POROUS METALLIC BIOMATERIALS PROCESSING (REVIEW) PART 1: COMPACTION, SINTERING BEHAVIOR, PROPERTIES AND MEDICAL APPLICATIONS

Ileana Nicoleta POPESCU 1, Ruxandra VIDU 2,3,*
Vasile BRATU 1

1Valahia University of Targoviste, Faculty of Materials Engineering and Mechanics, Str. Aleea Sinaia, No. 13, Targoviste, Romania
2University of California, Davis, Electrical and Computer Engineering, One Shields Ave, Davis, USA
3University POLITEHNICA Bucharest, ECOMET-UPB, 313 Splaiul Independentei, Bucharest, Romania

E-mail: pinicoleta24@yahoo.com, *rvidu@ucdavis.edu

Abstract. Over the last few decades, researchers have been focused on the study of processing using different methods of new biocompatible and/or biodegradable materials such as permanent or temporary medical implants in reconstructive surgery. The advantages of obtaining biomedical implants by Powder Metallurgy (P/M) techniques are (i) obtaining the near-net-shaped with complex forms, (ii) making materials with controlled porosity or (iii) making mechanically resistant sintered metallic materials used as reinforcing elements for ceramic/polymeric biocompatible materials. In this first part of the 2-part review, the most used and newest metallic biomaterials obtained by P/M methods are presented, along with their compaction and sintering behavior and the properties of the porous biomaterials studied in correlation with the biomedical domain of application.

Keywords: Porous metallic biomaterials, Powder Metallurgy (P/M) techniques, Compaction-Sintering behavior, Biomaterials properties, Medical applications.

1. INTRODUCTION

Metallic biomaterials such as stainless steel, magnesium, tantalum, titanium etc, have been widely used in many medical applications [1-9] for their good biocompatibility, good electrical conductivity, high strain energy (toughness), good wear resistance and outstanding combination of strength and ductility, compared with other materials. In terms of corrosion resistance, the most used metallic biomaterials are 316L stainless steel, Co-based alloys, and Ti-based alloy. Recent studies have shown that Zr-based alloys could be used as potential material for implants [2-11]. These characteristics along with relatively simple and common fabrication techniques (casting, forging, machining), or alternative conventional/advanced Powder Metallurgy techniques make metallic biomaterials suitable candidates for medical applications.

Biomaterials are used in orthopedic load-bearing application (e.g. screws, bone plates and joint replacement), as well as in cardiovascular devices and dental implants (e.g. artificial hearts, cardiac valve prostheses, vascular stents etc.), as porous scaffolds or neuro-vascular implants (aneurysm-clips). In the last years, biodegradable materials based on Mg, Fe or Zn for temporary implants such as stents and orthopedic fixation elements were also developed [1-11]. In Figure 1, the most used metallic biomaterials in the medical field are presented.

