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Open pore Titanium Foams via Metal Injection Molding of Metal Powder with a Space Holder

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Abstract

Powder methods are highly applicable for the processing of more challenging metals and forms. Examples of materials that encompass both of these are metallic foams, which are advanced materials that consist of a network of interconnected or randomly spaced macropores separated by dense or microporous cell walls. These macropores can be either open or closed, or mix of those two, depending on the manufacturing process. One popular metal foam that has received a huge amount of interest in the last decade is Ti foam, due to it offering a unique combination of properties, such as high strength to weight ratio and high permeability combined with excellent biocompatibility. In this study the use of metal injection molding of titanium powder in combination with a space holder (to create large pore spaces) is examined for the production of open pore Ti foams for biomedical applications. Potassium chloride with two different particle shapes (spherical and cubic) was used as a space holder. It was found that feedstocks prepared with spherical KCl particles had a lower viscosity and better flowability compared to those made using cubic particles. Ti foams with a total porosity of $61.25\% \pm 0.29$ were successfully produced. The structure of the foams produced was characterized using SEM and X-ray Micro-Computed Tomography.

Keywords:

Metal Injection Molding, Titanium powder, Foam, Micro-CT, Pores, Dental Implants

Introduction

Titanium foams are materials with reduced density, high specific strength and stiffness, good biocompatibility and excellent corrosion resistance [1]. These characteristics make them perfect candidates for bone substitute in biomedical implants, where the properties of these foams can be tailored depending on the amount of porosity introduced to match that of the surrounding tissue or bone, thus avoiding the stress shielding problem. This phenomenon results from the non-uniform partitioning of load between the implant and the surrounding tissue or bone and is one of the major causes of failure in implants [2]. This inhomogeneity in load transfer occurs due to the large difference between the elastic moduli of the dense implant and the surrounding tissue or bone, where the dense material of the implant carries stresses without transmitting them into the bone, thus shielding it and leading to its disintegration in the body environment. The presence of pores in the structure of the foams can solve this and also promote bone ingrowth as well as cell attachment and consequently, improve the osseointegration of these implants [3]. Although the optimum size of pores for bone ingrowth is still under debate, several studies reported that the ideal size range is about 100-400 μm [4-6]. Almost all production processes for titanium foams use metal powder. These include the impregnation of polymer foams [7], Gel casting [8], freeze

casting [9], slip casting [10] as well the space holder technique [11-13] with all of these the challenge is to control the process to achieve the desired structure, retaining porosity, while obtaining good integration of the powder for good mechanical properties . The first four techniques are relatively slow processes and need a long processing times resulting in low output in comparison with other foaming techniques, such as the space holder technique (i.e. press and sinter powders with a removable phase that makes the pores). Hence, many scholars have intensively investigated the use of the powder metallurgy with space holder technique for the production of Ti foams [12, 14]. However, there are several challenges associated with such method that are yet to be solved; for instance the breakage and deformation of the space holder particles due to the high pressure applied (which leads to deformed pores), and the segregation of powders due to differences in densities[1, 15]. One advanced powder processing technique with the potential to address these aforementioned issues, as well as offering the possibility of mass producing near net shaped Ti foams is Metal Injection Molding in combination with a Space Holder (MIM-SH). The space holder is a removable phase that acts to retain controlled porosity. In this study, the use of MIM-SH will be investigated to produce porous Ti parts with the aim of meeting the optimum pore size range for biomedical implants. In addition, the structure of the foam will be investigated via Scanning Electron Microscopy as well as micro-Computed Tomography (micro-CT).

