



Titre: Title:	Multi-material direct ink writing (DIW) for complex 3D metallic structures with removable supports
Auteurs: Authors:	Chao Xu, Bronagh Quinn, Louis Laberge Lebel, Daniel Therriault, & Gilles L'Espérance
Date:	2019
Туре:	Article de revue / Article
Référence: Citation:	Xu, C., Quinn, B., Laberge Lebel, L., Therriault, D., & L'Espérance, G. (2019). Multi- material direct ink writing (DIW) for complex 3D metallic structures with removable supports. ACS Applied Materials & Interfaces, 11(8), 8499-8506. <u>https://doi.org/10.1021/acsami.8b19986</u>

Document en libre accès dans PolyPublie Open Access document in PolyPublie

•

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/42883/
Version:	Version finale avant publication / Accepted version Révisé par les pairs / Refereed
Conditions d'utilisation: Terms of Use:	Tous droits réservés / All rights reserved

Document publié chez l'éditeur officiel \equiv Document issued by the official publisher

Titre de la revue: Journal Title:	ACS Applied Materials & Interfaces (vol. 11, no. 8)
Maison d'édition: Publisher:	American Chemical Society (ACS)
URL officiel: Official URL:	https://doi.org/10.1021/acsami.8b19986
Mention légale: Legal notice:	"This document is the Accepted Manuscript version of a Published Work that appeared in final form in ACS Applied Materials & Interfaces (vol. 11, no. 8), copyright © 2019 after peer review and technical editing by the publisher. To access the final edited and published work see doi: 10.1021/acsami.8b19986."

Ce fichier a été téléchargé à partir de PolyPublie, le dépôt institutionnel de Polytechnique Montréal This file has been downloaded from PolyPublie, the institutional repository of Polytechnique Montréal

Multi-material direct ink writing (DIW) for complex 3D metallic structures with removable supports

Chao Xu, Bronagh Quinn, Gilles L'Espérance, Louis Laberge Lebel, Daniel Therriault*

5 6

4

7 Chao Xu, Bronagh Quinn, Prof. Louis Laberge Lebel, Prof. Daniel Therriault

8 Mechanical engineering, Polytechnique Montreal

9 C.P. 6079, succ. Centre-Ville, Montreal, QC H3C 3A7, Canada

10 E-mail: Daniel.therriault@polymtl.ca

11 Prof. L'Espérance

12 Metallurgy engineering, Polytechnique Montreal

13 C.P. 6079, succ. Centre-Ville, Montreal, QC H3C 3A7, Canada

15 **Keywords:** additive manufacturing, direct ink writing, complex 3D metallic structures,

16 removable support, multi-material

17

14

18 Abstract

19 Direct ink writing (DIW) combined to post-deposition thermal treatments is a safe, cheap and 20 accessible additive manufacturing (AM) method for the creation of metallic structures. Single material DIW enables the creation of complex metallic 3D structures featuring overhangs, 21 22 lengthy bridges or enclosed hollows, but requires the printing supporting structures. However, 23 the support printed from the same material becomes inseparable from the building structure 24 after the thermal treatment. Here, a multi-material DIW method is developed to fabricate 25 complex three-dimensional (3D) steel structures by creating a removable support printed from 26 a lower melting temperature metal (i.e., copper) or a ceramic (i.e., alumina). The lower melting 27 temperature metal completely infiltrates the porous steel structures for a hybrid configuration, 28 while the ceramic offers a brittle support that can be easily removed. The influence of the 29 support materials on the steel structure properties is investigated by the characterizing the 30 dimensional shrinkage, surface roughness, filament porosity, electrical conductivity and tensile 31 properties. The hybrid configuration (i.e., copper infiltrated steel structures) improves the 32 electrical conductivity of the fabricated steel structure by 400% and the mechanical stiffness by 34%. The alumina support is physically and chemically stable during the thermal treatment,
 bringing no significant contamination to the steel structure.

