

PROCESSING AND CHARACTERIZATION OF TITANIUM SPONGES WITH DIFFERENT POROSITY LEVELS ¹

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Abstract:

Titanium sponges can be used in many industrial fields due to their specific properties like low density, low stiffness, high corrosion resistance and good energy absorption characteristics. The processing of titanium sponges is difficult in the liquid state due to its very high melting point and extreme reactivity. Therefore, the powder metallurgy route in the solid state has become an attractive alternative, due to the low temperature, the possibility of obtaining high porosity and a good control of the porous structure, which relates to the processing reproducibility. A previous research has developed a powder metallurgy methodology to produce pure titanium sponges for surgical implant application, by using titanium powders and a pore former material (urea). The aim of this work is to process pure titanium sponges with different porosity levels and to investigate the evolution of pore structure and porosity fraction. Porosity characterization was performed by SEM analysis and optical quantitative metallographic analysis. The results showed that there is a relationship between the sponge volume fraction of pores and pore morphology with the pore former material size and quantity.

Key words: Sponge; Titanium; Porosity; Powder metallurgy.

PROCESSAMENTO E CARACTERIZAÇÃO DE ESPONJAS DE TITÂNIO COM DIFERENTES NÍVEIS DE POROSIDADE

Resumo

Esponjas de titânio apresentam aplicações em vários campos industriais, devido as suas propriedades específicas como à baixa densidade, baixo módulo de rigidez, alta resistência á corrosão e boas características de absorção. O processamento de esponjas de titânio apresenta dificuldades no estado líquido devido ao seu alto ponto de fusão e alta reatividade. Assim, o processo de metalurgia do pó no estado sólido vem se tornando atrativo devido às baixas temperaturas utilizadas, à possibilidade de obtenção de alta porosidade e ao rígido controle da estrutura porosa, que está relacionado à reprodutibilidade do processo. Uma pesquisa anterior desenvolveu uma metodologia para a produção de esponjas de titânio puro para aplicação em implantes cirúrgicos, utilizando pó de titânio e um material formador de poros (uréia). O objetivo desse trabalho é a obtenção de esponjas de titânio com diferentes níveis de porosidade e investigar a evolução da microestrutura porosa e fração de poros. A caracterização da porosidade foi realizada através de microscopia eletrônica de varredura e análise metalográfica quantitativa. Os resultados mostraram que existe uma relação entre a fração volumétrica de poros das esponjas e a morfologia de poros com o tamanho de partícula e quantidade do material formador de poros.

Palavras-chave: Esponja; Titânio; Porosidade; Metalurgia do pó.

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Introduction

The term “metallic foam” is often used for any kind of metallic material which contains voids, but foams are only produced in the liquid or semisolid state. Nowadays there are many distinct definitions for these materials, according to the fabrication process or morphology. “Cellular metals” are materials with a high volume fraction of voids, have their space divided into distinct cells, whose boundaries are made of solid metal, the interior are voids and the individual cells are all separated from each other by metal; “porous metal” contains closed, roughly spherical pores and a porosity level of usually less than about 70%; “metal foams” originates from a liquid foam in which gas bubbles are finely dispersed in a liquid; “metal sponges” have their space filled by pieces of metal that form a continuous network and co-exist with a network of empty space which is also interconnected. These definitions are not mutually exclusive and the distinction between them is sometimes not easy. Thus, foam is also a porous and a cellular structure, but a sponge does not necessarily contain cells.^[1,2]

The specific properties of “metallic sponges”, like low stiffness, low density and a good combination of energy-absorbing, heat-transfer and mechanical properties, offer a large potential in many industrial fields, such as, lightweight structures (construction), chemical, petroleum and biomedical engineering. Their microstructure may exhibit closed and open (interconnected) porosity, with different ranges of pore size, volume fraction and morphology. Mechanical properties of porous materials can be modified and optimized by controlling porosity, pore size, pore shape and pore distribution.^[1] Many processes are available to produce metallic sponges, including casting techniques, metallic deposition (ex. sputtering) and powder metallurgy, being the main difficulties the process control and high cost.^[2]

