Paste-based 3D printing of metallic materials: effect of binders and precursor sizes

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Abstract

This study proposes a simple paste-based synthesis method for 3D printing (3DP) of metallic materials utilizing a modified polymeric printer (MPP), which comprised a three-step approach toward realizing the final product: (i) generation of a paste containing the metal precursors and the organic binders necessary to achieve the adequate viscosity; (ii) layer-by-layer deposition of the paste based on a computer-aided design file; and (iii) a post-processing step aimed at removing the sacrificial organic media and sintering the metallic particles. Two different binder formulations comprising a semi-solid saturated hydrocarbon paraffin or an alcohol-water-thickening agent based gel were tested as the fluid media, in which the metallic powders (Ti-6Al-4V or Ni and Ti) were dispersed. The decomposition behavior of the pastes was studied and compared with commercial metal infused polymer filaments. The gel binder was deemed as the most effective medium given its ability to evaporate cleanly without altering the sample composition or leaving behind unwanted residual by-products. Metal microparticles were found to provide adequate viscosity as compared to nanoparticles, which behaved as shear thinning agents in the gel based medium. Upon identification of the best-suited metal powder sizes and binder formulations, the 3D printed samples were thermally processed and characterized.

1. Introduction

In recent years, the field of additive manufacturing (AM) has gained significant attention in both the academic as well as the industrial sectors. AM based metallic materials including titanium (Ti) [1–3], aluminum (Al) [4–6], nickel (Ni) [7, 8] as well as stainless steels [9, 10] have been explored widely, for a variety of engineering applications. Emphasis has been put on the production of complex shapes such as hollow, lattice-like or truss-based structures with potential use in medical and space systems [11]. As compared to subtractive manufacturing, AM processes only utilize the necessary amount of materials for part fabrication, which can reduce the cost and time associated with the overall production. The essence of AM lies in depositing materials layer-by-layer based on a computer-aided design (CAD), also known as three-dimensional printing (3DP). The advantages of 3DP include the ability of producing versatile geometries with high precision with efficient use of materials, design flexibility, and customizability and without the need for complex tools [12].

Different manufacturing methods currently exist for metal production including casting and powder metallurgy (PM). Casting involves melting of materials at high temperatures that get deposited into a desired mold shape and then are allowed to solidify. However, the casted parts could present irregularities transferred from the imperfections in the mold, and require surface post-processing [11]. PM, on the other hand encompasses techniques that allow for the synthesis of consolidated parts from metallic powders. PM processes can be further subcategorized into AM and conventional PM strategies. In conventional PM techniques, raw
metal powders are compressed into desired shapes followed by sintering and annealing in order to gain the required density and porosity. Among powder-based AM methods, the most common are selective laser melting (SLM), selective laser sintering (SLS), and electron beam melting (EBM) [13]. Powders are utilized as the raw material and a laser or an electron beam is used to melt the powder layers selectively based on the sliced CAD information [14]. These methods hold significant promise for producing metal alloys but one of the drawbacks associated with the aforementioned processes is their high production costs since the machines used for these techniques generally require high energy and protected atmospheres [15, 16]. Moreover, these methods require thermal post-processing steps to reduce porosity and control the final microstructure, which may have significant impact on the mechanical properties of the final product. Conventional PM methods such as metal injection molding (MIM) can be appealing in terms of affordability and ease of operation; however these methods can impose limitations on the attainable specimen geometry and also require thermal post-processing.

More recently solvent-cast 3D printing (SC-3DP) has gained popularity as an alternative approach for AM-based synthesis of metallic materials [17, 18]. The essence of the SC-3DP method lies in the deposition of a liquid ink containing a volatile solvent, which evaporates rapidly after extrusion from a depository nozzle on a substrate [17]. Typically the ‘green’ structures generated after layer-by-layer or even freeform assembly are subject to post-processing steps to remove the sacrificial binder and sinter the metallic powders [19]. The ability to generate metallic structures without the incorporation of complex tools and high-powered lasers or electron beams, is what makes the SC-3DP method especially attractive. Xu et al [17] synthesized metallic structures combining metallic inks consisting of poly (lactic acid) (PLA), dichloromethane (DCM), and steel particles. Other metallic materials synthesized utilizing the SC-3DP include inks containing copper-thermoplastic organic binding agents [20], 316 L stainless steel- methacrylate-2-hydroxyethyl (HEMA) gelation systems [15] as well as steel-biodegradable polymers [21]. Despite the simplicity of the SC-3DP method, one of the most critical steps is the debinding or binder-removal step as carbon residues from the organic media can influence the metal sintering process and deteriorate the properties of the final product [19], which makes the identification of appropriate binders indispensable.