2. Materials and Methods

2.1. Starting Materials and feedstock preparation

Spherical Ti powder with mean particle size of 74.9 μm was used (Arcam AB, Sweden) as a raw material for the production of the foams. The space holders used for the formation of pores were spherical and cubic potassium chloride (Sigma-Aldrich, UK). The densities of the powders were measured using a helium pycnometer (AccuPyc II 1340, Micromeritics, USA) with a filling pressure of 10 psi over 10 cycles. The estimated densities were 4.5 and 1.98 g/cm^3 for the Ti powder and KCl respectively. The morphologies of the powder particles are shown in Figure 1 .The binder used in this study was a multi-polymer system that consists of PEG1500, Poly methyl methacrylate (PMMA) and stearic acid. The volume percentage of binder was equal to 42 % of which 70% was PEG, 25 % PMMA and 5 % stearic acid, while the volume percentage of solid content was equal to 58% of which 60% was KCl and 40 % titanium. The feedstocks were mixed and extruded using a similar procedure to that reported in our previous study[16].

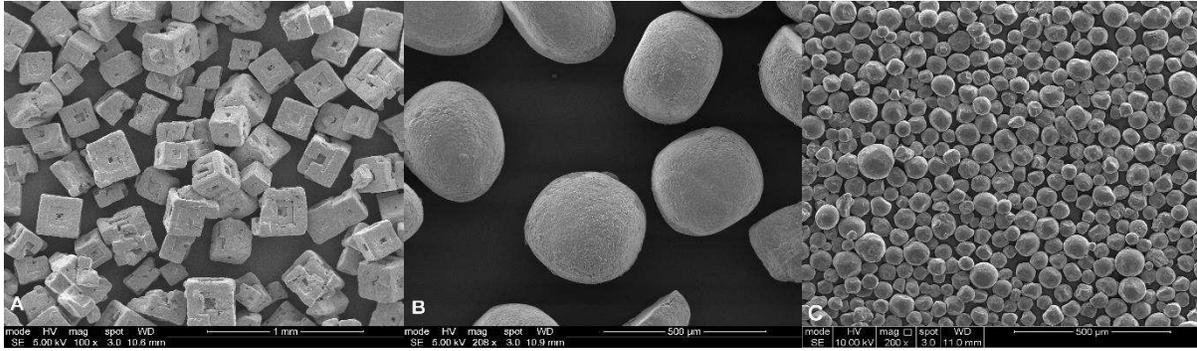


Figure 1. A. Cubic KCl, B. Spherical KCl, C. Ti powder

2.2. Rheological Testing

The rheological analyses of the feedstocks were performed using a capillary rheometer (Rosand RH2000, Malvern, UK) at a series of four temperatures starting with 120°C and ending with 150°C. A tungsten carbide die with a diameter of 2 mm and a length of 16 mm was used. Rabinowitsch correction was applied in order to obtain the true shear rate. The rheological tests were performed in order to assess the effect of the space holder particle shape on the viscosity of the feedstock as well as the dependency of viscosity on time.

2.2.1. The effect of the shape of the space holder particles

It is important to be able to produce foams with different pore morphologies (e.g. cubic, spherical, etc.) to meet different demands for different foam applications. This diversity in pore morphologies can be achieved by using space holders with different particle shapes. Thus, investigating the influence of the space holder particle shape on the viscosity of the feedstocks is important in assessing the suitability of these feedstocks for the production of foams with different pore morphologies by MIM-SH. The cubic and spherical KCl powders were both sieved through 710 μm , 500 μm and 250 μm sieves and were used in preparing two feedstocks. A third feedstock was prepared using a mixture of both cubic and spherical KCl powders (feedstock C). The particle size distributions of the sieved KCl powders were dry analysed using a Malvern Mastersizer 3000. The following table shows the particle size distributions of the Ti and KCl powders for the feedstocks prepared.