- 3
- 4

5 Introduction

6 Metallic structures fabricated through Additive manufacturing (AM), also referred to as threedimensional (3D) printing, have been used as batteries,^[1-2] medical implants,^[3-4] and sensors^{[5-} 7 ^{6]} due to their key advantages, i.e., high mechanical and electrical properties, complex 8 9 geometries, and mold-free manufacturing processes. The most established metal AM 10 approaches are powder-bed based methods such as selective laser melting (SLM) and electron beam melting (EBM).^[7-9] They use a laser beam or electron beam to locally fuse metallic 11 12 particles in a powder bed to build a 3D object layer-by-layer. These methods feature short 13 manufacturing time, high mechanical performance of the fabricated parts and very few 14 restrictions on the printed geometry. However, they are limited by high cost, laser induced excessive oxidation, and residual stresses in the fabricated parts.^[10-12] 15

16 Researchers developed many different metal AM methods to overcome the shortcomings of the 17 powder-bed methods. Skylar-Scott et al. built metallic architectures from a water-based silver ink. The silver ink was extruded from a micro nozzle as a filament. The filament was sintered 18 right after extrusion using a laser beam.^[13] Freeform 3D metallic architectures featuring high 19 20 resolution and high electrical conductivity were fabricated using this method. However, the 21 laser beam sintering in the air would cause excessive oxidation and loss of alloying elements. Wang et al. developed an initiator-integrated 3D printing method to build metallic structures.^[14] 22 23 First, a polymer template of the 3D structure was built. Then metallic particles were deposited 24 on the surface of the polymer template through electroless plating. Finally, the polymer 25 template was etched away to achieve ultralight cellular metallic structures. This method enables the fabrication of complex 3D metallic structures featuring low density. However, the metallic 26

architecture is hollow and relatively thin after the polymer template is etched away, which leads
 to poor mechanical performances.

3 Direct ink writing (DIW) is an AM method, which usually relies on the extrusion of polymer 4 solution (or melt), known as ink, through a micro-nozzle and the deposition of the extruded ink on a substrate layer by layer to create a 3D object.^[15-16] Researchers adapted it to metal AM by 5 printing from metallic inks.^[17-20] The metallic inks are prepared by adding metal micro- or nano-6 7 particles to the polymer solution (or melt), which are used in DIW to build a metal-polymer 8 composite 3D structure. To achieve a metallic structure featuring high mechanical and electrical 9 performances, a post-deposition thermal treatment is performed to pyrolyze the polymer and to 10 sinter the metal particles.

DIW of polymer can create complex 3D structures with large overhangs or lengthy bridges by 11 12 printing support underneath them to hold the structures. Once the printing is completed, the sacrificial support is removed.^[21-22] However, the utilization of a support does not work for 13 14 DIW of metal, where a post-deposition thermal treatment is performed. If the support is 15 removed before the thermal treatment at a moment when the polymer binder is pyrolyzed before 16 the sintering of the metallic particles, the overhang features will collapse. Whereas, if the support printed from the same material is not removed before the thermal treatment, the support 17 18 and the building structure will fuse together and become inseparable after the thermal treatment. 19 Thus, the existed DIW methods are unable to fabricated complex 3D metallic structures 20 featuring overhangs, length bridges or enclosed hollows.

Here, we propose a multi-material DIW method to fabricate complex 3D metallic structures with removable supports. This method consists of two steps: (a) room-temperature DIW of metal-polymer composite structures with metal- (or ceramic-) polymer composites supports, and (b) a post-deposition thermal treatment turning the as-printed metal-polymer composite structures to metal structures. **Figure 1a** shows a schematic of the multi-material DIW system and as-printed hollow sphere structures. The multi-material DIW system includes three major

1 components: (i) a computer controlled 3-axis robot, (ii) a pressure dispenser, and (iii) multiple 2 ink syringes containing steel, copper and alumina inks. The inks are concentrated steel, copper and alumina microparticle suspensions dispersed in a polymer solution (i.e., polylactic acid / 3 4 dichloromethane, referred to as PLA/DCM), respectively. The scanning electron microscope 5 (SEM) images of the microparticles are shown in Figure S1. To fabricate a 3D metallic 6 structure, e.g., a hollow sphere as shown in **Figure 1a**, supports are generated inside the hollow 7 sphere to support the top overhang part and underneath the sphere to create a flat bottom which 8 is compatible with the geometry of the substrate. Here, as a proof of concept, the supports are 9 built using a secondary material (i.e., copper or alumina ink), while the building structure is 10 printed with the primary material (i.e., steel ink). The steel-PLA composite structure with 11 copper-PLA composite support is referred to as as-printed S-Cu, while the one with alumina-12 PLA composite support is referred to as as-printed S-Al₂O₃. These two types of supports are 13 differently removed through the post-deposition thermal treatment. The lower melting 14 temperature metallic support (i.e., copper) could be completely melted and infiltrated into the 15 pores within the filament of the sintered structure to achieve a hybrid configuration. The 16 ceramic support (i.e., ceramic) survives the temperature cycle without any significant sintering 17 and can be easily removed without affecting the metallic structure.

