LEHIGH
UNIVERSITY

Lehigh University
Department of Materials Science and Engineering

Whitaker Laboratory
5 East Packer Avenue
Bethlehem, PA 18015

Die-Less MIM-style Additive Manufacturing with Controlled Porosity: A Proof of Concept

A proof of concept submitted to:

The Clayton Family Scholarship Fund
for Studies in Powder Metallurgy

Lehigh University

27 Memorial Dr W, Bethlehem, PA 18015

Jack Edgerton
Lehigh University
June 1, 2015

Abstract

Current manufacturing methods for orthopedic implants produce parts that have much greater elastic moduli than natural bone. This study was done to determine the viability of a new method of producing implants with controlled porosity using recently developed additive manufacturing technology with a metal injection molding feedstock in combination with a space holder to provide porosity. While the final piece of printing equipment is under development, a basic proof of concept was done to provide a way of testing the process. Three separate feedstocks of RYER Cu MIM mixed with 30, 40, and 50 volume percent NaCl spaceholder. The samples underwent debinding, spaceholder removal, and sintering before being examined using standard light optical microscopy. The samples were analysed for porosity content using ImageJ, and showed an increase in porosity with an increase in space holder content. The overall basic test of the process was successful, however further steps are needed for the compete proof of concept of the project.

Project Significance

The principal purpose of the project is to determine a viable method of manufacturing inorganic medical implants with controlled porosity through additive manufacturing. By introducing controlled porosity into medical implants, one would be able to tailor the part to the age of the patient, as well as improving fit through osseointegration [Barbosa et al.]. Osseointegration is when there is bone growth integrated within the implant. This creates improved mechanical interlocking between the bone and the implant, therefore making a better "fit" for the patient. Osseointegration is facilitated through open porosity or an interconnected network of pores [Barbosa et. al].

The primary significance of the porosity of the implant is to reduce or eliminate the risk of stress-shielding. Stress shielding is when the normal stresses on bones in contact with an implant are lowered or removed completely due to a mismatch of stiffness of the implant and surrounding bone structure. When implants are made with full density by typical manufacturing methods, the strength and elastic modulus of the part are much higher than that of natural bone. Titanium, a commonly used metal in implants, has an elastic modulus of 110 GPa at full density, whereas cortical bone has an elastic modulus typically ranging from 20-30 GPa [Torres et al]. This large discrepancy of stiffnesses between the implant and surrounding bones can cause bone density loss, which is obviously disadvantageous to the patient [mediLexicon]. Given that bone density varies with age, as well as the particular bone itself, the ability to control porosity and therefore elastic modulus could have a large, positive impact on the biomedical world. Correctly matching the modulus of an implant with the

modulus of bones in contact could potentially eliminate stress shielding completely. Through removing stress shielding, the implants would have a prolonged fit in the patient and would have much less of an effect on the surrounding bone structure.

The significance of using additive manufacturing is the ability to custom manufacture parts to the fit of the consumer without having to make special tooling or dies for the individual. This could improve the fit for the patient, as well as greatly reduce the time needed to manufacture the part. Furthermore, there is the possibility of making parts with a gradient of porosity to mimic two-part bone structure (cortical/trabecular bone), resulting in more natural mechanical behavior.

Material selection

This project will use a metal injection molding (MIM) feedstock. MIM feedstock consists of a metal powder held together by a polymer binder system that is removable from the part before or during sintering. This allows one to form freestanding green bodies that have enough strength to maintain geometry while sintering. One benefit of using a MIM feedstock is that it possible to change the powder metal in the feedstock, while using the same binder system without greatly changing how the feedstock behaves during printing. To clarify, sintering temperatures, times, and behavior will obviously change with a change in metal powder, however operating temperatures for printing will remain the same. This allows for using a MIM feedstock with a material like copper for the proof of concept portion of the project. Copper is not biocompatible, but is much less expensive. In the future, if this project develops past proof

of concept, a titanium alloy will likely be used because of its biocompatibility and high strength-to-weight ratio.

Copper was chosen as the powder metal of choice because of availability and price from local suppliers. For the initial stage of the project, a premade MIM feedstock was used. The feedstock is a RYER MIM feedstock with gas atomized Cu powder metal with spherical particles and a size distribution of 80 to 22 μm. The spherical particle shape was chosen because it has a higher tap density, which leads to improved MIM processing, as well as improved flow [Handbook of Metal Injection Molding]. This product was chosen based off of pricing, availability, and the potential simple switch to a Ti feedstock later on. The feedstock uses a SolvMIM, a proprietary binder system used by RYER in combination wish several different metal powders, including titanium. Assuming RYER maintains production of its SolvMIM feedstocks, it would be possible to simply replace the Cu feedstock with the Ti SolvMIM feedstock produced by RYER without needing to change the 'printing' processing parameters.