Table 1. Particle size distribution for the space holder and Ti powder

| | KCl Feedstock A | KCl Feedstock B | KCl Feedstock C | | Ti Powder |
|----------------|-------------------|-------------------|-------------------|--------------------|--------------------|
| Particle Shape | Cubic | Spherical | Cubic + Spherical | | Spherical |
| Dx (10) | 229 μm | 188 μm | 147 μm | 88.3 μm | 52 μm |
| Dx (50) | 329 μm | 307 μm | 222 μm | 201 μm | 72.5 μm |
| Dx (90) | 461 μm | 476 μm | 325 μm | 340 μm | 102 μm |

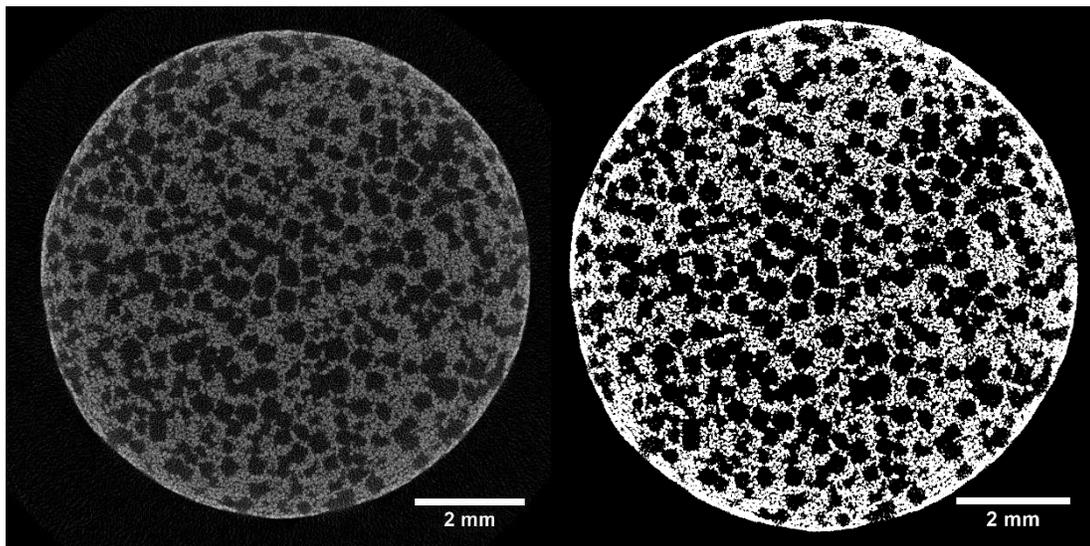
2.2.2 Dependency of Viscosity on Time

Some viscous materials exhibit time dependent shear thinning, a phenomenon called thixotropy. It is often related to the breakdown of the structure under shear with time leading to a reduced viscosity reading. This breakdown in the internal structure can be time-reversible where the structure of the material rebuilds once the shear stress is removed and the material is allowed to rest [17]. Feedstocks need to be checked for this phenomenon in order to make sure that there is no segregation among the polymeric binder and powders that might result from the breakage of the structure under shear. This can be carried out by subjecting them to ascending shear rate up to a maximum value and then decreasing it at the same rate to the starting value. Thixotropic materials often display a wide hysteresis loop, whereas normal materials do not show any hysteresis. Two feedstock samples were prepared using cubic KCl particles with mean particle size of 229 μm and tested for their structural stability by shearing them up to a maximum value of about 2200 1/s and then reducing it to the starting value at the same shear rate. These tests were carried out at two different temperatures, namely 140 and 150 °C.

2.3. Foams preparation and characterization

Cylindrical samples with a diameter of 10 mm and a height of approximately 13 mm were injection molded using a low pressure injection molder at a pressure of 45 MPa and a temperature of 150°C. The KCl particles used were spherical with a mean particle size of 319 μm as it was found during the rheological tests that more volume percentage of space holder can be added to the feedstock in the case of spherical compared to cubic, and that they flow better with reduced wall friction. The samples were then water debound ultrasonically at a temperature of 50°C in order to dissolve the space holder particles and remove the soluble part of the binder (PEG). The water debinding temperature was chosen based on the findings of our previous studies [16, 18]. After complete removal of the soluble part of the binder and space holder, the