Powder metallurgy is advantageous due to the possibility of obtaining pieces with complex geometry, the low temperature used in sintering treatment, effective especially for metals with high contamination susceptibility and the good control of the porous structure and chemical composition, which is related with processing reproducibility.^[3] This technology is used for fabrication of porous coatings and fully metallic sponges, which consists in compacting, binding and sintering metal powders steps. Mass transport between the particles is made by solid-state diffusion process. The porosity volume fraction of the sponge is associated with the degree of interconnectivity and particle size that it is controlled by process parameters such as powder green density, sintering temperature and time. The raw powder size and shape dictate the pore sizes and shape. An appropriate pore former material (space holder) is usually used to produce sponges with greater porosity, by removing the material in a low-temperature heat treatment.^[2]

Titanium and titanium alloys are widely used in the chemical and petroleum industries and especially for surgical implants, due to their low density, excellent combination of mechanical properties, high chemical and corrosion resistance and excellent biocompatibility. Concerning titanium powder metallurgy processing as this metal has good ductility and conformability the uniaxial or isostatic powder compaction step is usually successful. However, titanium sintering requires a high vacuum environment to avoid contamination due to its great reactivity and to achieve good particle bonding. When compared with other metallic biomaterials, titanium sponges exhibit the lower stiffness, that reduces de mismatch of elastic modulus between the metallic implant and bone, avoiding the implant loosening.^[3,4] Porosity characterization is considered essential for porous implants because the pore size

and morphology influence cellular adhesion. A high fraction of open porosity is required, because it improves implant to bone fixation (osseointegration) by the growing of bone-forming tissues inside de pores.^[5]

A previous research has developed a powder metallurgy processing route to produce pure titanium sponges in order to achieve the porosity requisites for porous surgical implants. In this study, pure titanium sponges processed with different porosity levels in order to investigate their pore morphology and porosity volume fraction. Porosity characterization was performed by SEM analysis and optical quantitative metallographic analysis.^[6-8]

METHODOLOGY

Cylindrical titanium sponges were processed by a powder metallurgy route. Pure titanium powder grade 2 (Micron Metals/EUA) was employed, with 0,014% N, 0,223% O, 0,040% H, 0,052 Fe, 0,006% Na, 0,006% Mg and 0,021 C. The titanium powders produced by HDH hydrogenation-dehydrogenation process have an acicular shape (Figure1a) and 149 – 177 μm particle size range. An organic additive, urea, with irregular shape (Figure 1b) was used for greater pore formation as a space holder. It was separated by sieving in four particle size ranges of 125 – 149 μm , 149 – 177 μm , 210 – 250 μm and 297 - 350 μm . Titanium powders were mixed with the proportions of 5%, 10%, 15%, 20%, 25% and 30%wt of the organic additive. There were four groups of samples (sponges). Each group corresponds to a particle size range of the space holder and includes six different conditions, in relation to the percentage of urea. Table 1 indicates the specifications of the 24 samples with different conditions. The particle size ranges of the titanium powder remained the same for all groups.

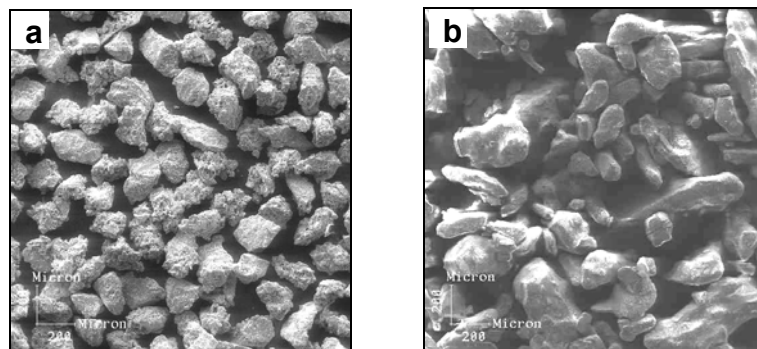


Figure 1. SEM photography's of titanium powders with acicular shape (a) and urea powders (b).

