Characterization of porous biomaterials of 316L stainless steel made from polyethylene waxes as pore-forming agents

Caracterização de biomateriais de aço inox 316L obtidos utilizando cera de polietileno como agente porogênico

DOI:10.34117/bjdv8n10-234

Recebimento dos originais: 20/09/2022
Aceitação para publicação: 20/10/2022

Rayana Fernanda Ribeiro Lourenço
MSc in Materials Engineering
Institution: Federal University of Itajubá (UNIFEI)
Address: Av. BPS, 1303, Itajubá - MG, CEP: 37500-903
E-mail: rayanafernanda@yahoo.com.br

Toni Jefferson Lopes
Postdoc in Chemical Engineering
Institution: Federal University of Rio Grande (FURG)
Address: R. Cel. Francisco Borges de Lima, 3005, Santo Antônio da Patrulha - RS, CEP: 95500-000
E-mail: tjlopes@furg.br

Gilbert Silva
DSc in Biomedical Engineering
Institution: Federal University of Itajubá (UNIFEI)
Address: Av. BPS, 1303, Itajubá - MG, CEP: 37500-903
E-mail: gilbert@unifei.edu.br

Gerson Avelino Fernandes
DSc in Chemical Engineering
Institution: Federal University of Itajubá (UNIFEI)
Address: Av. BPS, 1303, Itajubá - MG, CEP: 37500-903
E-mail: gersonfenandes@unifei.edu.br

ABSTRACT

For biomedical purposes, the 316L stainless steel has been used due to its high mechanical strength and its biotolerability by the human body. Its porosity allows the growth of living tissue within the implant, which improves fixation to hard tissues. Porous 316L stainless steel specimens were produced by powder metallurgy with controlled porosity by the addition of different polyethylene waxes granulometries (50 and 100 μm) and concentrations (0.0, 1.0, 2.0, 3.0 and 4.0%). The elastic modulus, porous morphologies and densities of the steel samples were determined. Thus, the densities and the elastic modulus were evaluated statistically through Tukey's test. The results showed that the porosity increases proportionally to polyethylene wax concentration, but the elastic modulus decreases. The Tukey's Test showed that there are no significant differences in most samples using the two waxes at most concentrations. Range values of 1.89 to 1.51 GPa using wax with 50 μm, and 1.72 to 1.19 GPa were respectively obtained using 100

μm particle size. The highest pore size (45 μm) and the lowest elastic modulus (1.19 GPa) were obtained by use of 4.0% of wax.

Keywords: biomaterials, 316L stainless steel, polyethylene, sintering.

RESUMO

O aço inox 316 vem sendo usado para aplicações biomédica, devido sua alta resistência mecânica e por ser biotolerável pelo corpo humano. Sua porosidade permite o crescimento de tecido no interior do implante, aumentando a sua fixação em ossos. Nesse estudo os corpos de prova porosos, de aço inox 316L, foram produzidos por metalurgia do pó, tendo a sua porosidade controlada pela adição de ceras de polietileno com diferentes granulometrias (50 e 100 μm) e diferentes concentrações (0,0; 1,0; 2,0; 3,0 e 4,0%). Foram determinados o módulo elástico e as densidades dos corpos de prova , os quais foram avaliados estatisticamente através do teste de Tukey, além de ter sido verificado a morfologia dos poros por microscopia eletrônica de varredura. Os resultados mostraram que a porosidade aumenta proporcionalmente à concentração de cera de polietileno aumenta, mas o módulo de elasticidade diminui. O teste de Tukey mostrou que não há diferenças significativas na maioria das amostras usando as duas ceras. Foram obtidos valores de 1,89 a 1,51 GPa usando cera com 50 μm e 1,72 a 1,19 GPa usando granulometria de 100 μm. O maior tamanho de poro (45 μm) e o menor módulo de elasticidade (1,19 GPa) foram obtidos com o uso de 4,0% de cera.

Palavras-chave: biomateriais, aço inox 316L, polietileno, sinterização, agente porogênico.

1 INTRODUCTION

Metallic materials, compared to ceramics and polymeric materials have superior mechanical properties when used as biomaterials for replacing structural components of the human body (Orefice et al., 2012).

Among the metallic biomaterials, 316L stainless steel is the most widely used in the biomedical field because of its high mechanical strength, resistance to corrosionin body fluids and it is biotolerable, that is, it is not easily rejected by organism (Zou and Ruan, 2004).