Porous materials are important for biomedical applications because they provide two major benefits for long-term clinical performances: (i) the porous structures on metallic materials allows for the bone to grow into the holes and help the artificial implant to lock in place and (ii) the rough surface acts as an interface for the stress transfer from the bone to implant. Also, porosity decreases material modulus of elasticity closer to those of human bone, which prevents the stress-shielding effect and enhances mechanical biocompatibility. The interconnected or open-cell porosity is more advantageous because it allows transport of body fluid through the implant to the healing tissue and will help adhesion of the cell while maintaining the growth of the cell into implant [3, 10, 12]. The general advantages of porous materials are property combinations and tailoring of properties [13]. In the first case, we can achieve unusual properties by combination; the porous metals can be thought of as composites and can display some of the properties of metals (such as high electrical and thermal conductivity, ductile failure at high stress, etc) with some of the properties of a porous structure (such as permeability to fluids, low density, etc) [13,14]. The second advantage refers to the properties that can be tailored to suit a certain need of a particular application and depends on the properties of both constituents: the metal in dense (non-porous) form, the metal with a porous structure. As a result, small structural changes can be used to adjust the properties (within certain limits), allowing the precise properties that are required to be obtained [13-15].
Porous metallic biomaterials are used as porous implants in living tissues. There are three distinct types of porous implants: (1) partly or fully porous-coated solid substrates; (2) fully porous materials; (3) porous metal segment joined to a solid metallic part [15-18]. Implants are designed with solid cores and porous coating when mechanical strength is required to stand physiological loads [15]. Porous metallic biomaterials can be made using different powder-based fabrication methods of porous alloys, such as: Conventional Press- and Sinter Techniques [1, 3, 16, 19, 20-36] combined or not with advanced P/M methods. Considering the advanced P/M techniques, many other methods have been developed over time to obtain porous or non-porous biomaterials, such as: Hot Isostatic Pressing (HIP) [1, 3, 13, 14, 22, 34-42], Porous Coatings such as: Vacuum Plasma Spraying (VPS), or Spark Plasma Sintering (SPS) [13, 14, 22, 40, 43-46], Microwave Sintering [10, 22, 47, 48], Reactive Sintering (including Self-Propagating High Temperature Synthesis, SHS) [3, 14, 49-52], Additive Layer Manufacturing (Selective Laser Melting/ Sintering (SLM/SLS) or Electron Beam Melting (EBM) [5, 10, 13-15, 20, 22 , 36, 40, 53-56]. Additionally, advanced P/M techniques also use Metal Injection Molding (MIM) [13, 18, 22, 36, 56-61], Space Holder Method [3, 13, 15, 20, 39, 48, 62, 63], Foaming of Metallic Powders [3, 10, 13-15, 20, 39], and Replication Method [14, 15, 20].

All these types and properties of the metallic biomaterials studied in correlation with the biomedical domain of their applicability are important aspect of the study of materials and are briefly presented in the following sections of this paper.

2. METALLIC BIOMATERIALS USED IN MEDICAL APPLICATIONS

Iron-based alloys are considered very good candidates for biodegradable medical materials [1]. Alloys of interest as biodegradable medical materials due to the fact that neither the corrosion rates nor the mechanical properties of pure iron do not meet the criteria required for medical use. Therefore, alloying can improve both corrosion rate and mechanical properties [64]. The Fe-Mn system is investigated as a promising material for biodegradable stents [1, 4, 29-31], and Fe-P system seems to be interesting for the temporary replacement of bones [32]. Both phosphorus and iron are biogenic elements, so that the human body should tolerate well the implant itself and the decomposition products. Phosphorus brings into the picture an additional beneficial effect between osteogenic cell populations and Fe-P alloy. P-alloying of Fe allows controlling mechanical properties and corrosion rate [27].

Currently, metallic biomaterials used for long-term implantation are SS 316L corrosion resistant alloys as the most widely used alloy and it is often considered the standard reference for mechanical properties in developing new biomaterials. Over time, SS 316 L has been used as implant in medical field for joint replacement, screws and bone plates for fracture fixations. According to Dewidar's study [16] the lifetime of hip synthetic joints is about 10 years, due to polymer degradation, wear of metallic materials or other factors. Because the growing number of young people (up to 40 years of age) with osteoarthritis, the demand for such implants that have a life more than 25 years has increased [16].
**Co-Cr alloys** are used for artificial joints including hip joints and knee due to their biocompatibility and high corrosion resistance and wear-resistance. Co-Cr alloy has been widely used in the manufacture of stents and other surgical implants as Co-Cr alloy demonstrates excellent biocompatibility with blood and soft tissues. Cobalt-chrome has a very high specific strength and is commonly used in dental implants, and orthopedic implants [5]. In comparison with other biomaterials used in medical applications such as stainless steel and Ti alloys, the wear resistance of Co alloys is higher. The head of the joint in the artificial hip joints is exposed to wear. Thus, high strength and ductility Co alloys, such as Co-Cr-Mo alloys were used in hip joints. To increase the resistance to wear of these alloys, carbide has been dispersed in Co alloys [5, 65].