samples were dried at 50°C for 3h in order to remove any moisture. Next, the green foams were thermally debound at a temperature of 450°C for 1h in order to remove the PMMA and sintered at a temperature of 1250°C for 2h under a flow of argon gas in a vacuum furnace. The volume percentage of porosity in the foams produced was determined by subtracting the true volume of the foams (the solid part only), which was obtained using the pycnometer, from the bulk volume that was calculated using the dimensions of the sample via a vernier caliper with a resolution of 0.01mm. One foam was cut into small slices or sections and cold mounted using epoxy resin under vacuum in order to fill the pores with resin, thereby providing mechanical support for later grinding. The samples were ground using silicon carbide papers with grits of 500 and then 1000 for 5 minutes before characterizing them using Scanning Electron Microscopy (SEM). Micro-CT scanning was carried out on one of the foams produced using a SkyScan1172 Bruker system with a voxel size of 6 μm using 1mm Al filter. To ease data processing and analysis in three dimensions, a section of 4 mm in height (a total of 657 cross-sectional images) was chosen to be analysed using CTAn analysis software and a threshold value of 70 was applied during the analysis. This value is of critical importance in determining which voxels will be identified as solid and included in the volume model. Figure 2 shows a CT cross-section image of the sample before and after binarization.



3. Re: *Figure 2. Transverse Cross-section before and after binarization*

Rheograms of the feedstocks prepared with different particle shape of space holders are shown in Figure 3.