18 **Figure 1b** presents the temperature profile of the thermal treatment, the thermal gravity analysis 19 (TGA) result of the polymer binder PLA under this temperature profile, the sintering temperature range and melting temperature of stainless steel 316L and copper.^[23-24] In addition, 20 21 a schematic is shown in Figure 1b illustrating the microstructure variations of the two-phase 22 interface in the as-printed structures at five different stages during the thermal treatment. For 23 S-Cu structures, Stage I is an as-printed structure at room temperature, where the steel and 24 copper particles are bound by the PLA binder, respectively. Stage II consists of a one-hour plateau at 400°C for debinding. PLA binder is completely pyrolyzed as shown in the TGA curve, 25 26 where the weight of the PLA binder rapidly drops within 7 min. The structure is held by the

1 friction forces among the steel particles and among copper particles, respectively. The 2 temperature then is increased to reach a temperature plateau at 950°C for one hour (Stage III). 3 This plateau temperature is selected to be in the sintering temperature range of S316L and 4 copper, but is lower than their melting temperatures. The S-Cu structure is mechanically 5 enhanced by initial sintering, where the necks appear among steel particles and among copper 6 particles, respectively. After this stage, even if the support is removed, the bonding between the 7 steel particles is strong enough to hold the building structure. During Stage IV, the temperature 8 increases from 950°C to 1165°C, surpassing the melting temperature of copper (i.e. 1085°C). 9 The copper support starts melting, while the steel structure is held in its original geometry by 10 the sintering bonds generated during Stage III. Stage V is a four-hour plateau at 1165°C, where 11 the steel particles are further sintered and the melted copper completely infiltrates the pores of 12 the sintered steel structure by capillary forces. After this temperature profile, the as-printed S-13 Cu is turned into a steel structure infiltrated by the copper.

14 For S-Al₂O₃ structures, Stages I and II are the as-printed structure at room temperature and the 15 debinding process respectively, like those of the S-Cu structures. Since both the melting 16 temperature of alumina (2040°C) and the lower limit of alumina sintering temperature (1800°C)^[25] are much higher than the maximum imposed temperature (1165°C), the alumina 17 18 particles are neither melted nor sintered, but remain as individual particles during the whole 19 thermal treatment. Therefore, in Stages III to V, the alumina support preserves its shape mostly 20 due to the friction forces among the alumina particles. The steel particles are sintered and form 21 a strong steel keeping the original geometry. As the alumina support is weakly held by the 22 friction forces, it does not fuse with the building structure and can be easily removed by hand 23 after the thermal treatment.

Figure 1c shows the as-printed and sintered S-Cu and S-Al₂O₃ printed using this method as a structure shaped as a human thigh bones at a scale of 1:7. The steel bone structure is 50% of

volume filled, while the support structure is 30% of volume filled. The supports provide a flat 1 2 bottom and hold up the overhang features for the bone to facilitate the printing on a flat substrate. 3 After the thermal treatment, the copper support melts and infiltrates into the sintered steel 4 structure, while the alumina support is removed easily by hand. Both sintered structures 5 preserve the original geometry of the human thigh bone with a uniform linear dimensional 6 shrinkage of 11%. To demonstrate the ability to build complex 3D metallic structure featuring 7 overhangs, an inverted "L" shape structure featuring a large overhang part is fabricated through 8 this method with a cubic support structure printed from a secondary material (Figure S2).



Figure 1. Multi-material DIW for complex 3D metallic structures with removable supports consists of two steps: (a) room-temperature DIW of metal-polymer composite structures with metal- (or ceramic-) polymer composites supports, and (b) a post-deposition thermal treatment turning the as-printed metal-polymer composites structures to metal structures, and a schematic shows the two-phase interface microstructures variations of the as-printed structures at five

different stages during the thermal treatment. (c) Optical images of as-printed and sintered S Cu and S-Al₂O₃ structures printed as a human thigh bones at a scale of 1:7.