However, this material does not induce bone growth since it does not have any calcium or phosphorous ions to promote physical-chemical binding of the implant with the bone tissue (Heimke, 1995).

Nevertheless, the stainless steel can release ions which provide the formation of a fibrous tissue capsule around the implant, which may cause deterioration of their function or of the tissue in their interface depending on the amount of movement(Zanin and Rigo,

2007). On the other hand, the 316L stainless steel has the lowest production cost among metallic biomaterials; this reason explains its wide use as bone replacement prosthesis.

One way to improve the fibro-osseous integration of stainless steel implants is to make them with high porosity. The presence of pores on their surface allows cellular growth through the pores, thereby promoting fixation of living tissue by mechanical anchorage. This tissue connection with porous implant is called biological fixation and can withstand complex loads (Cao and Hench, 1996).

The size and pore interconnectivity, as well as permeability and chemical composition of biomaterials surface have a great influence on bone formation (Jones et al., 2007; Otsuki et al., 2006). optimal pore size between 100 and 150 μm was established as the most important criterion for continued growth of bone into the pores due to cell size, needs of vascularity and diffusion of nutrients.

But, the optimum pore size is still controversial because some studies have shown a good bone ingrowth pore sizes range from 50 to 125 μm (Itala et al., 2001)

Stainless steel can be produced in porous form by techniques of powder metallurgy, which is based on pressing of powders in a closed metal cavity under pressure, and the material compacted is sintered by controlled heating (Brito et al., 2007). This technique allows the addition of pore forming agents and biocompatible substances to the metal powder, thereby increasing its biofunctionality (Dewidar et al., 2006).

The fusible component, which can also to be the porogenic agent, in a liquid phase sintering has a decisive role in determining sintering mechanisms and in the final appearance of the structure (Brito et al., 2007), mainly in the formation of interconnected pores.

The polyethylene (PE) wax, which is a low molecular weight polymer is commonly used as a meltable binder, because they have low melting point and good fluidity. In this study the PE was also used as a pore-forming agent.

The objectives of this study is to develop and characterize a 316L stainless steel, with porosity and mechanical strength suitable for use as bone replacement grafts or for bone tissue regeneration obtained through powder metallurgical process using polyethylene waxes of different particle sizes.

2 MATERIAL AND METHODS

Porous samples were supplied by Hoganas Sweden Company. They were produced through powder metallurgy process using 316L stainless steelobtained by gas

atomization.. Polyethylene waxes (PE) with different mean particle sizes were used as pore-forming agents (porogenic agents). They were supplied by Megh Industry and Trade company: Meghprint C-15020 (50 μm), and Meghwax CPB112M (100 μm) which were specified in this article as 50-WAX and 100-WAX, respectively.

The 316L stainless steel powder was mixed with the PE waxes in the following concentration: 0.0, 1.0, 2.0, 3.0 and 4.0 wt (%). The powders were manually homogenized using mortar with pestle.

Powder mixture was consolidated by uniaxial compression under constant pressure of 3 ton. For each concentration and kind of wax Seven cylindrical green compacts of 12.0 mm diameter and 8.0 mm height were prepared.

The compacted samples were heated in a resistance furnace at 450 ºC for 30 minutes to remove the waxes and to form pores. Thereafter, the temperature was increased to 1200ºC and the samples were sintered for 2 h in the presence of an inert (argon) at a heating rate of 10 ºC/min. After sintering, the 316L stainless steel compacts were cooled at 20 ºC/min.

Sintered sample morphologies were analyzed by scanning electron microscopy-SEM (Zeiss microscope model LEO-1420VP).

For each composition, the apparent density of green samples was calculated from the mass and volumes of six samples. The density of sintered samples was determined by Archimedes' methods (Shimadzu, model AY220).

The mechanical strength was determined through diametral compressive strength, according to ASTM C 496-90 standard on a universal test machine (EMIC model DL-2000) with loading speed of 0.5 mm/min. Six cylindrical samples (12.0 mm diameter and 8.0 mm height) were used for each composition.

The mean densities and elastic modulus of the samples were calculated and analyzed through the determination of the variance coefficient and multiple comparisons test for the average treatment effects of Tukey's test ($p < 0.05$) . The statistical analyses had been carried through by Statistica 6.0® software.