**Titanium alloys** are the most attractive metallic materials for biomedical applications. Examples include pacemakers, cardiac valve prostheses, artificial knee joints, bone plates, artificial hip joints, screws for fracture fixation and valve of artificial heart (Figure 1). Titanium alloys with aluminum and vanadium (Ti-6Al-4V) have been widely used as implant materials, but certain studies revealed that the release of the Al and V ions can be harmful to the human body [5, 12, 17]. Consequently, other alloy stabilizers were searched to decrease the hostile biological impacts. Also, introducing biocompatible alloying element could improve the mechanical properties of the implant. That is why V and Al-free alloys have been announced for implant applications, based on the Ti-6Al-4V (ASTM F 1295, ISO 5832-11) implants. New alloying elements in Ti alloys are tantalum (Ta), tin (Sn), niobium (Nb), and zirconium (Zr) [12, 66], to form new biocompatible Ti based alloys as: Ti-6Al-7Nb (ASTM F1295, ISO 5832-11), Ti-13Nb-13Zr (ASTM F1713), and Ti-12Mo-6Zr-2Fe (ASTM F1813-97) [5, 66]. The choice of these new alloying elements is based on the fact that they are non-cytotoxicity elements that have revealed good corrosion resistant and biocompatibility, and they form solid solution with Ti. [12, 66]

**Nickel-Titanium Alloys** have the property to trans-form plastically deformed specimens in to their original shape by just heating it. This feature is called the shape memory effect. Some biomaterials applications where the shape memory effect is required are as follows: orthodonty wires, dental bridges, self-expanding stents, and orthopedic prostheses to artificial heart.

**Porous NiTi shape memory alloys** have recently attracted extensive interest for their potential use as biomedical materials. Stress–strain behaviors of porous NiTi alloy [21] fabricated by element powder sintering in argon atmosphere and investigated by compression and flexural tests has indicated that the ultimate compressive strength and the flexural strength of the porous NiTi alloy depended on the densities of the porous NiTi alloy and the sintering conditions [19, 21].

**Nickel-Chrome based Dental Alloys.** At present, Ni-based alloys are increasingly used for economic reasons as substitutes for precious metal dental alloys. In terms of their biocompatibility, although new requirements and limitations have been imposed by the European Union on the use of dental alloys, especially Ni-Cr alloys, the demand for such materials is increasing.

Thus, in this context, recent studies and researches have been made regarding corrosion behaviour, cytotoxic effects or inflammatory response on 8 Ni-Cr dental alloys [67]. The results of research have shown that the amount of nickel ions released is higher than EU required limitation, but the corrosion behavior was poor. Also, biological tests on Nickel-Chrome based dental alloys revealed that: there are no cytotoxic effects on Hella and L929 cells, nor do they have a pro-inflammatory response in endothelial cells [67].

**Tantalum alloys.** The open-cell porous Ta materials are best suited for use as coatings or non-load-bearing implants because of their low mechanical properties. Recent studies (e.g. in vitro, in vivo, and clinical) have demonstrated that tantalum is a bioactive metal that recommended it as a promising metal for load-bearing orthopedic applications [68]. Tantalum is a ductile, hard, and chemically resistant material with good apposition to human bone. Tantalum spontaneously form a passive oxide layer with a very good adherence to the metal, which facilitate the bone in-growth under in vivo conditions via the development of bone-like apatite that promotes hard-and soft-tissue adhesion [69]. Generally, both bulk form (usually porous) and in coating form are available for the tantalum based implants, depending on the required application [62].

**Magnesium alloys** are of great interest as new degradable biomaterials. The foremost advantages of magnesium alloys used as provisional biomaterials are their biocompatibilities and good mechanical properties. The magnesium and Mg alloys are lightweight metals (1.74 to 2.0 g/cm³). The elastic modulus (41–45 GPa) is close to that of the bone while the fracture toughness of magnesium is greater than ceramic biomaterials, which avoids the stress shielding effect. Magnesium is the fourth most abundant cation in the human body and it is essential to human metabolism. Research directions of the biomedical magnesium alloys are built on both self-designed biomedical and industrial magnesium alloys system [70].