Table 1. Sample specifications related with the amount and particle size of urea.

Urea – % weight →	5(%)	10(%)	15(%)	20(%)	25(%)	30(%)
Urea – Particle size ↓						
Group I – (125 - 149 μm)	A ₁	B ₁	C ₁	D ₁	E ₁	F ₁
Group II – (149 - 177 μm)	A ₂	B ₂	C ₂	D ₂	E ₂	F ₂
Group III – (210 – 250 μm)	A ₃	B ₃	C ₃	D ₃	E ₃	F ₃
Group IV – (297 - 350 μm)	A ₄	B ₄	C ₄	D ₄	E ₄	F ₄

Manual mixing of titanium powders with the organic additive was performed using petroleum ether as a binder. Then the mixture was encapsulated in flexible moulds, compacted by cold isostatic pressing at 300 MPa. The compacted samples were removed from the moulds and treated at 200°C for 2 hours in order to evaporate the organic additive. Sintering of compacted samples was performed at 1200°C in a vacuum furnace (better than 10^{-6} Torr) for 1 hour. After sintering, interstitial chemical analysis results were 0,240% O and 0,022% N, according with pure titanium grade 2 specifications (ASTM F67-89). Figure 1 shows the macrophotograph of the sponge A_1 with diameter from 7.80 mm to 8.10 mm and 5,10 mm medium height (Figure 1). All samples have similar sizes.

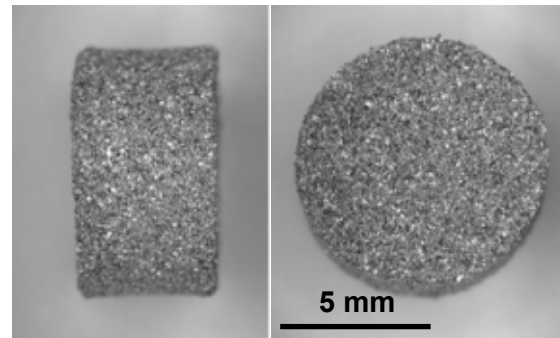


Figure 1. Macrophotograph of the sample A_1 with 5% urea/125 - 149 μm .

Transversal metallographic cut sections along the longitudinal axis of the samples were prepared for optical microscopy, using the standard methodology. In each prepared surface, at least 20 images were taken, to register the entire section surface. Porosity volume fraction evaluation was carried out by quantitative metallographic analysis, using an Image Pro Plus version 4.0 software. This program bases in ranges of grey scale and determines, amongst other parameters, the pore volume fraction and the pore size.

RESULTS AND DISCUSSION

The SEM topographic views of sample C_1 (Figure 2a, 2b) show that the porous microstructure consists of macropores, some of them higher than 100 μm , and rounded micropores with sizes lower than 10 μm . It can be observed that the macropore surfaces are rough, due to the titanium powder nature, which is a desired feature for implant osseointegration.^[9] Figure 3 (a-f) shows the optical micrographs of samples from group I and Figure 4 (a-f) the samples from group III. Pores are the dark regions in the micrographs.

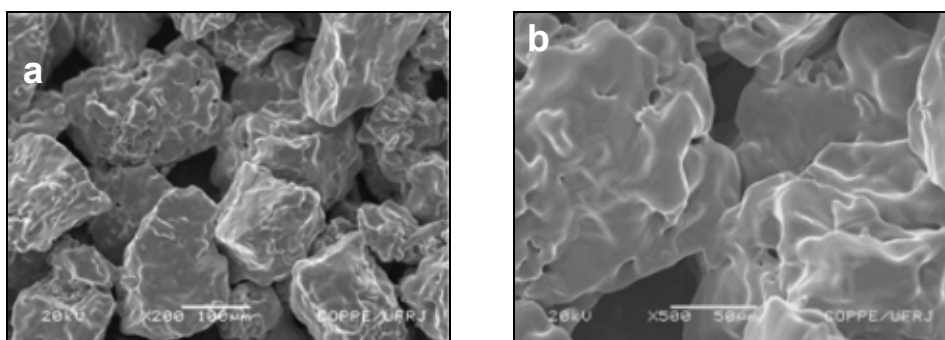


Figure 2. SEM microtopography from sponge C_1 with 15% urea/125 - 149 μm .