3 RESULTS AND DISCUSSION

3.1 MORPHOLOGY

SEM micrographs taken from the specimens sintered with the different waxes of PE are shown in Fig. 1 and Fig. 2. For both waxes investigated in this study, the microstructures illustrate an increase of porosity as the wax content increases.

Figure 1: SEM micrograph of the specimen sintered with different concentrations of 50-WAX: a) 0.0%, b) 1.0%, c) 2.0%, d) 3.0%, e) 4.0% and f) 4.0% (zoom at 3,000x).

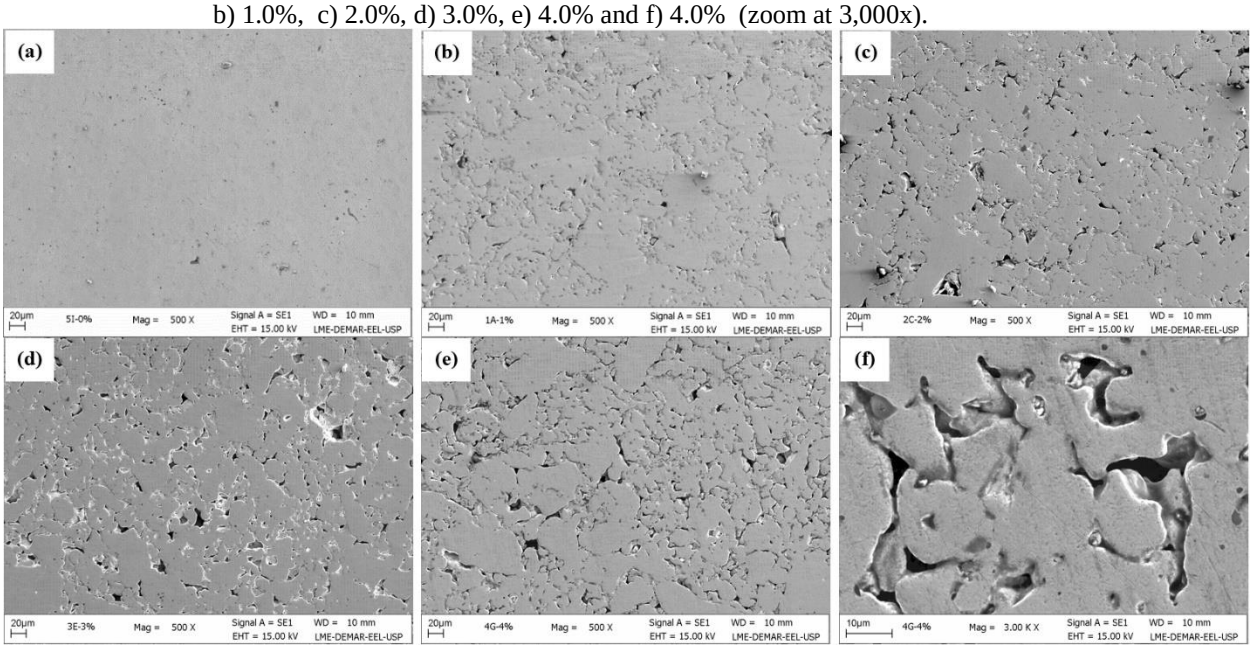
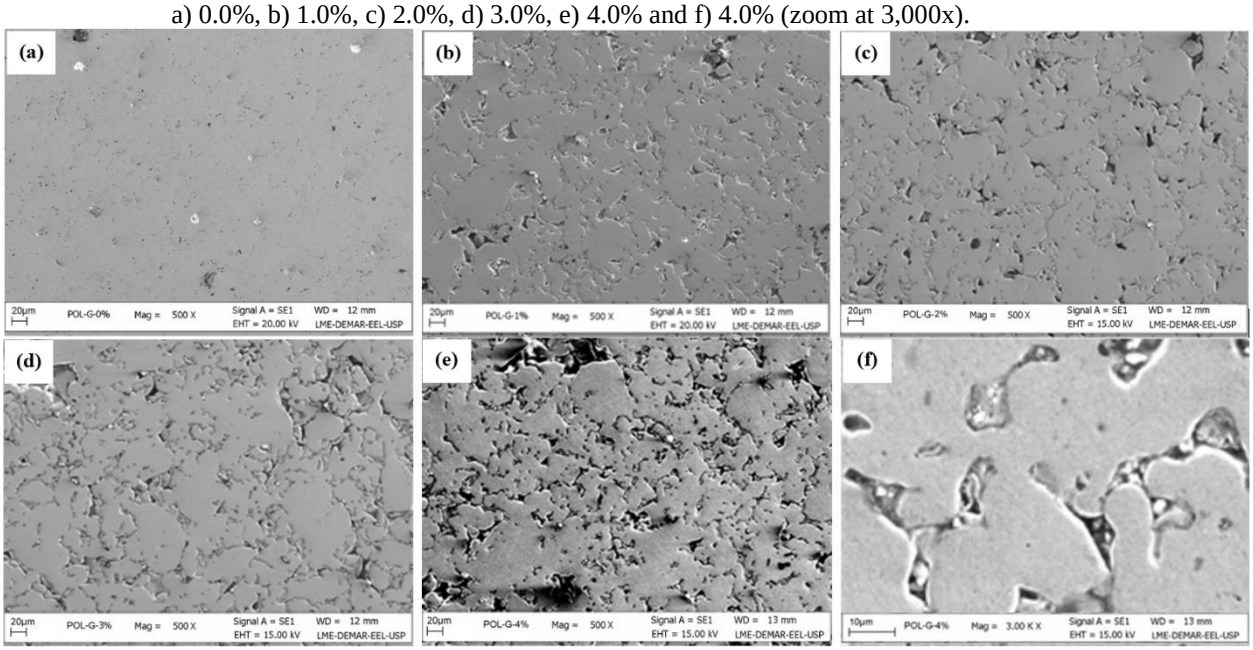