3

5

4 Experimental Section

6 Ink preparation: The steel particles are stainless steel 316L with a spherical shape and a 7 diameter less than 20µm. The copper particles are spherical and less than 20µm in diameter. 8 The steel and copper particles are purchased from US Research Nanomaterials, Inc. The 9 alumina particles are irregular in shape and less than 10µm in size (265497, Sigma-Aldrich). 10 The SEM images of the three types of particles are presented in Figure S1. The polymer binder 11 solution is produced by adding 2g polylactic acid (PLA, 4032D, Natureworks LLC) to 8g 12 dichloromethane (DCM, Sigma-Aldrich) and left to dissolve for 24 h to ensure homogenization. 13 The steel, copper and alumina inks are prepared by mixing the corresponding particles with the 14 polymer solution at a weight ratio of 3:1, 3:1, and 1.2:1, respectively, using a ball mill mixer 15 (8000M Mixer/Mill, SPEX SamplePrep) for 15 min.

16

17 Multi-material DIW: The CAD model of the building structure is either designed in a computer 18 aided design software (CATIA) or downloaded from internet (thingerverse.com). The support 19 is generated where it is needed to hold building structure through a software, Simplify 3D 20 (version 4.0). Both the building and support structures are converted into a G-code using 21 Simplify 3D. Then the G-code is converted into a point-to-point program that can be read by 22 the JR Point software to control the 3-axis positioning robot (I&J2200-4, I&J Fisnar). The ink 23 is loaded in a syringe (3mL, Nordson EFD) attached with a smooth-flow tapered nozzle (exit 24 inner diameter = $250\mu m$, Nordson EFD). DIW is performed using the positioning robot and 25 pressure dispensing systems (HP-7X, Nordson EFD). The structures are deposited on a glass 26 slide (PN 16004-422, VWR) at room temperature. All the structures in this work are deposited at a linear printing speed of 15mm/s and under an applied pressure of 0.7 - 1.2 MPa. The spacing
 between each layer is 80% of the nozzle inner diameter to compensate the solvent evaporation
 induced filament shrinkage and ensure tight bonding between the adjacent layers.

4

Post-deposition thermal treatment: The as-printed structures are thermal treated in a laboratory
electric tubular furnace (59256-P-COM, Lindberg) on a ceramic substrate. To prevent oxidation,
a gas flow (97.5% Ar and 2.5% H₂, flow rate = 5 L/min) is circulated inside the quartz tube.
The temperature profile is presented in Figure 1b, wherein all the heating rates are 600°C/h
and the cooling rate is 900°C/h.

10

11 Surface roughness measurement: The roughness of the top surface of the sintered steel 12 structures is measured using a profilometer (SV-C4000, Mitutoyo) following the AISI standard 13 in accordance with ASME B.46.1-2002. The measuring direction is perpendicular to the 14 filament orientation. The sampling length of meso R_a is 7.5mm, while the sampling length of 15 micro R_a is 0.1mm. Ten specimens are measured for each sample type.

16

Porosity analysis: The sintered steel scaffold is cut parallel to the Z direction to observe the vertical cross section. The sliced steel scaffold is sealed in a resin (EpoFix resin, Struers) block and the cross section is polished for observation under an optical microscope (Zeiss Axioplan EL-Einsatz). The porosity is determined using an image analysis software (ImageJ). The filament porosity is calculated as the ratio of void area inside the filament over the filament area. Ten cross sections of each sample are analyzed.

23

Electrical conductivity analysis: The electrical conductivity of the sintered steel structures is
measured using the four-point probes method. A constant current of 1A is provided by a power

supply (Agilent, E3633A). The voltage is acquired by a multimeter (HP, 3457A). Five
 specimens of each sample type are tested.

3

4 Tensile test and DIC: The samples are sintered steel tensile bars, of which the cross-section of 5 the neck is $\sim 3.6 \times 1.8$ mm. The tensile tests are carried out in a MTS Insight machine with a 50 6 kN load cell (MTS 569332-01) at a crosshead speed of 1 mm/min and using DIC to measure 7 the strain of the tensile bars. The tensile bars are polished on both sides for a smooth surface. 8 A thin layer of white acrylic spray paint (Ultra 2X spray paint, Painter's Touch) is applied on 9 the surface. The speckle pattern (black dots of ~0.4mm) is painted on the white paint with a 10 roller brush to ensure the tracking of displacement. The images of the sample are taken by two 11 long range focus stereo microscopes at a frequency of 4Hz during the tensile test. The images 12 are analyzed by VIC3D micro (Correlated solutions, version 7.2.4) and the strain is calculated 13 by the displacement of the speckle pattern. Tensile tests were performed on the sintered S, S-14 Cu and S-Al₂O₃ samples and their DIC measured strains are presented in Video S1, S2 and S3, 15 respectively. Five specimens for each sample type are tested.