The samples of the type "A", with 5% urea (space-holder), presented usually closed pores with irregular shape. The samples of type "B", "C" and "D", with 10%, 15% and 20% of urea, respectively, presented great open pores and small closed pores, mostly located in the walls of the great pores. The samples type "E" and "F", with 25% and 30% of urea, respectively, presented an interconnected porosity more substantial than that presented in the samples type "B", "C" and "D". This behaviour can be observed in the correspondent micrographs of samples from group I (urea size 125 - 149 μm) and group III (urea size 210 - 250 μm), at Figures 3 and 4. Sample D₁ presented a pore structure quite similar to samples B₁ and C₁, while sample D₃ is much similar of samples E₃ and F₃, probably because the greater urea particle size (210 - 250 μm) of samples from group III, comparing with group I (125 - 149 μm). It was also observed that samples B₁, C₁, D₁, E₁ and F₁ shows lesser closed pores than samples B₃, C₃, D₃, E₃ and F₃, indicating that, as porosity increased a larger internal coalescence of pores has occurred in samples from group I, probably because the smaller urea particle size of samples from this group.

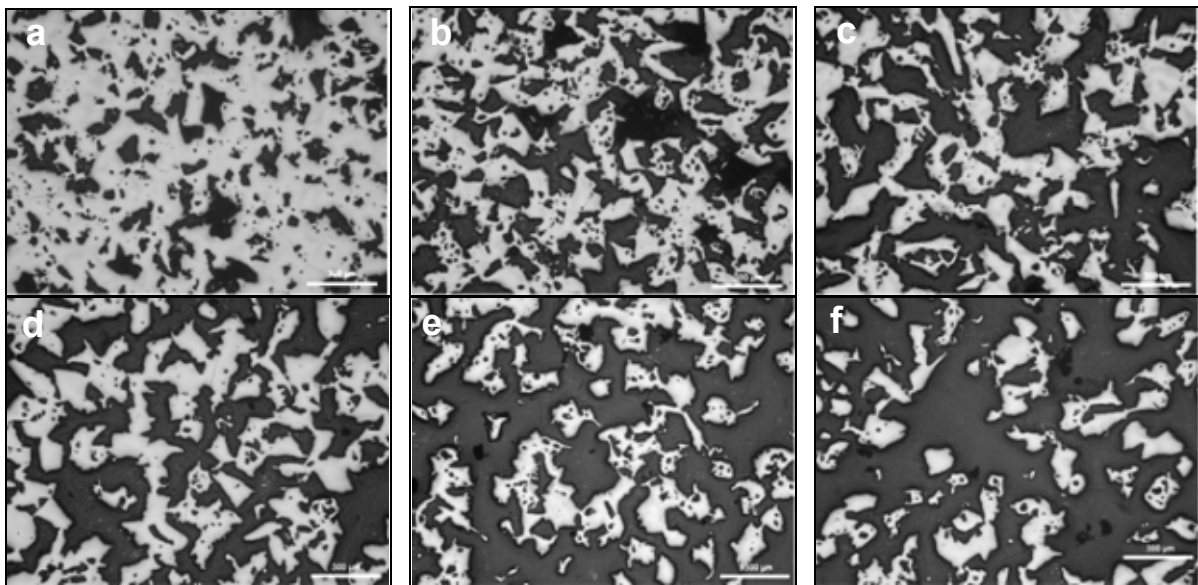


Figure 3. Optical micrographs of samples from group I (urea size 125 - 149 μm): a - A₁; b - B₁; c - C₁; d - D₁; e - E₁; f - F₁.