Herein, the SC-3DP method is extended to two different organic binder-metal pastes using a modified polymeric printer (MPP) setup, which allowed for facile paste extrusion with the help of a syringe pump and a plastic tube connecting the filament nozzle tip. The formulations comprised metallic powders dispersed in either a semi-solid saturated hydrocarbon paraffin or an alcohol-water-thickening agent based gel. The debinding behavior of the two formulations is compared with commercially available metal infused poly (lactic acid) (PLA) composite filaments. The effect of using metallic precursors in the nano or micron size range is also analyzed. The effects of thermal post-processing on the microstructure and composition of the final products are discussed.

2. Methodology

2.1. Fabrication of 3D printed metal/alloy specimens

2.1.1. Metal-binder formulations

The semi-solid saturated hydrocarbon paraffin, referred to as ‘paraffin’ henceforth, was used in a combination with Ti-6Al-4V (Ti-64) spherical metal powder in a gravimetric ratio of 1:4.1 (paraffin: Ti64) for adequate paste viscosity.

The alcohol-based gel, referred to as ‘gel’ henceforth, consisted of 29% deionized water, 70% ethanol, and 1% thickening agent (carbomer, glycercine and tri-isopropanolamine) by mass. The gel binder was used along with nanostructured Ni (<100 nm), Ni (5 μm), and Ti (45 μm) powders. The metal powders were mixed with the gel in gravimetric ratios varying from 0.3:1 to 1:1. All the aforementioned precursors were procured from Sigma-Aldrich (St Louis, Missouri, United States). The pastes were mixed using a Flacktek dual asymmetric speed mixer (Landrum, SC, United States).

Since PLA is a commonly used binder and can be easily acquired commercially, PLA infused with metallic filler was utilized to compare the debinding effect with the alcohol-based gel and paraffin binders. For comparative studies - steel-PLA, iron (Fe)-PLA, copper (Cu)-PLA, as well as the standard PLA, were procured from Protoplant, Inc. (Vancouver, WA, United States) and directly used as precursors for the filament 3D printing process.

2.1.2. 3D printing process

2.1.2.1. Metal-binder printing

For the paste printing process, a computer-aided design stereolithography (STL) file based on the shape and size of the Tensile Specimen E8 from the American Society of Testing and Materials (ASTM) was used. The sample
geometry was chosen based on the most common dimensions used for testing metals and alloys in tension. The G-code files were generated from the STL files using the open source Ultimaker Cura 3D printer slicing application (Ultimaker Corp., Geldermalsen, The Netherlands). Figure 1(a) depicts a schematic diagram of the modified polymer printer (MPP) setup - the metal-binder paste formulations were fed into an Ultimaker 3D printer using a plastic tubing that connected the syringe pump (Razel Model R-99) and the nozzle tip. A movable stage was used to adjust the pump height and provide facile paste flow under gravity. The flow rates for the syringe pump were kept between 20–40 cc · hr⁻¹. The most common parameters used for the printing process were layer height and wall thicknesses, each of 0.4 mm, and an infill density of 100% with both print and travel speeds set at 20 mm · s⁻¹. A thin layer of the material was deposited onto the build plate to form the outer layer wall followed by the inner part, as predefined by the G-code. The printer fan was turned on to dry the layers during the print process. After printing, the samples were placed in a desiccator overnight at room temperature, which allowed for any excess solvent evaporation. For the Ni–Ti powders, nozzle tips with internal diameter of 1.54 mm were used. The gel based formulations consisted of loose particles, which were thereafter subjected to thermal treatment. In the case of paraffin, the samples remained as a paste until the heat treatment was performed.