16

17 **Results and discussion**

18 Steel scaffolds (S), steel scaffolds with copper support (S-Cu) and steel scaffolds with alumina 19 support (S-Al₂O₃) are printed and thermally treated to investigate the influence of the support 20 materials to the building structures. Figure 2a shows optical and SEM images of as-printed and 21 sintered (thermally treated) S, S-Cu and S-Al₂O₃ scaffolds. The as-printed steel scaffolds 22 supported by copper and alumina are as neat and orderly structured as the as-printed steel 23 scaffold without support. The steel, copper and alumina particles are bound by the PLA binder 24 to hold the structures, respectively. After the thermal treatment, the steel scaffolds retain their geometry, but exhibit some dimensional shrinkage. The SEM images of the sintered (thermally 25 26 treated) scaffolds at different magnifications are presented in Figure S3. They have similar

linear size reduction ranging from 10.7% to 11.2% (Figure 2b). Each type of steel scaffolds
has a small size deviation of ≤1.3% (Figure 2b). The small deviation guarantees the
reproducibility of this method in terms of dimensional accuracy of the fabricated structures.
The steel particles of the S-Al₂O₃ scaffold are just as sintered as those in the S scaffold, but the
S-Al₂O₃ scaffold has a rougher surface. The steel particles in S-Cu scaffold are sintered as well.
In addition, the copper support melts and infiltrates into the sintered steel structure, leading to
a smoother surface.

8 Figure 2c shows the single filament surface roughness (named as micro R_a) and the inter-9 filament surface roughness (termed as meso R_a) of the sintered steel scaffolds, and SEM images 10 of the measured surfaces serving as an example of the micro and meso R_a . The profilometer 11 probe traveling direction (measuring direction) is perpendicular to the filament longitudinal 12 axis. The micro R_a of sintered S-Al₂O₃ (4.1µm) is greater than that of sintered S (2.5µm), while the micro R_a of sintered S-Cu (1.6µm) is smaller than that of sintered S. The meso R_a s of 13 sintered S and sintered S-Cu are similar (~5µm), which are smaller than that of sintered S-Al₂O₃ 14 (13.9µm). The thermally treated alumina scaffold is so fragile that the shrinkage and surface 15 16 roughness could not be measured. The shrinkage difference between the thermally treated ceramic particles and the sintered steel particles leads to a rougher surface. According to our 17 observations, the support materials have little influence on the dimensional shrinkage of the 18 19 steel scaffolds. The alumina support appears to increase the micro and meso surface roughness 20 of the sintered steel structure by 1.6µm and 9µm, respectively.



1

Figure 2. (a) Optical and SEM images of as-printed and sintered (thermal treated) scaffolds. (b) Linear size reduction of the sintered steel structures. (c) Single filament surface roughness (micro R_a) and inter-filament surface roughness (meso R_a) of the sintered steel structures, and SEM images of the measured surfaces serving as an example of the micro and meso R_a .

1 The influence of the support materials to the elemental composition and porosity of the building 2 structures is studied through SEM and elemental analysis. Figure 3a shows SEM images and 3 Energy-dispersive X-ray spectroscopy (EDS) elemental mappings of the cross sections of 4 sintered S, sintered S-Cu, and sintered S-Al₂O₃ structures. The cross sections of the three types 5 of sintered steel structures are characterized by the strong presence of iron. Copper is detected 6 only in the sintered S-Cu structures as expected. The detection of copper is located in the regions 7 between the iron rich zones. Aluminum and oxygen (i.e., the elements contained in the alumina 8 support) are not detected in the sintered S-Al₂O₃ structures. Neither in the sintered S and 9 sintered S-Cu structures. The elemental analysis result shows that: (i) the copper support 10 infiltrates into the building structure and fills the majority of the pores in the sintered steel 11 structure during the thermal treatment, and (ii) the alumina support is chemically stable during 12 the thermal treatment and does not contaminate the steel structure. The volume fractions of the 13 solid phases (iron for S and S-Al₂O₃, iron and copper for S-Cu) are similar in all three types of 14 sintered steel structures at $\sim 98\%$ (Figure 3b). In the sintered S-Cu structure, the iron phase 15 takes up about 87.2% and the copper phase accounts for around 10.4%. This value can be 16 controlled by the volume ratio of the support and building structure, which will be studied in 17 the future work. All the three types of sintered steel structures have similar and low porosity 18 (~2%), and small pore size between 2 and 3 μ m (Figure 3c-d). The supports do not have an 19 obvious influence on the porosity and pore size to the building structure.



