

A NOVEL MANUFACTURING METHOD FOR TITANIUM FOAM FOR BIOMEDICAL APPLICATIONS

Yuyuan Zhao and Laura E. Monaghan

**Department of Engineering
The University of Liverpool
Brownlow Hill
Liverpool
UK**

ABSTRACT

The excellent biocompatible properties of porous titanium make it a popular choice for many biomedical applications, especially due to its high specific strength. This paper introduces a new method for manufacturing titanium foam, where titanium powder is sintered with sodium chloride as the space-holder. The process is capable of producing open-cell titanium foam with controlled cell morphology, cell size and porosity. The samples produced have spherical or angular cells with a cell size of 250 – 425 μm and different porosities of 60-80%. A range of processing conditions including sintering temperature have been investigated. Their effects on the quality of the final specimens, as determined by techniques including SEM, EDX and XPS, have been discussed. It has been found that additional sintering under vacuum produces higher quality samples. The manufacturing conditions can be varied to achieve optimum quality and cleanliness with this new manufacturing method.

INTRODUCTION

Open-cell structures have been investigated by many researchers and compared to human bone [1,2]. A key application for these lies in the area of structural implants. Research shows that open-cell (open-pore) structures can encourage cell growth, improve healing and reduce recovery time, the long term Stress Shielding Effect (SSE) and hence the loosening of the implant. The SSE is a critical issue in load-bearing implants [3,4] as loosening of the implant causes pain and discomfort and eventually leads to the need for a revision. The SSE is notably caused by a mismatch in modulus between the implant and the bone it replaces, although it should be noted that there are several other contributing factors to implant loosening.

For key structural applications such as Total Knee Arthroplasty (TKA) and Total Hip Arthroplasty (THA) primary options include either cemented or cementless fixation. Much research has

investigated the success rate of each and the varieties within the field [5-7]. The bone-implant interface is significant and a variety of materials are now available for the manufacture of biomedical implants of this nature. Porous materials can offer improved surfaces for such implants, as well as address the issue of the modulus mismatch. It has been found that pore size and interconnectivity are key factors for bone in-growth [8-10] and this influences the design of such materials.

The most common material choices for orthopaedic implants include stainless steel, titanium (and its alloys) and cobalt chrome alloys [11]. Although there are many options available, titanium remains one of the typical choices; commercially pure (ASTM F67) titanium is still used, although there are several alloys that are also commonly used [11]. Titanium provides excellent corrosion resistance combined with high specific strength and high availability.

Titanium foams can be manufactured via several routes, although some are in early stages of development [2]. Solid-state sintering is normally used for the manufacture of Titanium foam due to the high melting point. A variety of sintering temperatures can be used with much research using temperatures in the region of 1000-1200 °C [12].

This paper develops a method for manufacturing titanium foams, based on the sintering and dissolution process (SDP) [13], and studies the compositional and structural quality of the resultant foams.

EXPERIMENTAL PROCEDURE

The porous titanium samples were manufactured using a variation of the SDP process. Grade 2 commercially pure HDH titanium powder with angular and irregular particle morphology as shown in Figure 1, and composition as shown in Table 1, was mixed with a sodium chloride (NaCl) powder at a pre-specified volume ratio depending on the desired specimen porosity.