2.1.2.2. Commercial metal-infused polymer filament printing
To 3D print the commercial PLA-metal composites, the same software tools were utilized along with 1.75 mm filaments and a Monoprice printer (Rancho Cucamonga, CA, United States) operating between 200 °C–
215 °C. No syringe pump was used in this case since the raw material was directly fed as the filament. An infill density of 100% was used with the layer height and wall thickness, each set at 0.1 mm.

2.1.3. Thermal processing
The Ti-64-paraffin (1:1.4 gravimetric ratio) paste formulations were heat-treated in N2/O2 (80/20, v/v) or Ar/O2 (80/20, v/v) from room temperature to 550 °C followed by a hold time of 2 h. The choice of temperature stemmed from the thermal treatments carried out using simultaneous thermal analysis (STA) on the Ti-64 powders in N2 and N2/O2 atmospheres. The onset temperatures of oxidation and nitridization were determined as ~680 °C and ~850 °C, respectively, and therefore thermal treatment at 550 °C was considered appropriate to remove the paraffin binder without oxidizing or nitridizing the samples. Once the binder was removed, the samples were sintered at 1000 °C in inert atmospheres using a Lindberg Blue M furnace.

The gel binder in the Ni–Ti 3D printed samples evaporated at room temperature. However, to promote sintering among metallic particulates, the samples were either heated to 1000 °C in inert atmospheres using a Lindberg Blue M furnace at atmospheric pressure or thermally processed using hot isostatic pressing (HIP) in inert atmospheres. The HIP service was contracted with American Isostatic Presses, Inc. (AIP, Columbus, Ohio) where the AIP 6–45 H HIP system was used. The sample formulations were HIPed at 1000 °C for 3 h using either 20,000 or 25,000 psi. The temperature was chosen as 1000 °C based on other studies reporting non-additive manufacturing synthesis routes of NiTi alloys [22].

The commercial metal infused PLA samples were printed and then heat treated; the first part of the heat treatment was carried out in air atmosphere in order to burn off the polymeric component, whereas the second part was completed in argon as an attempt to sinter the remaining metal. The temperature employed to burn off the polymer was 300 °C. The second step of the thermal processing consisted of heating the sample to intermediate temperatures (530 °C in Ar) followed by a 2 h hold time and a final step of heating to 900 °C in Ar followed by an 8 h hold time.

2.2. Rheological measurements
In order to determine the viscosity and shear stress behavior of the gel based 3DP pastes, rheological measurements were carried out on different metal-gel mixtures using a Bohlin C-VOR Shear Rheometer. Nano- as well as micron-sized Ni powders were studied in conjunction to micron-sized Ti powders dispersed in the gel media. The tests were performed at room temperature over shear rates ranging from 0.1 to 1000 s⁻¹ with delay and integration times of 5 and 60 s, respectively.

2.3. Material characterization
Microstructural characterization on the samples was performed using a scanning electron microscope (Zeiss Neon 40 FE-SEM) equipped with an x-ray energy dispersive spectroscope (EDS, EDAX). Diffraction studies were carried out using x-ray diffraction (XRD) with a Rigaku Miniflex 600 x-ray Diffractometer with Cu-Kα radiation. Thermal analysis was carried out using a Netzsch STA 449 F3 Jupiter simultaneous thermogravimetric analysis (STA) capable of acquiring both the differential scanning calorimetry (DSC) and thermogravimetric (TG) data of the samples under investigation. Hardness tests were carried out using a Struers Durascan Vickers Microhardness tester.

3. Results and discussion

3.1. Paraffin-Ti64 formulations
The paraffin binder imposed challenges with effective paste delivery to the printer tubing owing to its high viscosity (640 poise at 25 °C). The semi-solid nature of the paraffin made homogeneous dispersion of metal particles very difficult, requiring multiple cycles in the asymmetric mixer to achieve homogeneity.