Figure 3. Elemental and porosity analysis of the sintered steel structures. (a) SEM images and
EDS elemental mappings of the cross sections of sintered S, sintered S-Cu, and sintered SAl₂O₃ structures. Scale bar = 50µm. (b) Volume percentage of iron and copper phase, (c)
filament porosity, and (d) filament pore size of the various sintered steel structures.

6

7 Figure 4 shows the results for the electrical and tensile tests conducted on the sintered steel 8 structures manufactured using different support materials.. Figure 4a presents typical tensile 9 stress-strain curves and representative optical image of the sintered S, S-Cu and S-Al₂O₃ tensile 10 bars in the inset. Figure S4 presents the SEM images of the sintered S, S-Cu and S-Al₂O₃ fully 11 dense tensile bars. Stereoscopic digital image correlation (DIC) technique is used to measure 12 the strain in the tensile bars during the tensile tests (Figure S5). The measured tensile properties 13 of the sintered steel structures are shown in Figure 4b. Sintered S-Cu exhibits higher Young's 14 modulus E (174 \pm 10 GPa), yield strength (YS) (284 \pm 16 MPa) and ultimate tensile strength

1 (UTS) (521 \pm 57 MPa) and elongation at failure (11.3% \pm 3.6%) compared to those of sintered S (~30% - 45% superior). This increase in tensile properties is the result of copper infiltration 2 3 of the sintered steel structure. Sintered S-Al₂O₃ has weaker tensile properties compared to the 4 sintered S. The E (108 \pm 6 GPa), the YS (165 \pm 8 MPa) and the UTS (304 \pm 18 MPa) of sintered 5 S-Al₂O₃ are 15% - 21% less than those of sintered S. The elongation at failure $(10.1\% \pm 1.4\%)$ 6 of sintered S-Al₂O₃ is similar to that of sintered S. We believe that the dimensional shrinkage 7 difference between the steel structure and the alumina support might affect the sintering of the 8 steel structure and lead to weaker tensile properties. Figure 4c shows the SEM images of the 9 tensile fracture surfaces of the sintered steel tensile bars. More SEM images of the tensile 10 fracture surfaces at different magnification are presented in Figure S6. The tensile fracture surface of the sintered S shows the shape and orientation of individual filaments at 45° relative 11 12 to the tensile direction and orthogonal with the filaments from adjacent layers. Each individual 13 filament is dense and the filaments from the same and the neighboring layers are fused together. 14 The individual filament shape and orientation are recognizable but not very clear in the sintered 15 S-Al₂O₃. The filaments in sintered S-Cu are completely fused together with the presence of 16 copper, making a fully dense structure. The electrical conductivity of the sintered S-Al₂O₃ is $(6.9 \pm 3.4) \times 10^5$ S/m and the sintered S, $(7.4 \pm 0.4) \times 10^5$ S/m are similar (Figure 4d). The 17 electrical conductivity of sintered S-Cu, $(27.9 \pm 4.2) \times 10^5$ S/m, is approximately four times 18 19 higher than the value measure for the sintered S due to the presence of copper (Figure 4d). The 20 properties of the sintered steel structures are summarized in Table S1. The overall electrical 21 and mechanical properties of the sintered S-Cu are superior to those of the sintered S. Sintered 22 S-Al₂O₃ has comparable electrical properties, but slightly weaker mechanical properties 23 compared to the sintered S.



Figure 4. Electrical and mechanical characterizations of the sintered steel structures. (a) Typical tensile stress-strain curves of sintered steel structures and representative optical image of the different sintered steel tensile bars (inset). (b) Young's modulus, yield strength, ultimate tensile strength and elongation at failure of the sintered steel structures. (c) SEM images of the tensile fracture surfaces of the sintered steel structures. (d) Electrical conductivity of the sintered steel structures.