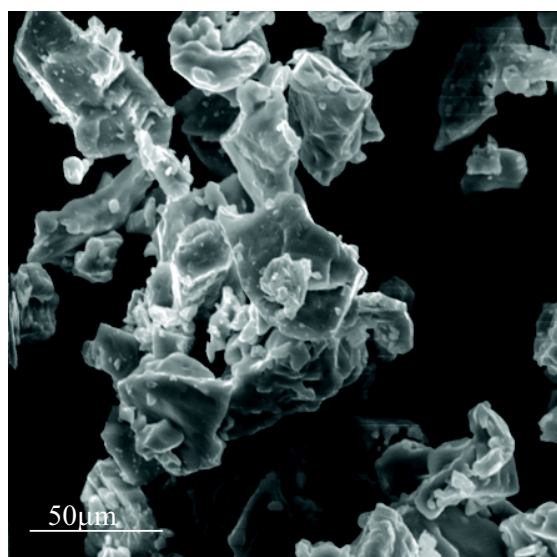


Figure 1: Morphology of as received HDH titanium powder

Table 1: Composition of commercially pure grade 2 titanium powder

<i>Element</i>	C	H	Fe	N	O	Ti
<i>%</i>	<0.1	<0.015	<0.3	<0.03	<0.25	<i>Bal</i>

The NaCl powders used were 95-99 % in purity and contained anti-caking agents of sodium hexacyanoferrate II and magnesium oxide. Two NaCl powders were used, one with angular and irregular particles and one with regular, near spherical, particles. Ideal pore size for microporous materials in biomedical applications is in the range of 50 - 500 μm , with a general minimum of 100 μm for cell penetration, tissue in-growth and vascularisation [14], and a maximum of 500 μm to prevent the increased event of non-healing. Others recommend an optimum maximum of 400 μm for greatest fixation strength in a defined time period [10]. For this paper each NaCl powder was sieved to the particle size range of 250 – 425 μm , to reflect the desired foam pore size.

The Ti/NaCl mixtures were bound with 10% ethanol and compacted into green samples in steel tubes with an inside diameter of 50 mm under a pressure of 250 MPa using a hydraulic press [15]. Iron powder was compacted at both ends to seal the tube and protect the green samples from excessive oxidation in atmospheric conditions during sintering. Additional NaCl powder was used to separate the green samples from the iron powder seals to prevent interference with the Ti/NaCl compact. The green samples together with the steel tubes were sintered in a standard electric furnace under normal atmospheric conditions, at temperatures ranging from 750 – 950 $^{\circ}\text{C}$ for 2, 4 and 6 hours. The sintered samples were air cooled to room temperature and removed from the steel tube. Specimens of 60 – 80 % porosity were made in 50 mm diameter discs. Any crystals or salt layers formed, due to the melting of NaCl during high temperature sintering, were removed using grinding paper and each cylindrical disc was sectioned into four cuboids. Further integral residual NaCl was removed using an ultrasonic dissolution process in heated water for three hours. They were dried in a furnace at low temperature for 1 hour resulting in porous titanium samples whose pores were direct negatives of the NaCl particles. Five samples ranging from 60 to 80 % porosity were made with spherical pore morphology and two (70 and 80 %) with irregular and angular pore morphology, with all pores being of a pre-specified size, determined by the size and shape of the NaCl powder used.

Two samples (70 % targeted porosity) were further sintered at 1000 $^{\circ}\text{C}$ for 2 hours under argon flow, one with regular and one with irregular pore morphology, and another two sintered at 1100 $^{\circ}\text{C}$ for 2 hours in a vacuum furnace.

One specimen, of 70% porosity sintered at 790 $^{\circ}\text{C}$ for 4 hours, was soaked in aqueous sodium hydroxide (45%) for 15 min. This was not heated in a bath as the heat provided from the exothermic nature of mixing granular NaOH with distilled water was sufficient. The foam was rinsed thoroughly with water and fully immersed into a nitric acid (33 %) and hydrofluoric acid (1.6 %) solution. This was heated to 40 $^{\circ}\text{C}$ with a soak time of no more than 5 min to avoid excessive metal removal [16].

The pore structure of the samples was checked using SEM and stereoscope microscopic imaging. The porosity of the foams was measured by the Archimedes method. The compositional changes of the foam surface were studied by XPS and EDX.

RESULTS AND DISCUSSION

Foam Structure

Pore distribution was typically uniform, although it was found to be non-uniform in places (Figure 2). Analysing the full discs produced showed that porosity decreased towards the outer edge. Porosity measurements were taken using sectioned foam cuboids from the centre of the discs.