The printed and heated samples were very sensitive to the atmospheres that they were treated in. Figure 2(a) shows the microstructure of the Ti-64-paraffin treated under N2/O2; the formulation remained as loose particles. The EDS analysis of the sample showed that the surface of the particles contained traces of nitrogen, which could explain the inability of the particles to sinter. The nitridization of titanium is usually expected from treating Ti containing samples in N2 at high temperatures, where Ti7N6, is commonly found [23]. Despite the moderate temperatures (close to 0.4Tm) employed for the thermal treatment and the absence of nitrogen containing crystalline components (when analyzed by XRD), it is surmised that there was enough nitrogen on the surface to prevent effective mass transport between the particles. Small amounts of Al and V were also detected from EDS, which is attributed to the makeup of the Ti-64 alloy. No residues from the paraffin binder were found, which indicates that a combination of N2/O2 and the chosen temperatures led to clean debinding of the paraffin. However, the presence of nitrogen might affect the mechanical properties of the specimen. Similar
compositions have been reported for samples produced by direct metal laser sintering methods [24, 25]. In contrast, the Ti-64-paraffin sample treated in Ar/O₂ atmospheres (figure 2(b)) showed the successful generation of a ‘green’ specimen that maintained its shape after the debinding step and did not contain residues. However, given the complications encountered during the mixing and printing steps, other binders with lower viscosities were investigated for facile sample fabrication.

3.2. Gel/Ni–Ti samples
As mentioned previously, 99% of the gel employed in the study contained water and ethanol with the remaining 1% consisting of a carbomer based thickening agent. Carbomers are polymers derived from acrylic acid, and are commonly used to suspend solids into liquids and control the flow and consistency of pharmaceutical products. The gel binder was selected due to its viscosity (10–170 poise at 25 °C) and its ease to evaporate at temperatures close to ambient conditions, thus avoiding debinding steps at higher temperatures that could promote oxidation or nitridization of the printed samples.

The samples containing gel and Ni nanoparticles suffered a phase separation during the speed mixing process, resulting in fluidic media with viscosity close to that of water (0.01 poise) and solid components that precipitated on the mixing container. The nanoparticles (initially sought after for their high reactivity) when mixed with the gel binder, formed shear thinning substances that complicated the printing process. When force was applied to the syringe pump, the gel became more fluid-like and deposited before the metal particulates, thereby either clogging the nozzle or producing high inhomogeneous 3D printed patterns. In contrast, the gel mixtures made with micron-sized Ni particles provided adequate viscosity for the 3DP process.

The viscosity versus shear rate behavior of the samples containing only gel, gel + Ni (5 μm) + Ti (45 μm), and gel + Ni (nano) + Ti (45 μm) has been depicted in figure 3(a). All the samples showed an initial steady decline in the viscosity with increasing shear rates. However, at about a rate of 19 s⁻¹, the viscosity of the sample containing nickel nanoparticles rapidly decreased from ~10 to ~0.005 Pa·s. Figure 3(b) illustrates shear stress as a function of the applied shear rate for the same samples. The sample containing only micron sized particles depicted a positive linear trend in the shear stress with increasing shear rates, which corresponds to a Newtonian fluid behavior. In contrast, the sample containing Ni nanoparticles exhibited an initial increase in shear stress but at a shear rate of 16 s⁻¹, the stress decreased dramatically. Both the viscosity as well as shear stress behaviors of the mixture containing nano-Ni were similar to those of non-Newtonian fluids. Shear thinning behavior of nickel nanoparticles in α-terpineol liquids and polymeric surfactants has also been reported in other studies [26]. Based on the rheological analyses, the micron-sized Ni particles were identified as appropriate precursors and utilized for the 3D printing and thermal processing.