Figure 2: SEM micrograph of the specimen sintered with different concentrations of 100-WAX: a) 0.0%, b) 1.0%, c) 2.0%, d) 3.0%, e) 4.0% and f) 4.0% (zoom at 3,000x).



Irregular shape and irregular size pores with distribution was obtained. Also, by increasing of wax concentration there was a tendency for the pores to connect.

With higher compaction forces, it was possible to produce pores with more regular shape. . And the pore size distribution could be improved using equipment to mix the powders. 316L samples made with 50-WAX showed more pores- a little bit larger and deeper than those produced with 100-WAX (Fig. 1-f and Fig. 2-f).

3.2 DENSITY

The powder densification began with pressing of powder particles to create the samples (green part) and ended with their sintering. The green and sintered density values of 316L stainless steels are shown in Table 1**.** It is understood from these values (Table 1) that the density of samples increases with the sintering, which is the normal tendency.

The density of 316L stainless steel powder compressed with both 50-WAX and 100-WAX tends to decrease with increase in the amount of the waxes. This happened due the waxes acting like lubricants which facilited steel powder packing.

The use of 50 -WAX produced samples with lower density values than the use of 100-WAX. Although the particle sizes of 100-WAX were bigger than those of 50-WAX, the former has showed to have been more compressible, therefore producing samples with higher densities.

Table 1. Medium density values of green (dg) and sintered samples (d_s).

PE waxes amounts [%]	**50-WAX**		**100-WAX**	
	d_g [g/cm^3]	**d_s [g/cm^3]**	**d_g [g/cm^3]**	**d_s [g/cm^3]**
0.0	5.3941	7.1384	5.3941	7.1384
1.0	5.2726	7.0039	5.2932	7.0708
2.0	5.2260	6.9172	5.2312	6.8649
3.0	5.2071	6.8565	5.1603	6.7713
4.0	5.1570	6.8508	5.0377	6.6280

The Tukey's test for mean differences between the densities as function of waxes percentages (using a 95% confidence level) are shown in Table 2 and Table 3

Table 2. Tukey's test for green stainless-steel samples with 50-WAX and 100-WAX (coefficient of variation (C.V.) = 1.54%).

Treatments		**50-WAX**				**100-WAX**			
		1.0 %	**2.0 %**	**3.0 %**	**4.0 %**	**1.0 %**	**2.0 %**	**3.0 %**	**4.0 %**
50-WAX	**1.0 %**		0.976	0.867	0.272	1.000	0.987	0.305	**0.001**
	2.0 %	0.976		1.000	0.833	0.851	1.000	0.865	**0.009**
	3.0 %	0.867	1.000		0.964	0.629	1.000	0.975	**0.025**
	4.0 %	0.272	0.833	0.964		0.121	0.778	1.000	0.238
100-WAX	**1.0 %**	1.000	0.851	0.629	0.121		0.895	0.139	**0.000**
	2.0 %	0.987	1.000	1.000	0.778	0.895		0.814	**0.007**
	3.0 %	0.305	0.865	0.975	1.000	0.139	0.814		0.210
	4.0 %	**0.001**	**0.009**	**0.025**	0.238	**0.000**	**0.007**	0.210	

Table 3. Tukey's test for sintered stainless steel samples with 50-WAX and 100-WAX (coefficient of variation (C.V.) = 1.97%).