The typical structures and pore morphology of the as produced Ti foam samples are shown in Figure 3. The pores of both regular and irregular pore samples are interlinked by small tunnels and have rough irregular walls as a result of the sintered HDH titanium particles. Enlargements of typical areas identified in Figure 3 can be seen in Figure 4. Pore walls are roughened due to the morphology of the titanium particles, as shown in Figure 4 (a). After the first sintering at 790 $^{\circ}\text{C}$ it can be seen that

towards the pore walls and edges full densification is not achieved (Figure 4 a, b). Some necking can be seen between particles at this sintering temperature (Figure 4 c). Higher temperature sintering in a protective environment provides greater coalescence and increased densification, with some angular particle morphology retained.

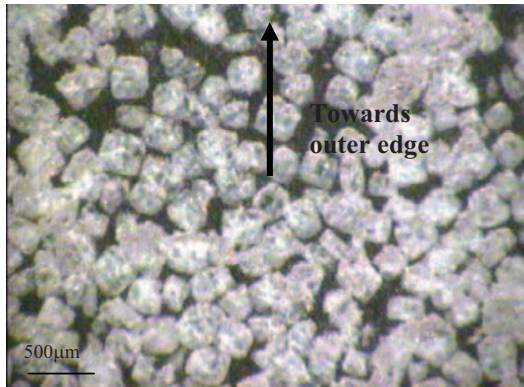


Figure 2: Stereoscope image of titanium specimen sintered at 790 °C for 4 hours, before removal of the NaCl

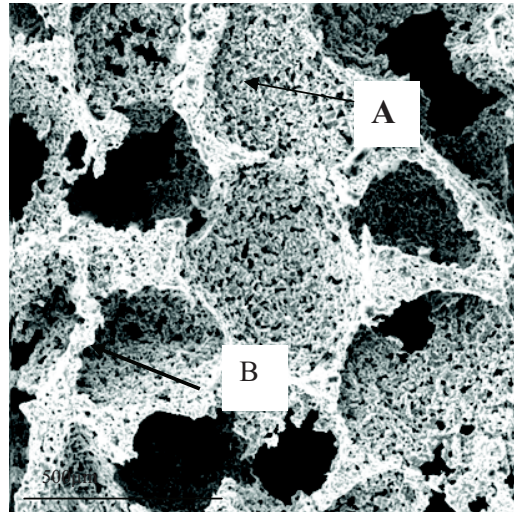


Figure 3: SEM image of a Ti foam sample produced by sintering at 790 °C for 4 hours under atmospheric conditions

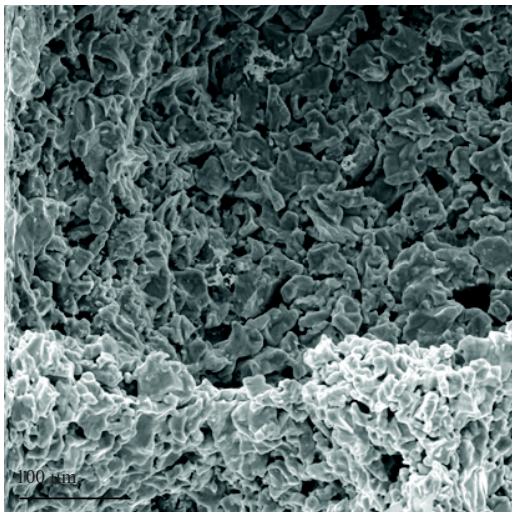


Figure 4 (a)

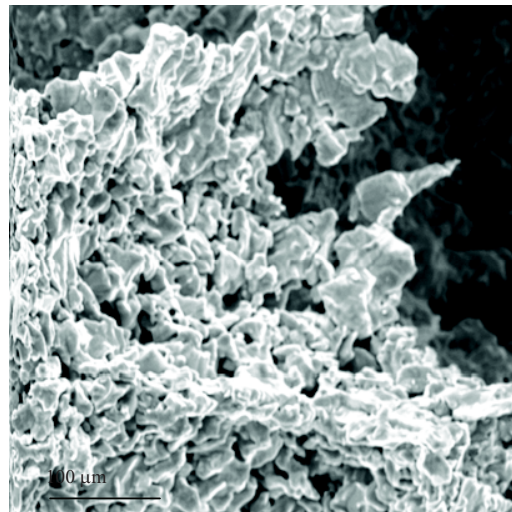


Figure 4(b)