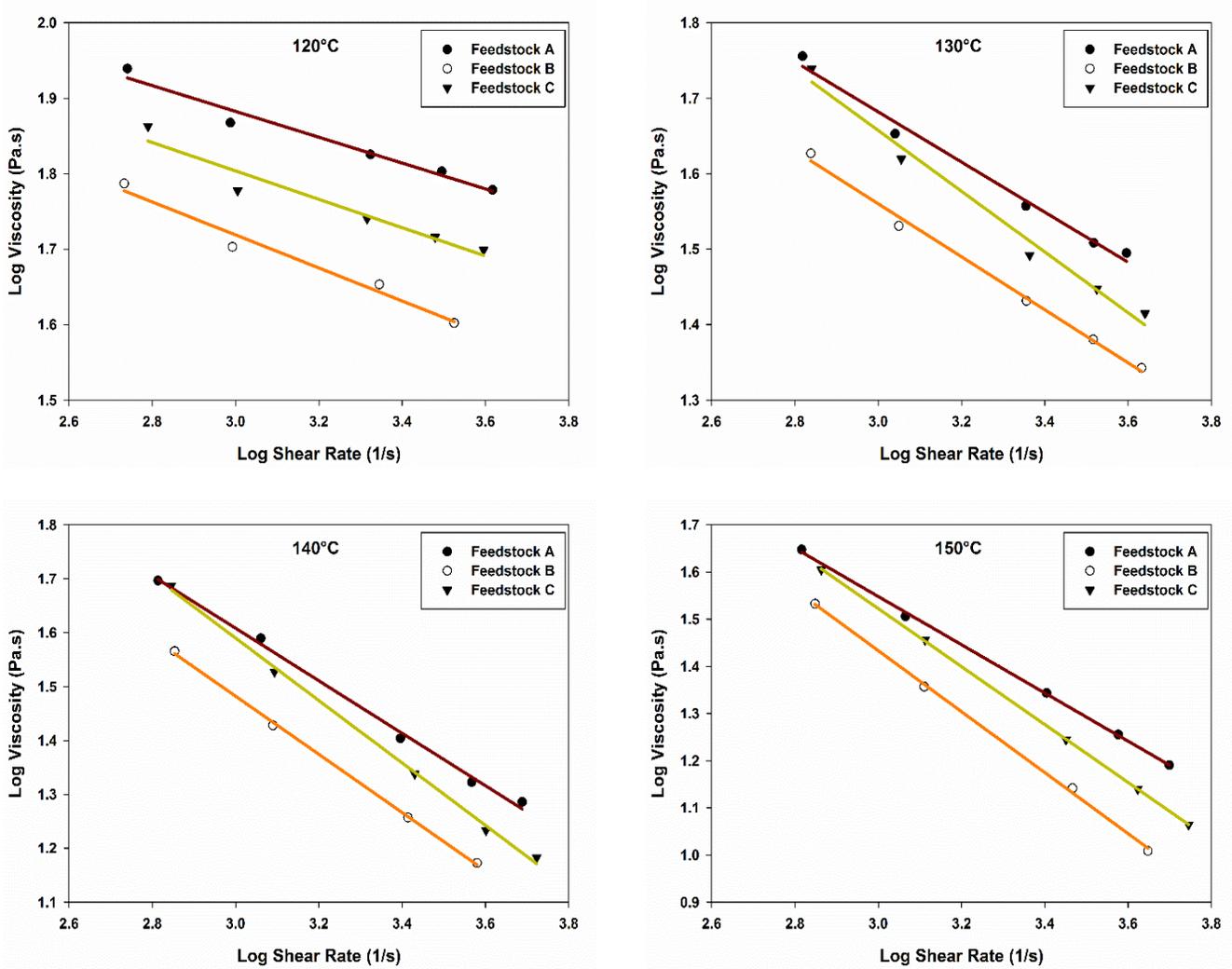


Figure 3. Viscosity rheograms of the feedstocks prepared at different temperatures

It was observed that feedstocks made with cubic KCl particles had a much higher viscosity than those made using spherical KCl particles and a slightly higher viscosity than that of feedstock made with a mixture of finer cubic and spherical KCl particles. Spherical KCl particles flow much better than cubic particles (moving past each other more easily) with reduced die wall friction resulting in lower viscosity and reduced resistivity to flow. This is also the reason why spherical powder was selected in feedstock formulations. Tuncer et al [19] favored KCl over NaCl as a space holder and reported that KCl powder can be compacted at lower pressure to almost theoretical density and can give lower wear of screw and valve compared to NaCl. However, one might argue that the shape of the space holder is a significant contributor for their

findings, rather than just the material as the KCl particles used in their study were approximately spherical, while the NaCl particles were cubic. It has also been reported in the literature that feedstocks made by spherical powders have lower viscosity than that of irregular powders and can have a higher maximum solid content in single-system Ti feedstocks [20]. In binary feedstock systems, the same effect has been observed on the viscosity in the case of adding secondary spherical powders compared to cubic or irregular powders. Thus, more spherical KCl can be added to the feedstock to produce foams with larger percentage of porosity compared to the cubic case. It can also be noted that feedstock prepared with a mixture of cubic and spherical KCl powders had a viscosity value between the spherical and cubic, albeit the particle size was finer. At lower shear rates, the viscosity of the feedstock with the cubic KCl and of that with the mixture of finer cubic and spherical were close to each other, however, this trend changes noticeably as the shear rate increases where spherical particles flow easily, yet their movement is still restricted by the presence of cubic KCl particles which keep the viscosity relatively high compared to viscosity of the feedstock made with spherical KCl. The results of the viscosity dependence on time for the investigated feedstocks are illustrated in Figure 4.