**Zinc alloys.** The newly developed Zn-xCu binary alloys (x = 1, 2, 3, and 4 wt%) could be promising candidates for biodegradable cardiovascular implant application due to their excellent combination of strength and ductility, low degradation rates, acceptable cytotoxicity and good antibacterial property [71]. In the work of Vojtech et al. [6], Zn-Mg alloys containing up to 3 wt% Mg were studied for their mechanical and corrosion properties and were compared with pure Mg, casting Zn-Al-Cu and AZ91HP alloys, as potential bio-degradable materials. Mechanical properties (tensile and hardness) were...
discussed in correlation with the structural features of these alloys and they found that the corrosion rates of the Zn-Mg alloys were lower than those of pure Mg and AZ91HP alloys. Zn-Mg alloys corroded at rates of the order of tens of microns per year, while the corrosion rates of Mg and AZ91HP alloys were of the order of hundreds of microns per year. Zinc toxicity was assessed from the corrosion performance and it was found that the toxicity is minor compared with the tolerable biological daily limit of zinc [6].

Zirconium (grade 702, 99.2%) is not commonly used as a medical material, but has several properties in common with titanium and it is chemically closely related to it. For example, both are transition metals with similar outer shell valence electron structure. They both are typically covered by thin, chemically stable, surface oxides. However, most chemical and physical properties, such as oxidation rates, transport properties, crystal structures, and water interactions of the two metals and/or their oxides differ quantitatively [72].

Zr–Ru alloys with various content of Ru were proposed and fabricated for new biomedical Zr alloys with ultralow magnetic susceptibility, enhanced mechanical properties, improved corrosion resistance, excellent biocompatibility and Magnetic Resonance Imaging (MRI) compatibility. Li et al. [11] have demonstrated that both the Yield Strength (YS) and the Ultimate Tensile Strength (UTS) of the Zr-Ru alloys are higher than that of pure Zirconium. Also, Ru alloy additions improved the corrosion resistance of pure Zr. Furthermore, the breakdown potentials (Etran) of Zr-Ru alloys are much higher than that of pure Zr, indicating the enhanced pitting corrosion resistance by adding the Ru alloying element. Among the Zr-Ru alloy series, Zr-1Ru is the optimal Zr-Ru alloy system as therapeutic devices under MRI diagnostics environments [11].

Niobium alloys. Nb and Zr are desirable elements in biological systems and biomedical applications thanks to their biocompatibility, resistance to corrosion, mechanical integrity and ionic cytotoxicity. The synthesized nano/sub-micron grain structured Nb-Zr alloy exhibited higher corrosion resistance in Simulated Body Fluids (SBF) medium, implying that these alloy specimens can be used as excellent implant materials [73].

Gold and gold alloys are useful metals in terms of stability, corrosion resistance, odontotherapy (because of its long-lasting). Since gold alloys have more mechanic property than pure gold, it is subjected to alloying process. These alloys consist of 75% or more than 75% gold, the remaining is comprise of noble metals. Copper increases strength, platinum also increases strength, but if it add more than 4%, the processing of this material gets difficult due to increase in melting temperature. Soft alloys which have more than 83% gold are used as packing material [5].

Gold is distinctly different from the other two metals (Zr and Ti). It is a noble metal which does not form surface oxides (except under extreme conditions). Thus, it exposes a real metallic surface to the biological environment, in contrast to titanium and zirconium which expose oxide (i.e. ceramic) surfaces. The surfaces of gold, zirconium and titanium have in common the fact that they are chemically very stable and highly corrosion resistant in most environments and therefore products released from the implants would probably not influence the biological response [72].

Platinum is inert. Unlike other metals, such as copper and nickel, platinum does not decompose inside the body and does not cause allergic reactions. Platinum can be fabricated into very tiny, complex shapes and it has some important properties not shared by base metals [74].

Platinum alloys have low corrosion rates, high biocompatibility and good mechanical resistance which make them suitable for medical applications [75]. Platinum biocompatibility makes it ideal for temporary and permanent implantation in the body, a quality which is exploited in a variety of treatments in addition to the heart implants, such as: catheters containing platinum components to detect the cardiac arrhythmia, Pt-Ir alloy rings for shocking electrodes, guidewire with coiled Pt-W tip and marker band (Pt, Pt-Ir or Au) of balloon-mounted stent used in percutaneous transluminal coronary angioplasty [74].