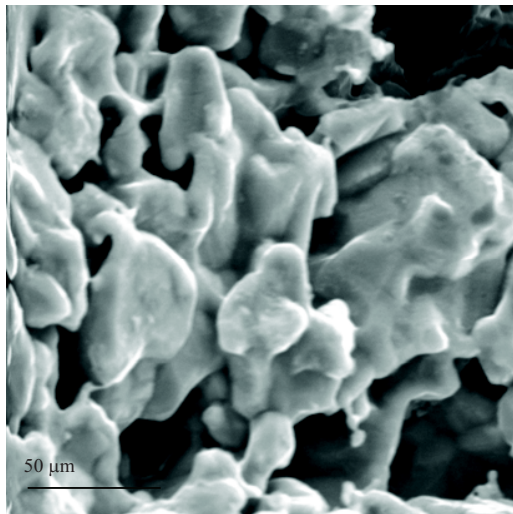


Figure 4 (c)

Figure 4: SEM images showing pore morphology and particle sintering of samples sintered at 790°C for 4 hours: (a) at the surface of a pore wall indicated as A in Fig. 3, (b) at a cross-section of a pore wall, indicated as B in Fig. 3 and (c) enlarged at the pore wall

Final porosity was generally higher than the targeted porosity, which is the volume fraction of NaCl in the NaCl/Ti mixture. Targeted porosity calculations assume full packing of titanium and sodium chloride particles, which is not true in this case. This is due to the presence of voids and air gaps created during the mixing and compacting of the Ti/NaCl mixtures. Twenty specimens manufactured under the basic conditions of 790 °C for four hours were measured and results show that final porosity is approximately 2% higher than the original target. Typical values for foams sintered at 790 °C for 4 hours with regular pore morphology are given in Table 2.

Table 2: Comparison of targeted porosity with measured porosity of the foams

Target Porosity (%)	65	65	70	70	75	75
Final Porosity (%)	67.6	68.4	70.2	71.9	76.9	78.9

Effects of sintering temperature

The samples sintered near and above the melting temperature of the NaCl powder were investigated. The melting temperature for the powder used in these experiments was expected to be lower than pure NaCl (801°C), due to impurities. Experimental investigation found it was around 785 °C. Sintering temperatures close to 800 °C provided stronger foams that were light in colour. At this temperature the molten salt experiences less flow and effectively seals and protects the titanium foam from greater exposure to the air, hence foams produced are light grey in colour. Sintering temperatures of around 850 °C (or higher) in the presence of air produced oxidised foams that were black in colour and weak, and would break on removal from the tube. Sintering temperatures of 900 °C and 950 °C in normal atmospheric conditions produced highly oxidised samples that easily crumbled. These higher temperatures produce fully molten salt resulting in movement of gas around the sample, which in air creates a highly oxidising environment. Oxide growth on titanium moves through a range of colours and finishes at black [16]. A sintering time of 4 hours was accepted as a reasonable time for initial sintering. A time of 2 hours was insufficient for sintering and 6 hours had no noticeable effect on the foam, but did cause greater oxide growth.

Sintering at a higher temperature of 1100 °C in vacuum or at 1000 °C under argon flow produced foams that were lighter grey in colour and generally brighter in appearance, with a clearly defined network. A polished foam surface of this type of foam with regular pore morphology can be seen in Figure 5. It can be seen that the structure of the foam is not changed, in terms of the network of pores. Primarily changes are seen in the appearance of the foam in colour and oxide presence, and secondly in the integrity and strength of the structure.