Outside of purchasing a MIM feedstock, there was some experimentation with mixing up a feedstock "in house". The feedstock consisted of copper metal powder and a polymer binder system. The requirements for the binder system were as follows: it had to have a low melting temperature and quickly solidify, at least 4 MPa in strength at room temperature for the strength of the green bodies, a low viscosity and good fluidity at molding temperature, must be chemically passive, easily removable while leaving little impurities, and commercially available while still being affordable [Wen et al.]. The binder system chosen was a simple three-component binder system. It consisted of a polymer "backbone" that provided most of the green strength, a wax component for improved flow, and a small amount of a third

component used for lubrication [Wen et al.]. High-density polyethylene was chosen for the "backbone", paraffin wax was chosen as the wax component, and a small amount of stearic acid was chosen for adding lubrication. The main reasons for choosing this binder system were simplicity and relatively low cost, as well as this is a commonly used binder system in other MIM studies.

While it would be ideal to be able to tailor the viscosity and strength properties to best fit this process by making the feedstock in house, this proved to be a difficult and time consuming process. For the sake of this simplicity during proof of concept, the premade RYER MIM feedstock was chosen to be used first. If the commercial feedstock does not fit for this application, making a feedstock may be the next step.

Homogeneity within the feedstock is highly important for the performance of manufacturing the part. If the feedstock is not fully mixed, poor flow behavior will likely occur which leads to difficulty with dimensional stability of the part [Wen et al.]. Additionally, well mixed feedstock will provide a more even distribution of porosity from the space holder. For homogenization, all components of the feedstock will be put into a heat bath with a mechanical mixer. Regardless if it is a premade feedstock or not, the feedstock will still need the addition of the space holder, after which the feedstock will require homogenization.

Process Selection

The equipment chosen for the project is a Hyrel 3D System 30 additive manufacturing system. Hyrel is very new to the market, but was chosen because they offer a special extrusion nozzle, the EMO-25. This extrusion nozzle is distinctive in that it does not feed filament into the

nozzle but instead uses a cartridge with ejection driven by a mechanical plunger. This allows for using a MIM feedstock, without needing to extrude the feedstock into 3mm filament first. Producing MIM filament that would work with the typical fusion deposition modeling style printer would be very difficult and time consuming, if at all possible. The primary issue that arises with the EMO-25 is that it was not designed to operate at the high temperatures required for extruding the MIM feedstock (about 200 °C). However it is unique to the additive manufacturing market and there are no better available options. Therefore, before the printing system will be of use in this project, the extrusion nozzle must be modified so that it can operate at the temperature needed for this application. Beyond the EMO-25, the Hyrel 3D System 30 has the capability of operating multiple extruders simultaneously. This would allow for simultaneously printing with two separate feedstocks with different amounts of space holder, to mimic the porosity levels (or stiffness values) of both cortical and trabecular bone in one part.

As previously stated, MIM feedstock consists of a powder metal bound together using a polymer binder system. This polymer binder must be removed from the part after it is formed. Removal of the binder through burnout is possible, however it is relatively inefficient and will leave impurities in the part. To solve this issue, the part will be immersed in n-hexane for 24 hours to remove majority of the primary binder from the part. The residual binder content can be removed by burnout prior to sintering and after desalination, which is explained below.

The chosen method for creating porosity in the part was to use a space holder technique. The idea behind using a space holder is introducing a material in particle form into the feedstock that can be removed after printing that will leave macrovoids in its place [Engin et al.]

The two typical types of space holders that have been used in MIM research in the past are salts and polymers. When using a polymer space holder, the space holder must be removed through heat treatment. The main issue with using this method is that burning off the polymer space holder from the sample leaves large amounts of interstitial carbon and oxygen, which results in higher amounts of internal oxidation. NaCl powder was chosen for the space holder because it can be removed by immersing the part in water [Torres et al.]. This eliminates the issue of adding impurities to the part from burn off of the space holder. Salt removal can be expedited using ultrasonic vibratory equipment or through heating the water to increase solubility.

