not cause sintering between the larger powders (also witnessed by the loose powder surrounding the printed part following the build). While some nanoparticles are randomly distributed across the copper powder surface, a large amount of copper nanoparticles have concentrated to the necking regions between copper particles. Nanoparticle bonding was consistently observed in randomly picked regions on both green part surfaces and between layers.

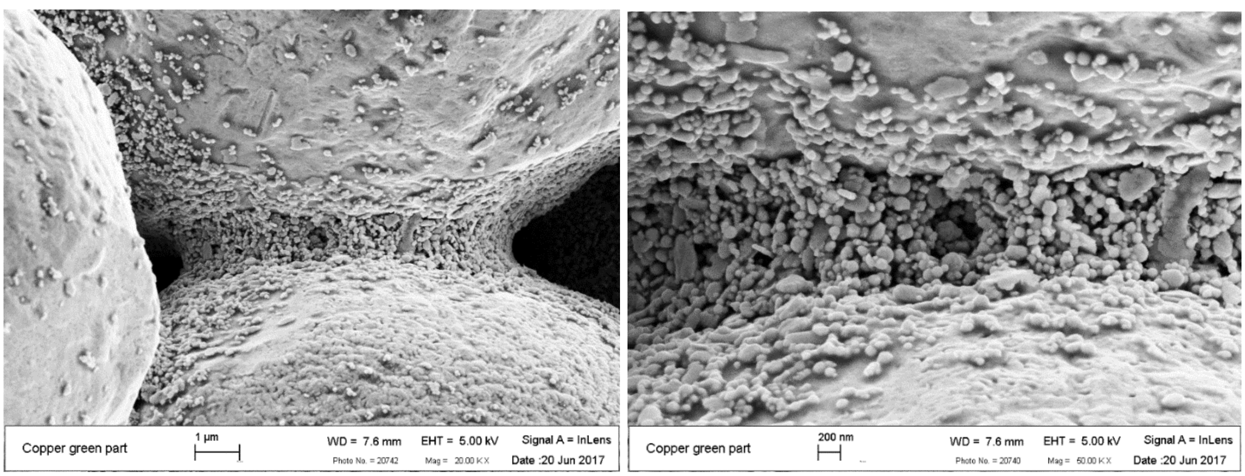

Figure 7. Nanoparticle bonding between copper powder particles in copper nanosuspension printed green parts

4.3 Green strength

Figure 8 compares the green strength of polymer binder printed parts (cured at 200 °C for 1 hour after printing) and copper nanosuspension printed parts (printed with 260 °C bed temperature; directly retrieved from the powder bed without post-printing curing).

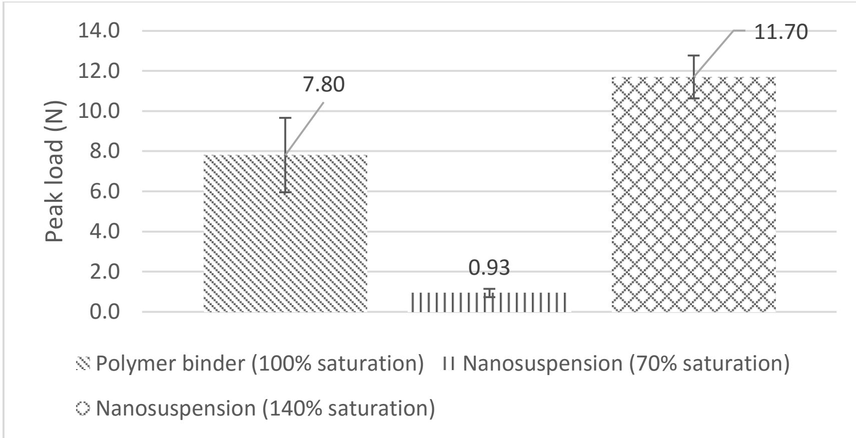

Figure 8. Green strength of nanosuspension printed parts, in comparison to the polymer binder printed counterparts (evaluated by the rupture loading force in 3-point bending test)

The green parts printed by copper nanosuspension with both saturations ratios were able to be retrieved from the powder bed without breaking. Green parts made with the lower saturation setting (70%) are significantly more fragile than the parts made with 140%. When sufficiently saturated, the nanosuspension printed parts could have a green strength that is comparable to the polymer binder printed parts, which can typically ensure safe handling and depowdering without part damage.

4.4 Green and sintered density

The green density of parts printed with polymer binder and copper nanosuspension is compared in Figure 9. Despite the presence of copper nanoparticles at the interstices of the powder bed, the measured green density of parts made via the nanosuspension was not improved substantially.