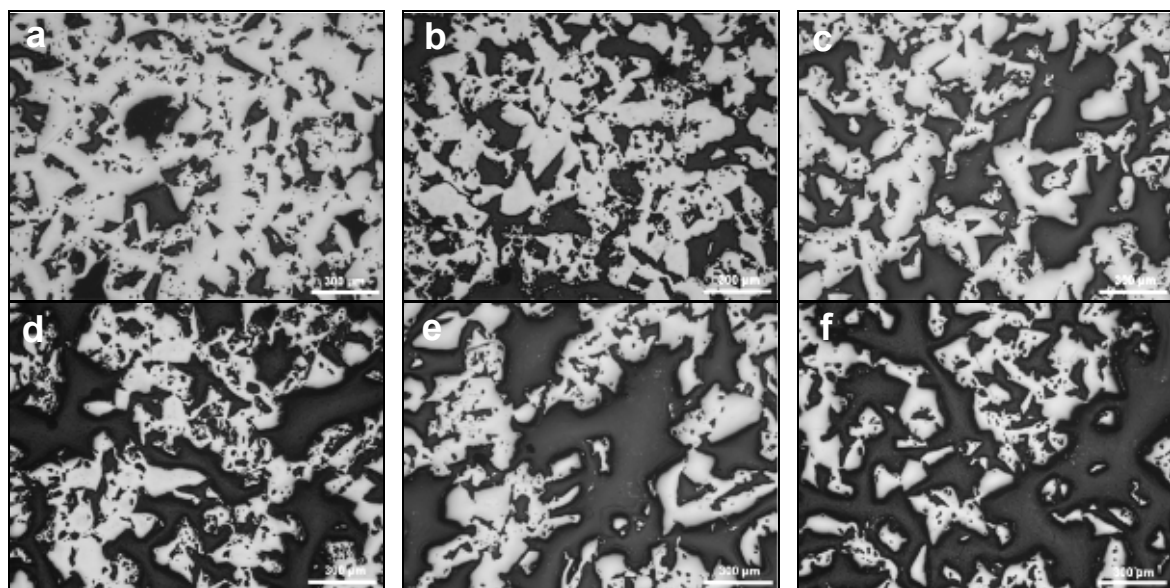


Figure 4. Optical micrographs of samples from group III (urea size 210 - 250 μm): a - A₃; b - B₃; c - C₃; d - D₃; e - E₃; f - F₃.

Although Figures 3 and 4 shows samples micrographics of groups I and III, the microstructure evolution from samples A type to samples F type was very similar for the four groups. All sponges exhibit microstructure characteristics of isotropy and uniformity along the transverse sections observed. The quantitative analysis results for pore volume fraction ranges (minimum and maximum values) for each sponge group were: group I – A₁ (36,42 ± 5,16) and F₁ (74,24 ± 3,86); group II – A₂ (37,13 ± 4,82) and F₂ (68,14 ± 4,88); group III – A₃ (34,36 ± 4,56) and F₃ (70,73 ± 6,82); group IV – A₄ (38,05 ± 5,01) and F₄ (72,30 ± 4,43). A graphic bar in Figure 5 is based on the quantitative analysis results, reporting the pore volume fraction variation with the quantity of the space holder used (urea), according to each particle size range of urea (groups I, II, III, IV).