There will be porosity that naturally occurs through this process that was not caused by the space holders. Microporosity will occur from incomplete sintering of metal particles; microvoids will form from binder removal as well. These pores will be of much smaller size and will have a very small degree of interconnectivity, if any. This microporosity will be largely uncontrolled, will contribute much less, if anything, to driving down the elastic modulus, and will not provide the ability for osseointegration [CHEN et al.]. Therefore, macroporosity is necessary, and the microporosity can largely be ignored for this project.

For the sake of simplicity, and because the metal powder will change after the proof of concept, the effects of varying the heat treatment will be examined minimally. A simple sintering and heat treatment process determined from copper metal injection molding research and recommendations by the feedstock manufacturer will be used. After debinding and desalination, the part will be sintered at 1000 °C for 90 minutes. The furnace will have an argon atmosphere to reduce oxidation [N. Tuncer et al.].

At this stage of the process, Hyrel is currently developing a custom extruder similar to the EMO-25 with a heating element so it can be used at the necessary elevated temperature (170-200 °C) for the MIM feedstock. During this time, a base characterization was done to test the effects of the space holder content on porosity. Additionally this was a way to test the mixing and heat treatment processes, and give a base characterization of the entire process.

Process Characterization

Three separate feedstocks were mixed together using varying volume percentages of space holder content for determining the effects of space holder content on porosity. Table 1 below has the compositions listed for the three feedstocks.

Table 1: Feedstock compositions by weight and volume

	Composition by Volume	**MIM Feedstock Content**	**Space Holder Content**
Feedstock 1	70 vol% FS, 30 vol% NaCl	142.6 g	19.33g
Feedstock 2	60 vol% FS, 40 vol% NaCl	140.95 g	42.82g
Feedstock 3	50 vol% FS, 50 vol% NaCl	137.94 g	64.99g

The feedstocks were prepared by mixing the RYER MIM feedstock with salt in a heated jar monitored with a thermocouple. The jars were heated to 185 °C, which allowed for the viscosity to drop low enough for mixing without burning off any of the binder. Several samples of each feedstock were made to ensure that similarly sized samples would be available for the three feedstocks. By using similar sized samples, there would more uniformity in binder removal as well as sintering across the three samples. Samples were created by 'scooping' the heated feedstock and letting it flow into free-formed small ellipsoid shaped samples. This was the simplest way to mimic the additive manufacturing application.

After the samples were made, they were first debinded through immersion in n-hexane for 24 hours. This removed majority of the primary binder to avoid having high amounts of impurities in the samples from a thermal burnout. The secondary binder component of the SolvMIM binder remains behind, which provides green strength needed to handle the part before sintering. The secondary binder was removed thermally during the heat treatment process. After debinding, the samples were immersed in water and placed in an ultrasonic vibratory apparatus for removal of the salt placeholder. The samples were then sintered in an argon atmosphere controlled furnace. The argon atmosphere was used to limit the amount of oxidation within the samples. The sintering profile can be seen in Table 2 and Figure 1 below. This sintering profile was designed based off of the recommendations of the manufacturer and the constraints of the furnace. After the samples were sintered, they were mounted, ground, and polished using standard metallographic procedures.

Table 2: Sintering Profile

Command	Temp (°C)	Ramp Rate (°C/min)	Step Time (min)	Elapsed Time (min)
Ramp	275	15	30	30
Dwell	275		78	108
Ramp	700	10	96	204
Dwell	700		48	252
Ramp	1000	10	30	282
Dwell	1000		90	372
Ramp	100	8	150	522