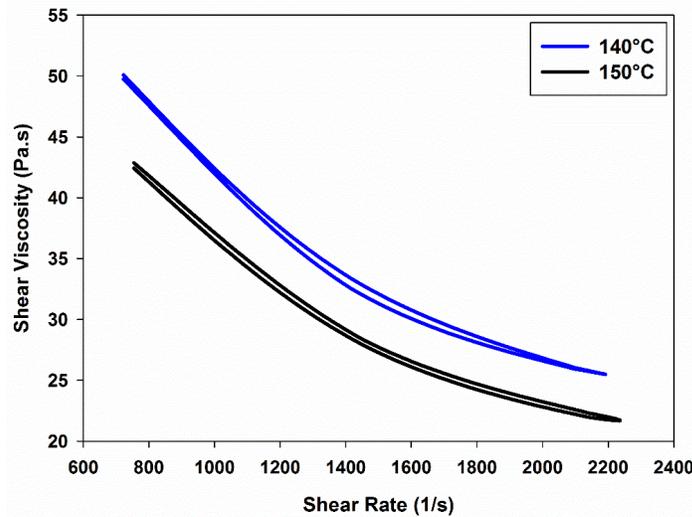


Figure 4. The hysteresis behaviour of feedstock

It can be seen from Figure 4 that there is not an obvious hysteresis loop at the injection temperatures, which is an indication of the feedstock having good structural stability and consistency, sufficient to inject the feedstock into different parts shapes.

SEM images of a cross-section of the foam produced are displayed in Figure 5. It can be clearly seen that the foam is composed of relatively large interconnected or spaced macropores separated by microporous cell walls. The micropores are formed due to partial sintering and incomplete densification of the powder particles. The true densities of the foams were found to be equal to 4.55 g/cm^3 .

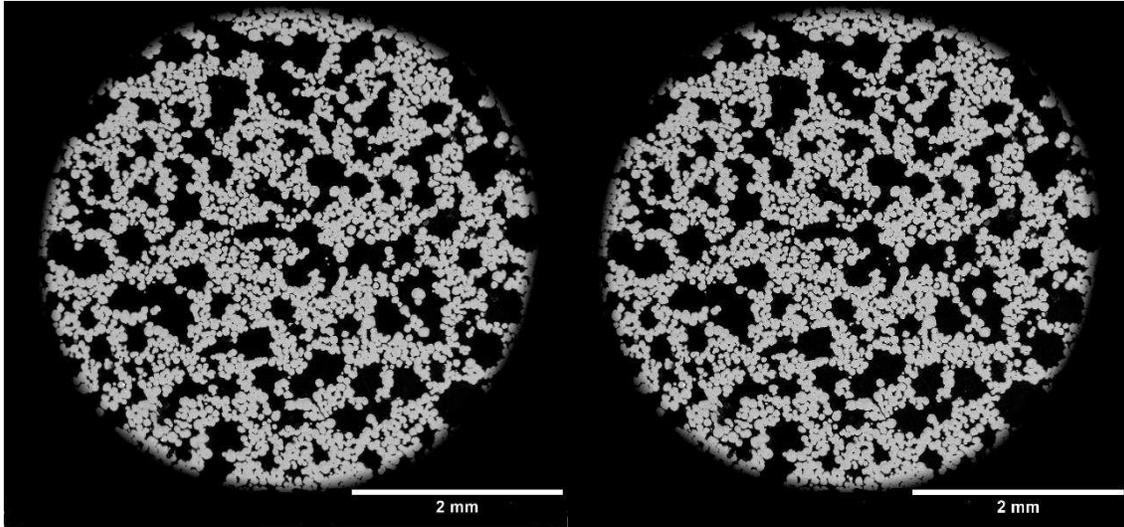


Figure 5. SEM Images of a cross-section of the foam produced. While the sintering process produces bonds, individual metal powder particle shapes can still be discerned, indicating the presence of micro porosity.