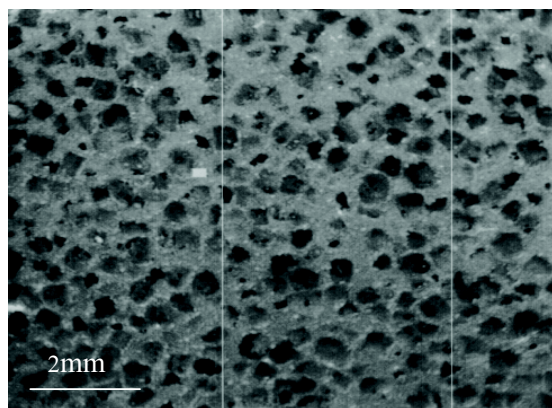


Figure 5: SEM image of titanium foam sintered at 790 °C for 4 hours, then sintered at 1000 °C under argon flow for 2 hours

Surface Chemistry

An XPS spectrum of the surface chemistry of a specimen sintered once at 790 °C followed by ultrasonic cleaning in water is shown in Figure 6. The presence of residual sodium chloride is evident from peaks of sodium and chlorine. Low titanium counts of less than 1500 cps is the result of surface scales and oxide.

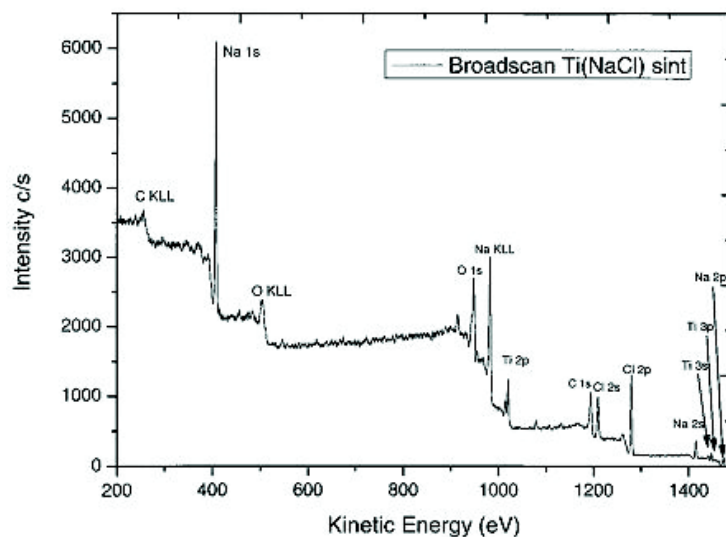


Figure 6: XPS data for titanium foam sintered at 790 °C

Removal of unwanted NaCl was carried out by either sintering at 1100 °C under vacuum or at 1000 °C in a protective argon environment, or by cleaning in an aqueous sodium hydroxide bath followed by a

nitric/hydrofluoric dip. High temperature sintering not only increased mechanical properties as a result of increased densification, but also resulted in cleaner foams that were light grey in colour. Foams without the second stage of processing were compared to those which had been additionally sintered as shown in Figure 7 (a) and (b). EDX analysis showed higher titanium counts, with reduced chlorine counts, after additional sintering. Sublimation of sodium chloride occurs at elevated temperatures and at low pressures [17]. In the vacuum environment sublimation is the more favourable event hence the sodium chloride removes itself from the porous titanium structure via its gaseous state. In the argon environment the molten salt flows out of the structure.

The cleaning treatment improved the surface quality of the Ti foam considerably. EDX spectra of a foam after the chemical cleaning (Figure 7 (c)) presented excellent results with Cl peaks significantly reduced, and titanium counts greatly increased, compared to the spectra in 7 (a), confirming that surface contaminants and oxide/scale (s) were successfully removed. Counts of Ti increased from several thousand to nearly 160,000, with the chlorine peak reduced to minimal counts. The improvements in surface quality were visible by the naked eye with foams being bright and shiny. Under stereoscope microscope a well defined porous network can be seen (Figure 8).