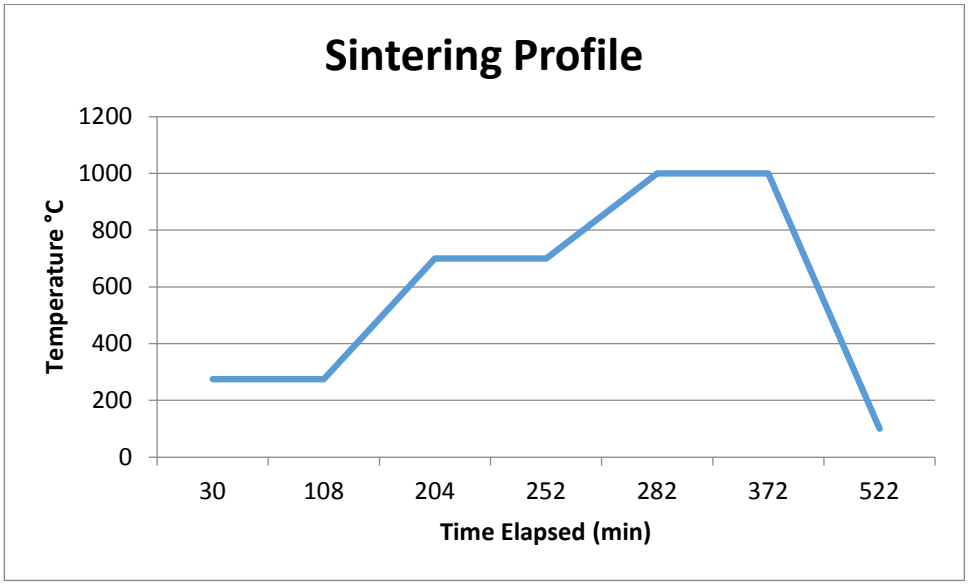

Figure 1: Temp vs time graph of sintering profile

Results and Discussion

Micrographs of samples 1, 2, and 3 can be seen in Figures 2, 3, and 4 respectively below. The sintering profile appeared to be successful with the exception of some incomplete sintering in sample 3 which can be seen in the bottom left corner of Figure 3. This was most likely due to sample 3 having a greater wall thickness than samples 1 and 2. The samples are black on the surface most likely from the burnout of remaining primary binder. Table 3 shows the weight of the samples before and after debinding. The debinding process theoretically was supposed to remove 3.5% of the weight of the green body in primary binder content. However the weight change averaged to be about 3% meaning there was residual primary binder that was burned off. Additional time in the n-hexane is likely needed.

Table 3: Before and after debinding weights

Sample	Pre Debinding Weight (g)	Post Debinding Weight (g)
1	20.927	20.428
2	18.689	18.128
3	10.208	9.98

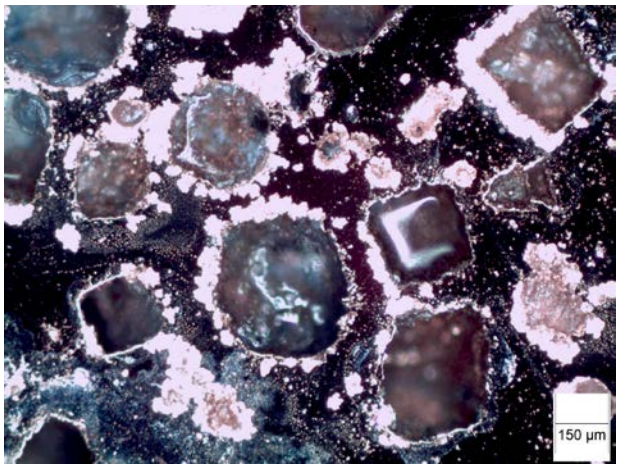

Figure 2: Micrograph of sample 1 (feedstock 1)

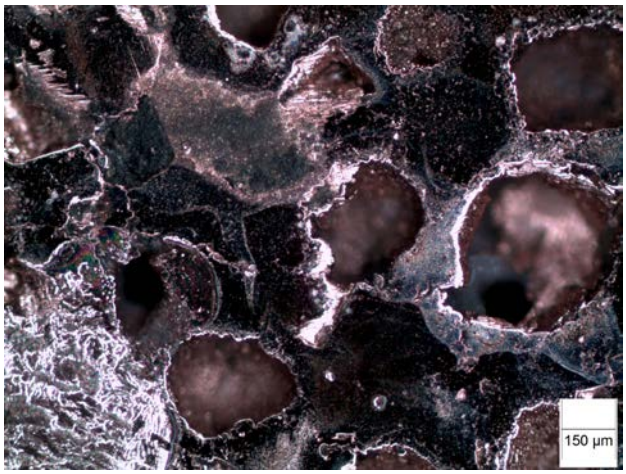

Figure 3: Micrograph of sample 2 (feedstock 2)

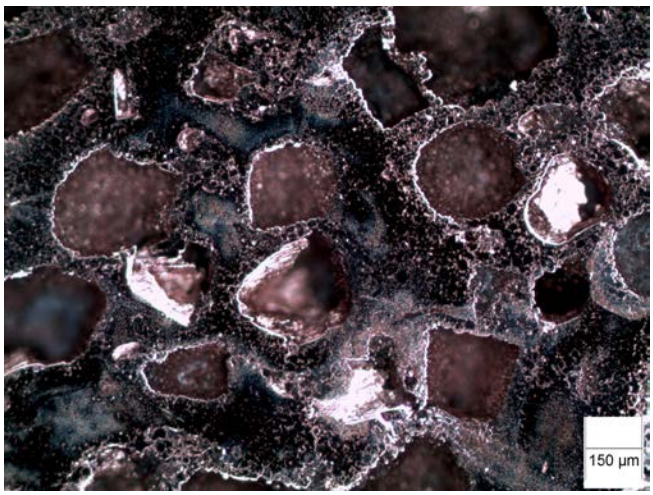

Figure 4: Micrograph of sample 3 (feedstock 3)

ImageJ analysis was done on five separate micrographs of each sample to determine area fraction of porosity. The data results from which can be found in Table 4 below.