The total volume percentage of pores for the foams produced was equal to $61.25\% \pm 0.29$. The average volume shrinkage of samples after sintering was about $34.45\% \pm 0.84$. Three dimensional volume rendered CT of a 4mm section of the foam produced is illustrated in Figure 6. The color bar is indicative of the density difference between different regions in the foam, where the blue color refers to the densest part of the foam and dark red the lowest. It was observed that the foam had an outer layer generally denser than other parts of the foam. This is expected due to the fact that the space holder particles cannot get closer to the surface than when they were touching the mold. The volume percentage of total porosity estimated by 3D analysis of the CT images was equal to 61.5% of which 99.7% is open porosity. This result is in a good agreement with the value calculated by using the true and bulk volume values. Pore sizes ranged from 6 to 100 μm for micropores and from 100-480 μm for macropores. Although these ranges intersect, the distribution showed concentrations around these two separate size ranges, leading to the description in terms of the two pore types. These macropores are well suited for bone ingrowth, where several scholars reported that the optimum pore size range is 100-400 micron, while some extend this range up to 500 microns[21]. Furthermore, the presence of micropores can be of potential benefit as it has been found that micropores as small as 50 μm can promote blood vessel growth within the implant [5, 6].

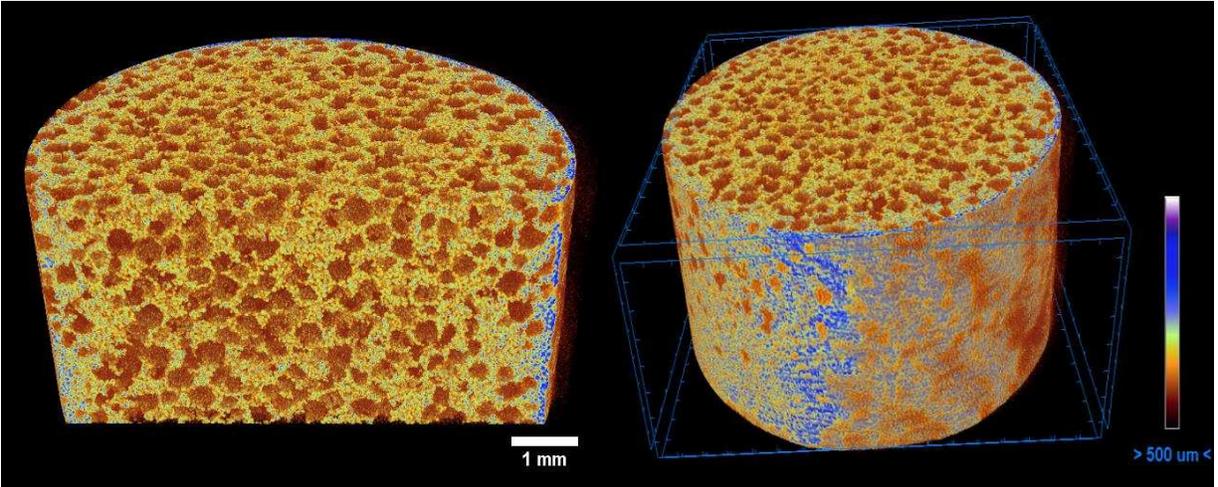


Figure 6. Volume rendered CT images of the foam produced

4. Conclusion

Titanium foams are potentially useful materials which will require powder processing. The potential use of Metal Injection Molding in combination with a Space Holder for (mass) producing open pore Ti foams has been investigated. In addition, the effect of the shape of the space holder on the viscosity of the feedstock as well as the dependency of viscosity on time have been examined. Two shapes of space holder particles were used in this study, namely spherical and cubic KCl with different particle sizes. It was found that feedstocks made with cubic KCl particles had a much higher viscosity than those prepared using spherical KCl particles. Spherical particles flow much better than cubic ones with reduced die wall friction resulting in lower viscosity and reduced resistivity to flow than cubic ones, thereby offering the possibility of achieving a higher space holder content resulting in higher volume percentage of pores. Ti foams with a total volume percentage of porosity of 61.25% were produced of which 99.7 % was open porosity. Two types of pores were apparent in the foams produced, namely micropores and macropores. Micropore sizes were ranging from 6 to 100 μm , whereas macropore sizes ranged from 100-480 μm . These pores are apparently well suited for bone and blood vessel growth, thus showing great potential for biomedical applications. Pending further verification of the interaction with the body, such powder-based products may be used within dental implants or potentially joints replacements.

5. References

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