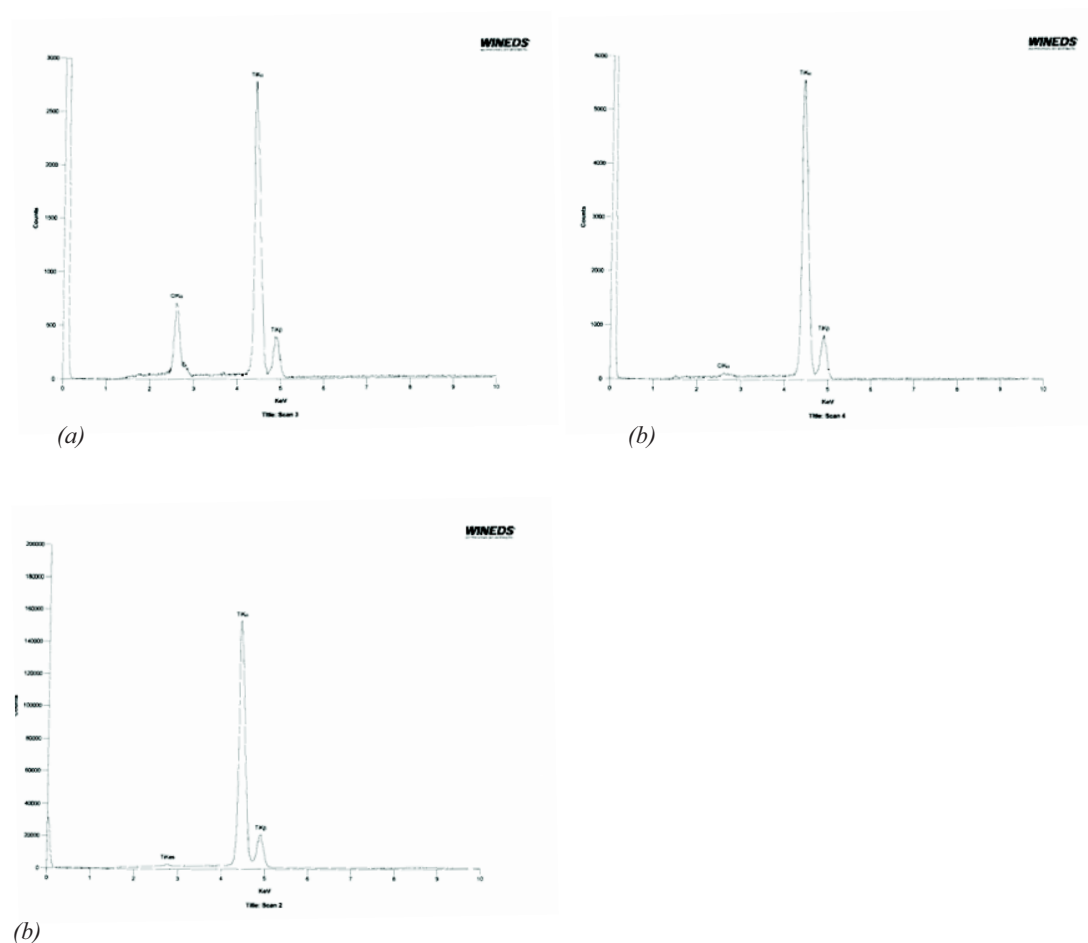


Figure 7 (a-c): EDX spectra of titanium foam surfaces after treatments (a) Sintered at 790 °C for 4 hrs and cleaned in distilled water, (b) Sintered at 790 °C for 4 hours and cleaned in distilled water, followed by second sintering at 1000 °C under argon flow for 2 hours, and (c) Sintered at 790 °C for 4 hours, cleaned in distilled water followed by cleaning in aqueous NaOH and HF

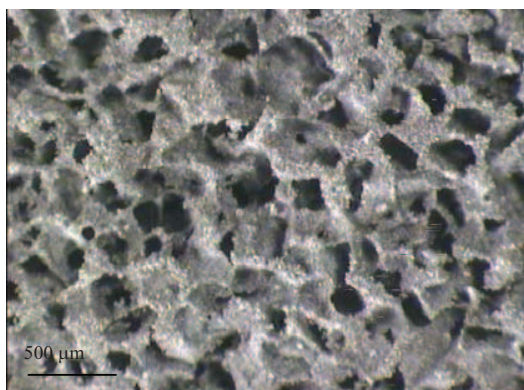


Figure 8: Titanium foam structure after cleaning treatment (790 °C for 4 hours, 70 % target porosity)

CONCLUSIONS

Titanium foams with pore size in the range of 250 – 425 μm and porosity in the range of 60 – 80 % have been manufactured successfully using this powder metallurgy process. Porous titanium samples can be produced at a low production cost with control over foam structure and pore size. High temperature sintering, in a protective environment, improves quality and strength. Surface chemistry can be controlled, with oxides and contaminants easily removed using cleaning treatments of an aqueous NaOH bath followed by dipping in nitric/hydrofluoric acid solution. This provides a surface for testing biological compatibility.