8

9 Conclusion

10 A multi-material direct ink writing method is developed to fabricate complex 3D metallic 11 structures by printing removable supports using two different secondary materials. As a proof 12 of concept, steel structures are fabricated through this method with the help of copper and 13 alumina supports, respectively. The influence of the support materials on the steel structure is

1 investigated. The supports lead to no significant difference to the building structures on the 2 dimensional shrinkage, surface roughness and porosity of the building structure. The copper 3 support brings a hybrid metallic composition to the steel structure and improves its electrical 4 conductivity by four times and stiffness by 34%. Although the alumina supports lower the 5 stiffness of the building structure by 17%, it brings no contamination to the steel structure. It is 6 worth mentioning that the support materials are not only limited to copper or alumina. Any 7 desired alloying metal with a lower melting point than the building material can be the metal 8 support material, e.g., zinc and aluminum. Any ceramic material that is physically and 9 chemically stable during the thermal treatment can be the ceramic support materials such as 10 tungsten carbide. The proposed method broadens the geometry possibilities of metallic 3D structures that DIW can create. It provides the metal additive manufacturing of medical 11 12 implants, sensors and batteries featuring complex geometries a readily accessible choice.

13

14 Supporting Information

SEM images, the strain distribution measured by DIC, a summary of the properties of the sintered steel structures, videos of the tensile test process with DIC measured strain showing on the samples.

18

19 Author Contributions

20 The manuscript was written through contributions of all authors. All authors have given21 approval to the final version of the manuscript.

22

23 Corresponding Author

24 (Daniel Therriault) Email: daniel.therriault@polymtl.ca

1 **Conflict of Interest**

2 The authors declare no conflict of interest.

3

4 Acknowledgements

5 The authors acknowledge the financial support from NSERC (Natural Sciences and 6 Engineering Research Council of Canada, grant number: RGPIN 312568-2013) and Auto 21 of 7 the Canadian Network of Centers of Excellence (NCE) program. The authors also acknowledge 8 the scientific discussions from Olivier Sioui-Latulippe and Vincent Wuelfrath-Poirier on 9 metallurgy science. A scholarship for Mr. Xu was also provided by the China scholarship 10 Council (CSC) and the Fonds de recherche du Quebec - Nature et technologies (FRQNT).

1 References

2	1.	Cheng, M., Jiang, Y., Yao, W., Yuan, Y., Deivanayagam, R., Foroozan, T., Huang, Z.,
3		Song, B., Rojaee, R., Shokuhfar, T., Pan, Y., Lu, J., Shahbazian-Yassar, R. Elevated-
4		Temperature 3D Printing of Hybrid Solid-State Electrolyte for Li-Ion Batteries. Adv.
5		Mater. 2018, 30, 1800615.
6	2.	Finsterbusch, M., Danner, T., Tsai, C.L., Uhlenbruck, S., Latz, A., Guillon, O. High
7		Capacity Garnet-Based All-Solid-State Lithium Batteries: Fabrication and 3D-
8		Microstructure Resolved Modeling. ACS Appl. Mater. Interfaces 2018, 10, 22329-
9		22339.
10	3.	Elahinia, M., Moghaddam, N.S., Andani, M.T., Amerinatanzi, A., Bimber, B.A.,
11		Hamilton, R.F. Fabrication of NiTi through Additive Manufacturing: A Review. Prog.
12		Mater. Sci. 2016, 83, 630-663.
13	4.	Amin Yavari, S., Loozen, L., Paganelli, F.L., Bakhshandeh, S., Lietaert, K., Groot, J.A.,
14		Fluit, A.C., Boel, C.H.E., Alblas, J., Vogely, H.C., Weinans, H. Antibacterial Behavior
15		of Additively Manufactured Porous Titanium with Nanotubular Surfaces Releasing
16		Silver Ions. ACS Appl. Mater. Interfaces 2016, 8, 17080-17089.
17	5.	Rim, Y.S., Bae, S.H., Chen, H., De Marco, N., Yang, Y. Recent Progress in Materials
18		and Devices toward Printable and Flexible Sensors. Adv. Mater. 2016, 28, 4415-4440.
19	6.	Xu, L., Gutbrod, S.R., Bonifas, A.P., Su, Y., Sulkin, M.S., Lu, N., Chung, H.J., Jang,
20		K.I., Liu, Z., Ying, M., Lu, C., Webb, R. C., Kim, J. S., Laughner, J. I., Cheng, H., Liu,
21		Y., Ameen, A., Jeong, J. W., Kim, G. T., Huang, Y., Efimov, I. R., Rogers, J. A. 3D
22		Multifunctional Integumentary Membranes for Spatiotemporal Cardiac Measurements
23		and Stimulation across the Entire Epicardium. Nat. Commun. 2014, 5, 4329.
24 25 26	7.	Gu, D.D., Meiners, W., Wissenbach, K. Poprawe, R. Laser Additive Manufacturing of Metallic Components: Materials, Processes and Mechanisms. <i>Int. Mater. Rev.</i> 2012, 57, 133-164.