3. CONVENTIONAL PRESS-AND-SINTER METHODS OF POROUS ALLOYS

Powder Metallurgy (P/M) techniques has the advantage, in comparison with casting methods, to form near-net-shaped products and also to allow obtaining porous materials with tailored porosity, pore size and pore distribution [3]. The well-known technological steps of P/M are obtaining the raw material, dosing and homogeneous mixing of powders followed by their consolidation. Mixing depends on various factors, such as those related to powder characteristics, especially the different component densities. Consolidation can be accomplished by pressure-based densification (e.g., die pressing), densification based on sintering (e.g. MIM) or densification combining both press and simultaneous heat treatment (HIP). Following the application of P/M techniques, 80% densification of the powders can be obtained, resulting a dense, non-porous material. In this case, PM is advantageous to other techniques for obtaining materials with complex configurations at the final shape, so minimizing costs by eliminating intermediate operations.

Powder metallurgy has developed in the medical field as a technique alternative to conventional ones, especially in the production of materials for bone implants in surgery, such as in orthopedics and dentistry. In the latter two areas it is necessary load bearing ability and especially a rigid fixation of the implant to the bone [10].

The porous implants provide a more efficient fixation compared to dense materials due to the bone host via the growth of new bone tissue into the pores.
The porous implants provide a better fixation of implants to the bone host via the growth of new bone tissue into the pores.

Porosity resulting from powder metallurgy processing gives a decrease in the Young's implant module, and surrounding bone, thereby improving the fixation [16].

Sintering process is a key process in the P/M technology because furnace atmospheres affect the sintering development and the material being treated. The main mission of the process is to prevent the metal from coming into contact with the air. The properties of the porous or dense implants using P/M technique are dependent on processing parameters and the sintering atmosphere [16]. In addition, P/M could be advantageous for metallic biomaterials like Ti, Mg or Nitinol, which are difficult to machine by conventional methods [52, 65].

**P/M of Porous 316L Stainless Steel.** Montasser Dewidar [16] studied the effect of sintering parameters on densification behavior, micro-structure, properties (mechanical and tribological) of Porous SS 316L, with possible utilization in artificial knee or hip joints.

In Figure 2, the processing steps of fabrication of porous 316L stainless steel is schematically presented.

In Figure 3, the compressibility curve of 316L stainless steel powder is presented, showing that low applied pressures (between 150 MPa and 350 MPa) have been used to obtain samples with high porosity [16]. The compacted powder (SS 316L powders without lubricant addition), increases with increasing of applied pressure. Was obtain a minimum density (4.4 g/cm³) for applied pressure of 150 MPa (corresponding to 55% of theoretical density) and the highest value of density from experimental study, at 350 MPa was 5.12 g/cm³ (corresponding to 64% of theoretical density) [16].

In Figure 4 the effect of sintering temperature and sintering atmosphere on the compressive yield strength (a), compressive modulus of elasticity (b), and hardness (c) of 316 L samples compacted at 350 MPa are presented. These results [16] led to the following conclusions:

(i) the sintered SS 316L at the all three sintering temperatures had porosity values ranging from 39.25 % to 11.87 %;

(ii) the mechanical tests showed that as the porosity increases, both the modulus of elasticity and the strength of the material decrease;

(iii) the most efficacy sintering atmosphere used in processing of porous 316 L stainless steel (with highest strength, wear resistance and hardness values results obtained) was nitrogen atmosphere and

(iv) the optimum sintering temperature in nitrogen atmosphere was 1300 °C.

These mentioned above processing parameters and optimum results (mechanical properties, density and wear resistance) make the obtained porous 316 L SS suitable for use as biomaterial in hard-tissue applications.
P/M of Biodegradable Fe-Mn. Hermawan et al. [4, 29, 30] was the first researchers that studied biodegradable iron-manganese alloys with future applicability in the medical field, as implants in the cardiovascular system.

Hermawan [30] obtained the Fe-Mn alloys by P/M processing, and he pursued the fulfillment of the following targeted properties: (a) good mechanical properties (yield strength more than 190 MPa, maximum elongation higher than 20%); (b) physical properties (non-ferromagnetic and magnetic properties comparable with SS 316L), and (c) controlled degradation process and biological performance (non or less toxic elements, etc.). One of the reasons for choosing the manganese as alloying element was that it is an essential element of the proper functioning of living organisms, it is nontoxic, and as an alloy, Fe-Mn alloys are nonmagnetic. In Figure 5 the schematic P/M processing route of Biodegradable Fe-Mn alloy for biodegradable stents applications is presented [30].