Treatments		50-WAX				100-WAX			
		1.0 %	**2.0 %**	**3.0 %**	**4.0 %**	**1.0 %**	**2.0 %**	**3.0 %**	**4.0 %**
50-WAX	**1.0 %**		0,834	0,256	0,217	0,950	0,323	**0,011**	**0,000**
	2.0 %	0,834		0,970	0,952	0,213	0,987	0,267	**0,001**
	3.0 %	0,256	0,970		1,000	**0,024**	1,000	0,846	**0,013**
	4.0 %	0,217	0,952	1,000		**0,019**	1,000	0,885	**0,017**
100-WAX	**1.0 %**	0,950	0,213	**0,024**	**0,019**		**0,033**	**0,001**	**0,000**
	2.0 %	0,323	0,987	1,000	1,000	**0,033**		0,775	**0,009**
	3.0 %	**0,011**	0,267	0,846	0,885	**0,001**	0,775		0,288
	4.0 %	**0,000**	**0,001**	**0,013**	**0,017**	**0,000**	**0,009**	0,288	

Statistically, the Tukey's Test (Table 2) using different wax concentrations (with 95% of significance) showed no significant differences between the densities of most green samples. At the highest concentration (4.0%), the lowest density for 100-WAX samples was registered.

This fact might have occurred because the particles of 100-WAX were larger than those of 50-WAX. The first wax had greater compressibility than the second, which produced higher density samples. In Table 3, the Tukey Test for mean density differences (in percentage of waxes) between the sintered samples (50-WAX and 100-WAX) were similar to those observed in green samples. Statistically, the Tukey Test showed that there were no significant differences among the 50-WAX concentration percentages in the samples.

However, in relation to the use of 100-WAX in the treatment of the samples, a difference was observed in the green samples. Two statistically different regions appeared; the first relative to the lowest concentration 1.0% (higher sintered density) and the second for the 4% concentration of 100-WAX (lowest sintered density).

Comparing the densities results, before and after sintering, it is possible to notice a similar average increase of almost 32.0% for all the samples.

3.3 DIAMETRAL COMPRESSION TEST

The elastic modulus was obtained by diameter compression test. Table 4 shows the effect of different content and kinds of waxes on the elastic modulus of sintered body samples.

Table 4. Effect of different concentrations waxes on the compressive elastic modulus of sintered samples.

PE waxes amounts (%)	50-WAX		100-WAX	
	Elastic modulus [GPa]	Standard-deviation [GPa]	Elastic modulus [GPa]	Standard-deviation [GPa]
0.0	1.78	0.08	1.78	0.08
1.0	1.87	0.06	1.72	0.09
2.0	1.57	0.13	1.69	0.16
3.0	1.51	0.13	1.54	0.03
4.0	1.55	0.19	1.19	0.06

The increase of wax concentration increased the porosity, which decreased the mechanical properties.

Also, for sintered samples with porosity obtained by use of 100-WAX, the results show that the elastic modulus increased for 1.0% of wax, and after it decreased with increase of wax concentration (tending to stabilizes).

Table shows Tukey's test to check the difference between the mean elastic modulus of the specimens, after sintering with 50-WAX and 100-WAX, using a 95% confidence level.

Table 5. Tukey's test for sintered stainless steel samples with 50-WAX and 100-WAX (coefficient of variation (C.V.) = 6.52%).