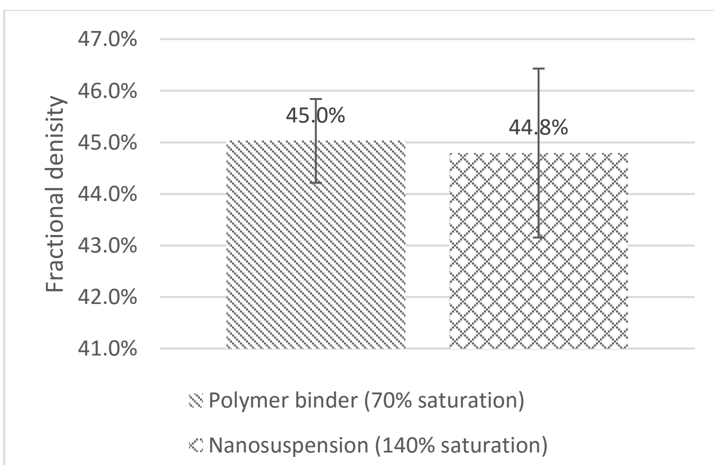

Figure 9. Green density of polymer binder and nanosuspension printed parts

In addition to green density, there is also a lack of evidence to show that the sintered density is substantially improved by the inkjetted nanoparticles (Figure 10). While increasing powder bed packing through depositing fine particles into powder bed interstices could potentially improve sintered density, its effectiveness is limited by the total amount of interstitial particles. In addition, sintering densification is complicated by many factors including sintering conditions and binder-powder interactions.

However, the sintered density difference in 70% and 140% saturated parts suggests that a further increase in binder saturation ratio has a potential to improve sintered density furthermore. Therefore, there is a need to expand binder saturation ratio values for further investigation of interstitial nanoparticles' effect on sintered density.

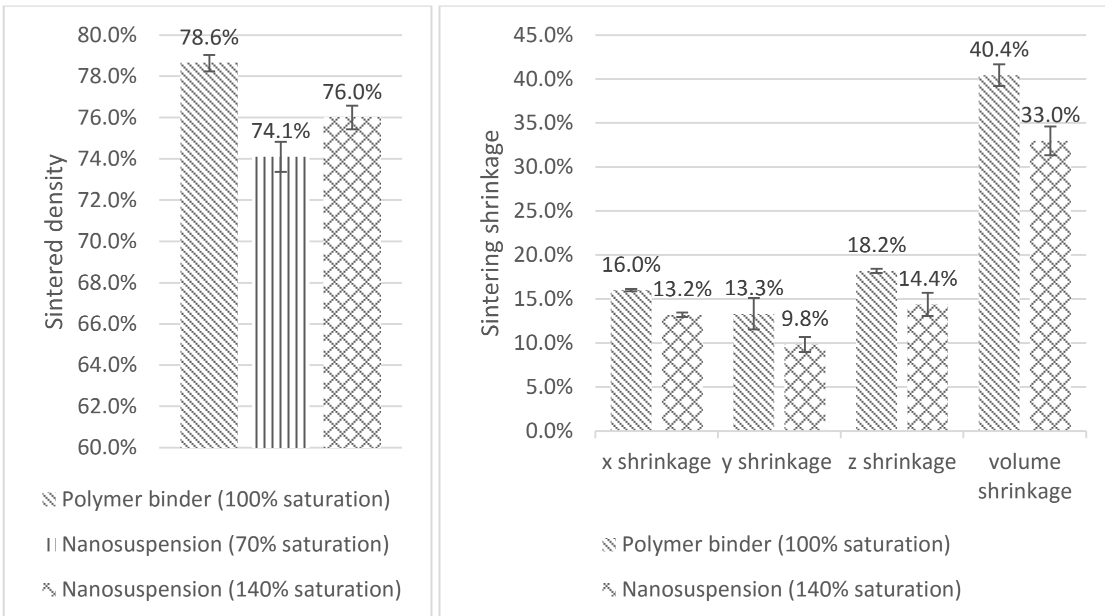

Figure 10. (a) sintered density and (b) sintering shrinkage of polymer binder and nanosuspension printed parts (sintered at 1075 °C for 2 hours)

5. Conclusion and future work

This work represents (i) a preliminary investigation into the concept of printing metals using the nanoparticles of same material as a permanent and structural binder and (ii) an exploration of the interstitial copper nanoparticle's effects on green and sintered part properties in Binder Jetting printed copper.

With adjusted inter-layer drying and curing conditions (2-minuate interlayer heating at 260 °C), the copper nanosuspension can be successfully printed into powder beds without recoating defects and sintering the surrounding powder bed (Section 4.1). The copper green parts printed with copper nanosuspension have obtained satisfactory green strength compared with the polymer binder printed parts without a need for post-print sintering of the powder bed (Figure 8). Nanoparticle bonding between copper powder particles is evident in nanosuspension printed green parts (Figure 6 and Figure 7).

While the copper nanosuspension can be used to successfully print green parts with high quality and strength, the nanoparticle binder's impact on sintered part properties and sintering densification remains uncertain. With the binder saturation ratios (140%) explored in this work, no density increase was observed in green and sintered parts. This ongoing research will focus on expanding the investigated binder saturation ratios, sintering conditions, and base powder packing density to further explore the nanoparticle binder's impact on sintering.

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