![Figure 4](image1.png)

![Figure 5](image2.png)

Unauthentifiziert | Heruntergeladen 10.09.19 09:01 UTC
exception of Fe–20%Mn alloy. In comparison with pure iron, the corrosion rate was slightly higher. The tests’ results on the four alloys showed that the optimum alloy for biodegradable stent application is Fe–35%Mn alloy. In terms of mechanical properties Fe-30Mn and Fe-35Mn alloys (the alloys that contained single austenitic phase) are closest to 316 L stainless steels. In addition, the iron based alloys with 30 and 35 % Mn have the degradation rate two times higher in comparison with pure iron, and also they have low inhibition in the metabolic activity of fibroblast cells during the cell viability studies. All these results make these obtained Fe-Mn alloys suitable for application as coronary biodegradable stent in vitro and in vivo conditions.

The Fe-P biomaterials prepared by powder metallurgy process (see Fig. 5b) starting with a new class of powders, i.e. carbonyl-iron particles coated with a layer of phosphates, were studied by Kupková et al. [27]. The aim of their work was to investigate how the phosphorus addition in an amount of 0.5 wt% and 1.0wt% to the iron powder as a coating layer affected the microstructure of sintered samples and their corrosion behavior in Hank’s solution.

The obtained microstructure (Figure 6) can be described as a spatial network of globalized iron particles or iron oxides surrounded by a solidified liquid phase consisting of a variety of ferric phosphates [27].

The results showed that the addition of 0.5 by weight of P give in a positive displacement of the corrosion potential at steady state and the addition of 1.0% by weight of P resulted in a slight negative displacement of the corrosion potential of the electrodes submerged in Hank’s solution with respect to the corrosion potential of un-deped iron.

It was found from the electrochemical experimental results that the corrosion rate is higher for Fe-1.0P material in comparison with Fe-0.5P alloy.

A porous structure of the sintered iron sample allowed the rate of degradation to be increased relative to the "bulk" iron.
The Fe-0.5P sample showed the lowest corrosion tendency with a corrosion rate similar to that of the Fe-1.0P sample. Also they proposed future investigations to better understand the degradation of PM iron-phosphorus biomaterials in simulated body fluids, as well as to verify the practicality of the fractal geometry for the analysis of corrosion phenomena [27].

Commercially pure (CP) Ti and Ti based alloys can be obtained from powders through a variety of techniques, such as: press-and-sinter, press-sinter-and-hot-work, hot isostatic pressing, extrusion or direct roll compaction of loose powders, hot-press-and-machine and metal-injection-molding-and-sinter. The press-and-sinter route is the most attractive approach due to its simplicity and cost. The main difficulties of processing by casting when molten Ti reacts with most metallic and non-metallic materials used as crucibles for melting, and high purity argon atmosphere is required in the crucible and in the mold during melting and casting, make Ti P/M attractive.

Compaction of titanium powder can be carried out at room temperature using standard presses in closed steel dies. For a better compaction, the irregular shape of sponge fines is recommended. The compaction behavior of sponge Ti powder shows a rapid increase in green density with compaction pressure up to 690 MPa, after that remaining constant. At 690 MPa the resulting green density is above 80% of the theoretical density. Similar compaction behavior and pressing characteristics have been observed for fine electrolytic titanium powder (250 μm), coarse electrolytic titanium powder (250–1000 μm), and fine titanium powder (< 30 μm) reduced by calcium hydride (CaH2) except that the 80% theoretical density occurred at a lower compaction pressure, 500 MPa [24]. The pressing characteristics of a powder mixture, for the preparation of alloys via a blended elemental (BE) route, are, in general, determined by the base titanium powder, but may also be affected by the form of the alloying element powders. In the literature, there are numerous experimental data regarding the effect of particle size and size distribution on the green density [25]. The high green density obtained from titanium powder or BE powder mixtures at pressures < 700 MPa by cold pressing ensures good green strength, which is essential for the safe and rapid ejection of green shapes from various die cavities and their subsequent handling prior to sintering. Cold-pressed titanium green parts was sintered in the past in argon at 50 mm mercury pressure, but nowadays they are usually sintered in vacuum at pressures of the order of the 10^2 Pa because of the chemical affinity of titanium for oxygen, nitrogen, carbon and hydrogen [26].