The 3D printed NiTi samples were sintered at 1000 °C either in a tube furnace at atmospheric pressure or using a hot isostatic press (HIP) at pressures of 20,000 and 25,000 psi. The Ni–Ti sample HIPed at 25,000 psi exhibited lower porosity than both the sample treated at atmospheric pressure as well as the sample HIPed at 20,000 psi. Vickers hardness of 558 ± 32 was measured for the sample treated at 25,000 psi, which is within 10% of other reports on Ni–Ti alloys [27]. The SEM observations for the 3D printed Ni–Ti sample in the secondary (SE) and backscattered electron (BSE) modes are shown in figures 4(a) and (b), respectively. The microstructure consisted of alternating dark and light lamellar phases. The XRD spectra from the printed Ni–Ti-gel mixture and the mounted and polished HIPed Ni–Ti sample are shown in figure 4(c). The gel binder evaporated cleanly from the Ni–Ti mixture without leaving any residual crystalline impurities; the sharp distinct peaks observed in the diffraction pattern were attributed to the Ni (JCPDS card no. 01–078–7533) and Ti (JCPDS card no. 01–089–
For the HIPed and mounted Ni–Ti sample, peaks from NiTi (B2 phase—JCPDS card no. 01–076–3614), NiTi (B19' phase—JCPDS card no. 01–078–2546) and Ti2Ni (JCPDS card no. 00–018–0898) were identified in addition to the parent Ni and Ti. The formation of intermetallic compounds such as Ti2Ni, Ni3Ti, Ni4Ti3, and Ni3Ti2 in addition to NiTi phases has been reported with the use of Ni and Ti elemental powders [28–34].

The EDX analysis corresponding to the sample region (figure 5(a)) confirmed atomic percentages of 57% Ti and 43% Ni (figure 5(b)) approximately. Point elemental characterization performed on the darker phase revealed ~55–58 at% Ti and ~42–45 at% Ni, identified as Ti2Ni whereas the lighter phase comprised 48–50 at% Ni and 50–52 at% Ti, identified as NiTi [27]. The difference in the contrast between the two phases is attributed to the higher atomic number of Ni, which is also confirmed from compositional BSD image shown in figure 4(b). The compositions were near equiatomic indicating the presence of both NiTi and Ti2Ni phases, as inferred from the Ni–Ti phase diagram [28]. The elemental maps shown in figures 5(c) and (d) confirmed that the lighter phase (NiTi) corresponded to a stronger Ni signal, whereas the darker phase (Ti2Ni) corresponded to a stronger Ti signal.
As noted by other authors, the annealing temperatures and times can greatly influence the microstructure, and thereby affect the mechanical and shape memory properties of the resultant alloy [27–34]. The driving force for the shape memory effect has been linked to a transformation between the austenitic and martensitic phases [11]. However, given that the scope of this work is the raw material and conditions necessary to 3D print pastes in order to generate NiTi alloys, the discussion is limited to the fact that the presence of the phases including NiTi, Ti2Ni and other intermetallics was confirmed by SEM and XRD analyses.

3.3. 3D printed commercial metal-filled polymer composites

The only challenges encountered while 3D printing the commercial metal-infused PLA filaments were mostly related to the printer requiring higher temperatures (215 °C versus 200 °C for bare PLA), which caused the polymer to lose viscosity and clog the nozzle occasionally. The printed ‘green’ specimens retained the desired size and shape after cooling to room temperatures. Figure S1 is available online at stacks.iop.org/MRX/6/106561/mmedia shows the strain–strain curves of the 3D printed tensile bars using the metal-infused PLA filaments. Thermal treatments were performed on the samples to study the debinding behavior of the polymeric media and its effect on the metal particulate sintering. Of the different fillers investigated, Cu was selected to exemplify the microstructural features encountered during the experimental steps. Multiple STA experiments were conducted to determine the optimal temperatures, atmospheres and dwell times needed to remove the binder while maintaining the chemical composition of each metal. Attempts to burn off the polymer using air or oxygen atmospheres at low temperatures (between 200 °C–400 °C) in order to convert organic components into CO2 and H2O, followed by higher temperature treatments (600 °C–1200 °C) in Ar, rendered partially oxidized metal particulates (figure 6(a)). The external layer of the metal particles oxidized, thereby preventing effective sintering (figure 6(a) inset). Diverse temperature profiles with initial oxidizing atmospheres followed by inert or reducing atmospheres were tested. However, none of the samples produced a completely reduced metal/alloy.