Treatments		50-WAX				100-WAX			
		1.0 %	2.0 %	3.0 %	4.0 %	1.0 %	2.0 %	3.0 %	4.0 %
50-WAX	1.0 %		**0.005**	**0.001**	**0.008**	0.586	0.223	**0.002**	**0.000**
	2.0 %	**0.005**		0.995	1.000	0.563	0.702	1.000	**0.000**
	3.0 %	**0.001**	0.995		1.000	0.213	0.274	1.000	**0.002**
	4.0 %	**0.008**	1.000	1.000		0.400	0.647	1.000	**0.003**
100-WAX	1.0 %	0.586	0.563	0.213	0.400		1.000	0.379	**0.000**
	2.0 %	0.223	0.702	0.274	0.647	1.000		0.489	**0.000**
	3.0 %	**0.002**	1.000	1.000	1.000	0.379	0.489		**0.001**
	4.0 %	**0.000**	**0.000**	**0.002**	**0.003**	**0.000**	**0.000**	**0.001**	

The Tukey's Test (Table 5) for mean differences between the elastic modulus as functions of percentages of waxes (50-WAX and 100-WAX) showed that the percentages of 50-WAX presented a significant difference at the highest percentage (4.0%) compared to all the other means (1.0%, 2.0% and 3.0%). Also, the treatment with 100-WAX had significant differences on the means for treatment with 1.0% of wax, especially when larger percentages of wax (2.0, 3.0 and 4.0%) were used.

4 CONCLUSIONS

In this study, the addition of PE waxes via powder metallurgy route influenced the densification behavior and the porosity of the sintered 316L stainless steel samples.

The increase of waxes content increases the porosity into stainless steel parts, resulting in a decrease in the mismatch of elastic modulus between implants and bone tissue, thereby improving its fixation.

The porosity increase was verified by the density decreased when the waxes concentration increase.

For green sample densities and compressive elastic modulus, the analysis of the Tukey's test, indicated that the addition of different waxes influenced the samples with 4.0%; that were statistically different from other treatments. And for sintered simples there was statistical difference for 1.0 and 4.0%

For both waxes (50-WAX and 100-WAX), the maximum addition of wax (4.0% wt) analyzed in this study produced body samples with the largest pore sizes and the lowest values of densities and elastic modulus.

The maximum pore size obtained (35 μm), it isn't enough big to growth of cell, that should not be less than 50 μm and should have a regular shape. Then, according to this result, it is necessary to get better porosity with similar elastic modulus values obtained in this work.

ACKNOWLEDGEMENTS

Financial support from the CNPq and FAPEMIG is acknowledged. The authors would like to thank the Hoganas and Megh companies for providing the raw materials of this project.

REFERENCES

Orefice R.L., Pereira M. M., Mansur H.S., Biomateriais: Fundamentos e Aplicações, Guanabara Koogan, Rio de Janeiro, 2012.

Zou J.P., Ruan J.M., Physicochemical properties and microstructure of hydroxyapatite-316L stainless steel biomaterials, J. Centr. South Univ. Technol. 2004; 11: 113-118.

Heimke G., Biomechanical aspects of joint and tooth replacements. In: D.L. Wise, D.J. Trantolo, D.E. Altobelli (Eds.), Encyclopedic Handbook of Biomaterials and Bioengineering, Marcel Dekker, New York, 1995, 43-68.

Zanin M.S, Rigo E.C.S, Boschi A.O., Recobrimento biomimético de hidroxiapatita com pré-tratamento álcali-térmico sobre aços inoxidáveis austeníticos, Rev. Bras. Eng. Biom. 2007; 23: 117-122.

Cao W., Hench L.L., Bioactive materials, J. Ceram. Int. 1996; 22: 493-507.

Jones A.C., Arns C.H., Sheppard A.P, Hutmacher D.W., Milthorpe B.K., Knackstedt M.A., *Assessment* of *bone* ingrowth into porous *biomaterials* using micro-CT, Biomaterials. 2007; 28: 2491-2504.

Otsuki B., Takemoto M., Fujibayashi S., Neo M., Kokubo T., Nakamura T., Pore throat size and connectivity determine bone and tissue ingrowth into porous implants: three-dimensional micro-CT based structural analyses of porous bioactive titanium implants, Biomaterials. 2006; 27: 5892–5900.

Itala A.I., Ylanen H.O., Ekholm C., Karlsson K.H., Aro H.T., Pore diameter of more than 100 micron is not requisite for bone in growth in rabbits, J. Biomed. Mater. Res.2001; 58: 679-683.

Brito F.I.G., Medeiros K.F., Lourenço J.M., Um estudo teórico sobre a sinterização na metalurgia do pó, Holos. 2007; 3: 204-211.

Dewidar M.M., Yoon H.C., Lim J.K., Mechanical properties of metals for biomedical applications using, Powder metallurgy process: a review, Met. Mater. Int. 2006; 12: 193-206.