Torres et al. [33] have researched on Porous Titanium for Biomedical applications obtained by Conventional P/M process, and studied the influence of pressing and sintering parameters on structure and mechanical characteristics of CP Ti grade 4 porous specimens. The microstructure was investigated from porosity point of view (the type, shape, size, and number of pores).

The mechanical tests consisted in compressive yield strength, and conventional and dynamic Young’s modulus investigations. The elastic modulus, both conventional and dynamic, and the yield strength showed the same behavior. In the middle part of the cylindrical samples (the sample results from pressing at 38.5 MPa and sintering at 1000 and 1100 °C ) resulted a better stiffness. An assessment of porosity and elastic modulus on a three-part cylindrical sample showed that it is possible to obtain a titanium sample of graduated porosity that can be used in implant design. This approach opens up a new possibility to solve the bone resorption problems in association with the stress-shielding phenomenon. Bolzoni et al. [34] studied the processing of hydride-dehydride elemental titanium powder by conventional Press and sinter method and hot-pressing techniques. For the conventional P/M route, the green samples were subjected to uniaxial cold press at 700 MPa using a floating die and zinc stearate as a lubricant for the walls of the die. The sintering parameters used were: sintering temperatures ranging from 900 °C and 1300 °C, with a step of 200 °C for 2 hours, in high vacuum tubular furnace (the minimum vacuum level was 10^-5 mbar), using a heating and cooling rate of 5 °C/min.

They obtain dense titanium products with properties similar to those of the wrought materials which should reduce production costs and eventually extend the use of titanium in new industrial applications.

Vasconcellos et al. [17] et al. [17] assessed the in vivo response of rabbit tibia to porous titanium scaffolds and dense titanium samples prepared by powder metallurgy. Porous titanium scaffolds were prepared from a mixture of titanium / urea powder having a weight ratio of 80 to 20 percent. The blend was uniaxial pressed under 100 MPa in a stainless steel mold and then isostatically pressed below 200 MPa. The resulting samples were sintered at 1200 °C / 1 h under vacuum (10^-7 torr) and then heat treated at 180 °C / 2h in air to remove the spacer particles.

These parameters were used to prepare dense titanium samples also. The results demonstrated that both titanium devices presented osseointegration, with porous titanium scaffolds showing bone ingrowth in the pores, which augmented over time. These porous structures have promising potential as a biomaterial implant system, considering their interactions with bone cells [17]. Bone growth in porous metal depends on several factors, such as (i) surface porosity, (ii) stability of micromorphism (iii) degree of micromorphism between the implant and bone, whether the host bone is trabecular or cortical and (iv) the presence of gaps between the implant and the bone surface. In their study [17], the tight press fit of the implants into the osteotomic cavity was aimed at minimizing the gap and micro-motion of the implant. Osteointegration is strongly affected by (a) the
morphology of the porous structure and (b) the degree of bone ingrowth seems to depend on the size of the pores.

Few research studies have been published on the effect of Mn on Ti-based alloys, especially on second generation alloys such as Ti–13Nb–13Zr, Ti–35Nb–7Zr–5Ta, Ti–Mo or Ti–29–Nb–13Ta–4.6Zr [63, 76]. One way to obtain Ti alloys with lower elastic modulus is to use metallic foams by a powder metallurgy route. The use of space holders as a means of tailoring the morphology and properties, particularly stiffness, of titanium foams produced by the PM route has attracted significant recent interest.

Development of titanium foams with low Young’s modulus as a potential implant by P/M techniques was made by Guerra et al. [63]. In their work, the effect of manganese on the mechanical properties of compression of Ti-13Ta-30Nb-xMn foams (x=2-6% by weight) has been studied. Titanium alloys obtained from mechanical alloying were processed to produce foams (see Figure 7) using ammonium hydrogen carbonate with a 35 mm average particle size (50% v/v) as a space-holder. Powders and space holder were mixed and uniaxial pressed to form compacts. The space support was removed by heating the green parts at 180° C for 1.5 hours before sintering at 1300° C for 4 hours in argon.