4. Conclusions

A simple paste-based method for facile 3D printing of metallic materials utilizing a modified polymeric printer (MPP) was successfully demonstrated. The technique consisted of layer-by-layer metal-binder paste deposition

Figure 5. SEM (secondary electron) image of the sample region where the EDS analysis was performed; (d) the corresponding EDS spectrum and quantitative composition; (c) elemental maps corresponding to Ni and (d) Ti.
based on a CAD file followed by a post-deposition thermal treatment step. The study evaluated three different precursor formulations including (i) paraffin binder mixed with Ti64 alloy powders, (ii) alcohol based gel with Ni (micro and nano-sized) and Ti powders aimed to produce NiTi alloys and (iii) commercially available metal infused polymer composites. The polymer and paraffin binders were found to be ineffectual as they resulted in excessive complications during the printing step either due to the binder viscosity or residual unwanted by-products during the thermal processing and sintering steps. The alcohol-based gel was identified as the most effective medium for the 3DP process as it evaporated cleanly without altering the sample composition. Micro-sized Ni particles imparted adequate viscosity for facile 3DP paste flow in contrast with Ni nanoparticles, which behaved as shear thinning agents. Upon identifying the best suitable gel-Ni–Ti paste formulations, the 3D printed samples were thermally treated using hot isostatic pressing. Microstructural and x-ray spectroscopic measurements carried out on the 3DP Ni–Ti specimens revealed an average atomic composition in the vicinity of 43% Ni and 57% Ti, which could be particularly useful for functional properties such as superelasticity and shape memory effects. The presented method is anticipated to open avenues for alternatives to 3D print small metallic parts when the location or budget constraints cannot accommodate the use of larger metal printing systems, and where the application allows for flexibility in the tolerance of mechanical properties.

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References

[1] Uhlmann E, Kersting R, Klein T B, Cruz M F and Borille A V 2015 Additive manufacturing of titanium alloy for aircraft components Proc. CIRP 35 55–60
[2] Edwards P, O’connor A and Ramulu M 2013 Electron beam additive manufacturing of titanium components: properties and performance J. Manuf. Sci. Eng. 135 061016
[3] Froes F H and Dutta B 2014 The additive manufacturing (AM) of titanium alloys Advanced Materials Research Vol 1019 (Switzerland : Trans Tech Publications) pp 19–25
[4] Li Y and Gu D 2014 Parametric analysis of thermal behavior during selective laser melting additive manufacturing of aluminum alloy powder Mater. Des. 63 856–67
[5] Buchbinder D, Schleifenbaum H B, Heidrich S, Meiners W and Bültmann J 2011 High power selective laser melting (HP SLM) of aluminum parts Phys. Proc. 12 271–8
[6] Brice C, Shenor Y, Kral M and Buchanan K 2015 Precipitation behavior of aluminum alloy 2139 fabricated using additive manufacturing Materials Science and Engineering: A 648 9–14
[7] Nie P, Ojo O A and Li Z 2014 Numerical modeling of microstructure evolution during laser additive manufacturing of a nickel-based superalloy Acta Mater. 77 85–95
[8] Denlinger E R, Heigel J C, Michaleris P and Palmer T A 2015 Effect of inter-layer dwell time on distortion and residual stress in additive manufacturing of titanium and nickel alloys J. Mater. Process. Technol. 215 123–31
[9] Islam M, Purtonen T, Piihi H, Salminen A and Nyrhälä O 2013 Temperature profile and imaging analysis of laser additive manufacturing of stainless steel Phys. Proc. 41 835–42

[10] Wang Z, Palmer T A and Beese A M 2016 Effect of processing parameters on microstructure and tensile properties of austenitic stainless steel 304L made by directed energy deposition additive manufacturing Acta Mater. 110 226–35

[11] Elahinia M, Moghaddam N S, Andani M T, Amerinatanz M, Bimber B A and Hamilton R F 2016 Fabrication of NiTi through additive manufacturing: a review Prog. Mater. Sci. 83 630–63

[12] Ngo T D, Kashani A, Imbalzano G, Nguyen K T and Hui D 2018 Additive manufacturing (3D printing): a review of materials, methods, applications and challenges Composites Part B: Engineering 143 172–96

[13] Sharma N, Jiang K K and Raj T 2018 Fabrication of NiTi alloy: a review Proc. Inst. Mech. Eng. Part I: J. Mater. Des. Appl. 232 250–69

[14] Gu D 2015 Laser additive manufacturing (AM): classification, processing philosophy, and metallurgical mechanisms Laser Additive Manufacturing of High-Performance Materials 15–71 (Berlin, Heidelberg: Springer)