Table 4: Average area fraction of porosity determined by ImageJ software

Sample	Average Area Fraction Porosity
1	25.52%
2	32.14%
3	34.48%

The results show an increase in porosity content with increase in space holder content, successfully showing the space holder technique's potential within this process for controlling volume porosity content. However, the results were not perfect. The increase in porosity with increasing space holder content was not linear. ImageJ had a was unable to identify the pores using a color threshold due to the dark surface of the samples, so the pores were manually traced in ImageJ. Tracing the pores manually likely lead to less accurate results. The area porosity numbers could be improved upon by using more images of each sample, or using a completely different method. Once it is possible to print out specific geometries using the Hyrel system, it may be possible to use the Archimedes method for determining porosity. The Archimedes method could also give the percentage of open porosity content, which is another important metric for success of the process. Open porosity as previously stated is what provides the ability for osseointegration.

Next Steps and Conclusions

Overall the characterization of the process was successful. Samples were made with incremental increases space holder content, which resulted in higher amounts of porosity with increased amounts of space holder content. The sintering profile was successful, longer dwell times at 1000 °C may be necessary if samples are made with greater wall thicknesses. The debinding process can be improved upon. At the minimum, a greater amount of immersion time in n-hexane is needed. It is also possible to heat the n-hexane to improve debinding efficiency, as stated by RYER. Upon receiving the custom heated EMO-25 extruder, further characterization and proof of concept will be possible. The first step would be to test printing basic geometries using the feedstock. It may be necessary for measuring rheology of the feedstock to determine the precise operating temperature to achieve the correct viscosity during printing. The optimal viscosity could be determined through rheology of existing fused deposition modeling materials such as ABS or PLA at their operating temperatures. After the precise printing operating temperature was determined, the next step would be to print cylindrical samples of varying porosity content for compression testing to determine the effect of the porosity on stiffness and compressive strength.

References

- Barbosa, Ana Paula Cysne, Martin Bram, Detlev Stöver, and Hans Peter Buchkremer. "Realization of a Titanium Spinal Implant with a Gradient in Porosity by 2-Component-Metal Injection Moulding." *Advanced Engineering Materials* 15.6 (2013): 510-21. Web.

- Tuncer, Nihan, Martin Bram, Alexander Laptev, Tilmann Beck, Alexander Moser, and Hans Peter Buchkremer. "Study of Metal Injection Molding of Highly Porous Titanium by Physical Modeling and Direct Experiments." *Journal of Materials Processing Technology* 214.7 (2014): 1352-360. Web.

- Torres, Yadir, Sheila Lascano, Jorge Bris, Juan Pavón, and José A. Rodriguez. "Development of Porous Titanium for Biomedical Applications: A Comparison between Loose Sintering and Space-holder Techniques." *Materials Science and Engineering: C* 37 (2014): 148-55. Web.

- Chen, Liang-Jian, Ting Li, Yi-Min Li, Hao He, and You-Hua Hu. "Porous Titanium Implants Fabricated by Metal Injection Molding." *Transactions of Nonferrous Metals Society of China* 19.5 (2009): 1174-179. Web.

- Engin, Gülsah, Bülent Aydemir, and H. Özkan Gülsoy. "Injection Molding of Micro-porous Titanium Alloy with Space Holder Technique." *Rare Metals* 30.6 (2011): 565-71. Web.

- Wen, Guian, Peng Cao, Brian Gabbitas, Deliang Zhang, and Neil Edmonds. "Development and Design of Binder Systems for Titanium Metal Injection Molding: An Overview." *Metallurgical and Materials Transactions A* 44.3 (2013): 1530-547. Web.

- "Definition: 'Stress Shielding'" *MediLexicon*. Stedman's Medical Dictionary, n.d. Web. 16 Dec. 2014.

- "Metal Injection Molding (MIM) of Thermal Management Materials in Microelectronics." *Handbook of Metal Injection Molding*. Ed. Donald F. Heaney. 1st ed. Cambridge, UK: Woodhead, 2012. 451-52. Print.