ACKNOWLEDGEMENTS

The authors would like to thank Dr Liping Zhang for assistance in sample preparation and equipment arrangements. Laura Monaghan would like to thank the EPSRC for a DTA award.

REFERENCES

1. Lorna J. Gibson and Michael F, Ashby, *Cellular Solids: Structure and Properties*, 1988, Pergamon Press, Oxford.
2. Hans-Peter, Degischer and Brigitte, Kriszt, *Handbook of Cellular Metals: Production, Processing, Applications*, 2002, WILEY-VCH.
3. JJ. Jacobs, D.R. Sumner and J.O. Galante, “Mechanisms of bone loss associated with total hip replacement”, *Orthop Clin North America*, 1993, vol. 24, no 4, pp. 583–590.
4. H.C. Amstutz, “Hip arthroplasty”, 1991, Churchill Livingstone, New York.
5. C.A.F. Dodd, D.S. Hungerford and K.A. Krackow, “Total Knee Arthroplasty Fixation: Comparison of Early Results of Paired Cemented Versus Uncemented Porous Coated

- Anatomic Knee Prosthesis” *Fifth Open Scientific Meeting of the Knee Society*, New Orleans, Louisiana, 1990, No. 260.
6. Marko Pecina, Dapic Tomislav and Miroslav Haspel, “Survival of Cementless and Cemented Porous-coated Anatomic Knee Replacement: Retrospective Cohort Study”, *Croatian Medical Journal*, 2000, vol 41, no 2, pp. 168 – 172.
 7. Richard Berger et al., “Problems With Cementless Total Knee Arthroplasty at 11 Years Follow-up”, *Clinical Orthopaedics and Related Research*, 2001, No. 392, pp. 196 -207.
 8. J. Klawitter, S. Hulbert, “Application of porous ceramics for the attachment of load bearing internal orthopaedic applications”, *Journal of Biomedical Materials Research*, 1971, vol 6, pp. 161 – 229.
 9. S. Simske, R. Ayers and T. Bateman, “Porous materials for bone engineering”, *Materials Science Forum*, 1997, 250, pp. 151–182.
 10. J.D. Bobyn, R.M. Pilliar, H.U Cameron, G.C Weatherly, “The optimum pore size for the fixation of porous-surfaced metal implants by the in-growth of bone”, *Clinical Orthopaedics*, 1980, 150, pp. 263–270.
 11. Lawrence Katx et al., “Orthopaedic Biomaterials”, *Encyclopaedia of Biomaterials and Biomedical Engineering*, 2004, DOI: 10.1081/E-EBBE 120007368.
 12. W.R. Weinand, F.F.R. Goncalves and W.M. Lima, “Effect of sintering temperature in physical-mechanical behaviour and in titanium-hydroxyapatite composite sinterability”, *Materials Science Forum*, 2006, vol. 530, no 31, pp. 249-254.
 13. Y.Y. Zhao and D.X. Sun, “A Novel Sintering-Dissolution Process for Manufacturing Al Foams”, *Scripta Materialia*, 2001, vol. 46, pp. 273-282.
 14. Julian R. Jones, and Larry L. Hench, Larry, “Microporous Materials”, *Encyclopaedia of Biomaterials and Biomedical Engineering*, 2004, DOI: 1081/E-EBBE 120014101.
 15. Yuyuan Zhao, Fuheng Han, and Thomas Fung, “Optimisation of compaction and liquid-sate sintering in the sintering and dissolution process for manufacturing Al foams” *Materials Science and Engineering*, 2004, A364, pp. 117-125.
 16. Matthew J. Donachie, *Titanium: A Technical Guide*, 1st Edition, 1988, ASM International.
 17. Dale W. Kaufman, *Sodium Chloride: The production and properties of Salt and Brine*, 1960, Renhold Publishing Corporation, New York.