[15] Ren X, Shao H, Lin T and Zheng H 2016 3D gel printing—an additive manufacturing method for producing complex shape parts Mater. Des. 101 80–7

[16] Agrawal R and Wang C 2016 Laser beam machining ed B Bhushan Encyclopedia of Nanotechnology. (Dordrecht: Springer)

[17] Xu C, Bouchemti A, L’Espérance G, Lebel L L and Therriault D 2017 Solvent cast-based metal 3D printing and secondary metallic infiltration Journal of Materials Chemistry C 5 10448–55

[18] Ahn B Y, Shoji D, Hansen C J, Hong E, Dunand D C and Lewis J A 2010 Printed origami structures Adv. Mater. 22 2251–4

[19] Gonzalez-Gutierrez J, Cano S, Schuschnigg S, Kukla C, Sapkota J and Holzer C 2018 Additive manufacturing of metallic and ceramic components by the material extrusion of highly-filled polymers: a review and future perspectives Materials 11 840

[20] Ren L, Zhou X, Song Z, Zhao C, Liu Q, Xue J and Li X 2017 Process parameter optimization of extrusion-based 3D metal printing utilizing PW–LDPE–SA binder system Materials 10 305

[21] Xu C, Wu Q, L’Espérance G, Lebel L L and Therriault D 2018 Environment-friendly and reusable ink for 3D printing of metallic structures Mater. Des. 160 262–9

[22] Bram M, Ahmad-Khanlou A, Heckmann A, Fuchs B, Buchkremer H P and Stöver D 2002 Powder metallurgical fabrication processes for NiTi shape memory alloy parts Materials Science and Engineering: A 337 254–63

[23] Marchand C, Maître A, Grimaud A, Denoirjean A and Lefort P 2006 Nitridation of Ti Surf. Coat. Technol. 201 1988–94

[24] Abboud J H, Fidel A F and Benyounis K Y 2008 Surface nitriding of Ti Materials Science and Engineering: A 460 405–14

[25] Renishaw Plc, ‘White paper: investigating the effects of multiple powder re-use in AM: additive manufacturing titanium Ti6Al4V alloy AM250 ageing study.’

[26] Tseng W J and Chen C N 2006 Dispersion and rheology of nickel nanoparticle inks J. Mater. Sci. 41 1213–9

[27] Abioye T E, Farayibi P K, Kinnel P and Clare A T 2015 Functionally graded Ni–Ti microstructures synthesised in process by direct laser metal deposition The International Journal of Advanced Manufacturing Technology 79 843–50

[28] Sina H, Iyengar S and Melin S 2012 Sintering and reaction behaviour in Ni–Ti powder mixtures 2012 Int. Conf. on Powder Metallurgy & Particulate Materials Vol 5, pp05–57 (Metal Powder Industries Federation, Princeton, New Jersey)

[29] Swan B K, Bajpai S and Behera A 2019 Microstructural evolution of NiTiNiOL and their species formed by atmospheric plasma spraying Surface Topography: Metrology and Properties 7 015006

[30] Li B Y, Rong J J and Li Y Y 1998 Porous NiTi alloy prepared from elemental powder sintering J. Mater. Res. 13 2847–51

[31] Berthelot B, Neudenberger M and Bidaux J E 2004 Powder sintering and shape-memory behaviour of NiTi compacts synthesized from Ni and TiH agents Materials Science and Engineering: A 384 143–50

[32] Li B Y, Rong J J and Li Y Y 2000 Stress–strain behavior of porous Ni–Ti shape memory intermetallics synthesized from powder sintering Intermetallics 8 643–6

[33] Greiner C, Oppenheimer SM and Dunand DC 2005 High strength, low stiffness, porous NiTi with superelastic properties Acta Biomater. 1 705–16

[34] Bassani P, Panseri S, Ruffini A, Montesi M, Ghetti M, Zanotti C, Tampieri A and Tuissi A 2014 Porous NiTi shape memory alloys produced by SHS: microstructure and biocompatibility in comparison with Ti2Ni and TiNi J. Mater. Sci., Mater. Med. 25 2277–85