From the graphic in Figure 5, one can observe that by increasing the amount of space holder, it increases the total porosity level, or either, there is a direct relationship between the amount of space holder and the level of porosity. It also shows that, remaining constant the amount of urea and changing its particle size range, there is not so much difference in the level of porosity, with some exceptions (15% and 30% urea with 125 - 149 μm). Thus, the particle size range has little influence on the total porosity level. However, it has influence in the pore size and pore morphology, especially with the samples with highest percentages of urea, as can be seen comparing the micrographs in Figures 3 and 4 with the correspondent percentage of urea: 20% urea (samples D₁ and D₃); 25% urea (samples E₁ and E₃); 30% urea (samples F₁ and F₃). Thus, samples D₁, E₁ and F₁, from group I, present a different interconnected porosity type, comparing with samples D₃, E₃ and F₃, from group III. It seems that the samples from group III, which have greater urea particles, have a more continuum titanium areas than the samples from group I, probably due the agglomeration arrangement of titanium particles around the urea particles. The samples with lower percentage of urea, 5%, 10% and 15%, presented the same morphology pattern in both groups I and III (Figures 3a, 3b, 3c, 4a, 4b and 4c).

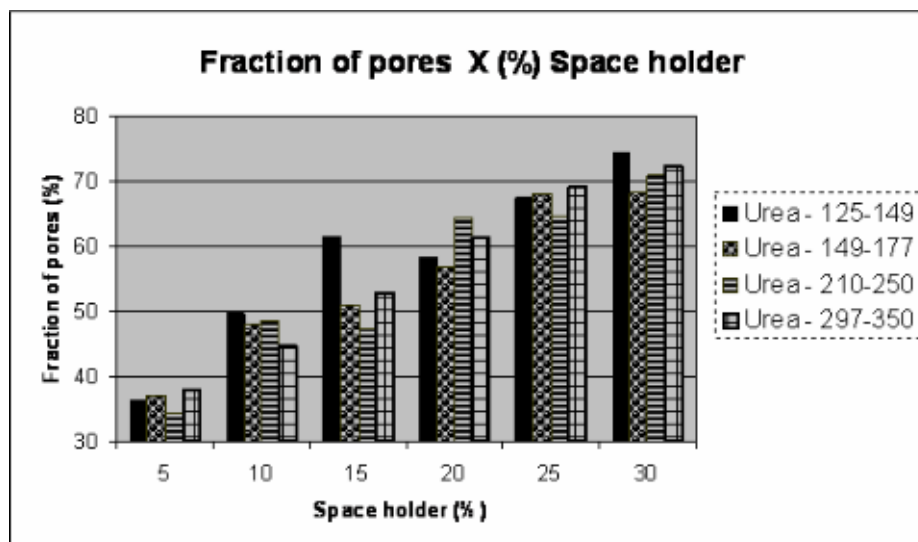


Figure 5. Volume fraction of pores related with space holder quantity for each particle size range of urea.

Figures 3a and 4a, from samples with 5% of urea, shows that the morphology of the pores can keep a direct relation with geometry of the space holder (urea). In both micrographs, pores are irregular like the urea pore morphology. For higher urea

percentages, it increases the amount of interconnected porosity and it is not possible to establish a direct relationship.

Pores can origin from particles compacting arrangement, changes in this arrangement due to the space holder elimination and from solid-state diffusion in sintering step. The combination of these three reasons gives origin to a certain type of porosity. Usually the powder compacting and sintering parameters, together with the size and morphology of the powders influence strongly the pore size and morphology. As the processing parameters remained the same for all samples, the unique difference among them is the compacting arrangement involving the contact points between titanium and urea particles. This explains why the sponge porosity morphologies were not significantly different, considering the same space holder quantity and the different size ranges of space holder groups. The continuity of this research will evaluate the influence of the titanium powder size and the powder compacting parameters, in order to study the influence of these parameters on the sponge porosities achieved.

CONCLUSION

The powder metallurgy route was successful to manufacture titanium sponges with a controlled porosity for samples with the addition of different quantities and different size ranges of a space holder material.

The sponges with porosities ranging from $34,36 \pm 4,56$ to $74,24 \pm 3,86$ presented a porosity morphology evolution changing from completely closed pores, closed and open pores and completely opened/interconnected pores, as the amount of space holder increased. All sponges exhibited microstructure characteristics of isotropy and uniformity.

Two-dimensional quantitative metallographic analysis was effective to determine the titanium sponges pore volume fraction and to allow a qualitative evaluation of pore size distribution and connectivity.

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