1	8. Herzog, D., Seyda, V., Wycisk, E., Emmelmann, C. Additive Manufacturing of Metals.
2	Acta Mater. 2016, 117, 371-392.
3	9. Martin, J.H., Yahata, B.D., Hundley, J.M., Mayer, J.A., Schaedler, T.A., Pollock, T.M.
4	3D Printing of High-strength Aluminium Alloys. Nature 2017, 549, 365.
5	10. Gong, H., Rafi, K., Gu, H., Ram, G.J., Starr, T., Stucker, B. Influence of Defects on
6	Mechanical Properties of Ti-6Al-4 V Components Produced by Selective Laser
7	Melting and Electron Beam Melting. Mater. Des. 2015, 86, 545-554.
8	11. Olakanmi, E.O.T., Cochrane, R.F., Dalgarno, K.W. A Review on Selective Laser
9	Sintering/Melting (SLS/SLM) of Aluminium Alloy Powders: Processing,
10	Microstructure, and Properties. Prog. Mater. Sci. 2015, 74, 401-477.
11	12. Chou, R., Milligan, J., Paliwal, M., Brochu, M. Additive manufacturing of Al-12Si
12	Alloy via Pulsed Selective Laser Melting. JOM 2015, 67, 590-596.
13	13. Skylar-Scott, M.A., Gunasekaran, S. and Lewis, J.A., Laser-assisted Direct Ink Writing
14	of Planar and 3D Metal Architectures. Proc. Natl. Acad. Sci. U. S. A. 2016, 113, 6137-
15	6142.
16	14. Wang, X., Guo, Q., Cai, X., Zhou, S., Kobe, B. and Yang, J., Initiator-integrated 3D
17	Printing Enables the Formation of Complex Metallic Architectures. ACS Appl. Mater.
18	Interfaces 2013, 6, 2583-2587.
19	15. Lewis, J. A. Direct Ink Writing of 3D Functional Materials. Adv. Funct. Mater. 2006,
20	16, 2193-2204.
21	16. Therriault, D., White, S.R., Lewis, J.A. Chaotic Mixing in Three-dimensional
22	Microvascular Networks Fabricated by Direct-write Assembly. Nat. Mater. 2003, 2, 265.
23	17. Ahn, B.Y., Shoji, D., Hansen, C.J., Hong, E., Dunand, D.C., Lewis, J.A. Printed
24	Origami Structures. Adv. Mater. 2010, 22, 2251-2254.

1	18. Jakus, A.E., Taylor, S.L., Geisendorfer, N.R., Dunand, D.C., Shah, R.N. Metallic
2	Architectures from 3D-printed Powder-based Liquid Inks. Adv. Funct. Mater. 2015, 25,
3	6985-6995.
4	19. Xu, C., Bouchemit, A., L'Espérance, G., Lebel, L.L., Therriault, D. Solvent-cast based
5	Metal 3D Printing and Secondary Metallic Infiltration. J. Mater. Chem. C 2017, 5,
6	10448-10455.
7	20. Xu, C., Wu, Q., L'Espérance, G., Lebel, L.L., Therriault, D. Environment-friendly and
8	Reusable Ink for 3D Printing of Metallic Structures. Mater. Des. 2018, 160, 262-269.
9	21. Ziemian, C.W., Crawn III, P.M. Computer Aided Decision Support for Fused
10	Deposition Modeling. Rapid Prototyp J 2001, 7, 138-147.
11	22. Waheed, S., Cabot, J.M., Macdonald, N.P., Lewis, T., Guijt, R.M., Paull, B., Breadmore,
12	M.C. 3D Printed Microfluidic Devices: Enablers and Barriers. Lab Chip 2016, 16, 1993-
13	2013.
14	23. Peckner, D., Bernstein, I. M. Handbook of Stainless Steels; McGraw-Hill Book
15	Company, New York, 1997.
16	24. Davis, J. R. Copper and Copper Alloys; ASM international, 2001.
17	25. Pradyot, P. Handbook of Inorganic Chemicals; McGraw-Hill, New York, 2003.

Table of Contents



- **Title:** Multi-material direct ink writing (DIW) for complex 3D metallic structures with
- 12 removable supports