The modulus of elasticity of the foam was lower than that of pure Ti and the yield strength increased with the addition of Mn.

![Figure 7. SEM images of foams: (a) Ti–30Nb–13Ta–2Mn; (b) Ti–30Nb–13Ta–4Mn; (c) Ti–30Nb–13Ta–6Mn; (d) small pores produced by sintering process [63]](image)

The increasing number of patients with cardiovascular disease has determined, in the last years, development of extensive researches in developed of different types of biomaterial including shape memory alloys (SMA) used as stents.

**Porous NiTi shape memory alloy** fabricated by element powder sintering in argon atmosphere were investigated by Zhu et al. [21] using compression and flexural tests. The results showed that the maximum compressive strength and flexural strength of the porous NiTi alloy depend on the NiTi porous alloy densities and the sintering conditions. In compression experiments, the pre-strain could recover completely while it was less than 2%.

Recovery of the NiTi porous alloy was based on the unique NiTi phase and pore structure. The pores have adverse effects on the recovery of the NiTi alloy form under experimental conditions.

**Powder Metallurgy fabrication of Co-Based Alloys** for Biomedical Applications [65] brings several advantages such as reduced machining, possibility of alloying by high-melting elements, preparation of nanocrystalline materials with enhanced mechanical
properties or producing of porous alloys with improved ability to integrate into issues. Cobalt-based materials with improved properties have been fabricated by means of powder metallurgy.

When compared with conventional alloys, the samples made by P/M process were found to result in good mechanical properties (high tensile and hardness, fatigue strength) and from structural point of view, fine grain size and more uniform structure that is less prone to segregation.

The P / M processed alloy also offers the same relative benefits even after exposure to high temperatures typically associated with the annealing or forging of hard-tissue implants [77].

In the work of Marek et al. [65] they focused on the basic preparation of Co28Cr6Mo0.25C by two methods of powder metallurgy. In the first method, pure metal powders were blended, pressed and sintered in a vacuum furnace. The second applied technology consisted of mechanical alloying using a planetary ball mill and compaction by sparking plasma sintering technique.

The preparation by conventional pressing and sintering technique consisted of a mixture of elemental powders of defined purity (Co from MERCK, 99.9%, 1 μm; Cr from Sigma Aldrich, 99.5%, 44 μm; Mo from Penta, 99.9%, 44 μm) and carbon (graphite, 10 μm) and then pressed at 630 MPa in 10 mm diameter green bodies, sintered in a vacuum induction furnace at 1250°C and 1350°C for 4, 8 and 12h. The dependence of the microstructure, phase composition and mechanical properties of samples prepared under the manufacturing conditions (milling parameters, sintering temperature, etc.) was studied.

The results were compared with the properties of the commercially available cobalt alloy used for medical applications. It has been found that simple cold compaction and subsequent sintering did not result in the desired phase composition and therefore the alloys exhibited a high porosity which was responsible for lowering the functional properties. Better results were obtained by using a combination of mechanical alloying and sparking plasma sintering. Thus, the Co28Cr6Mo0.25C alloy exhibited superior mechanical properties compared to the conventional molded counterpart.

Open-cell Porous Tantalum structure, with an appearance similar to cancellous bone (Zimmer Inc, Warsaw, IN) is made by pyrolysis of thermosetting polymer foam, which creates a low –density vitreous carbon skeleton with 98% porosity [68]. Trabecular metal is a portable structure of open porous tantalum, with repeated dodecahedrons, similar to the spongy bone. The pore size and mechanical properties of the Trabecular Metal can be adjusted by modifying the coating thickness of tantalum (40-60 mm). Current Trabecular Metal implants for hard-tissue applications have a porosity of 75-85% with a pore size between 400 and 600 μm. The open-cell porous Ta materials are best suited for use as coatings or non-load-bearing implants due to low mechanical properties. Porous tantalum structures can be prepared by applying the sponge impregnation technique and the powder metallurgy method [78].

Pore structure and morphology of the porous scaffolds evaluated by SEM showed that the porosity of the porous scaffolds was 66.7% and the pore size was 300-600μm, presenting a three-dimensional interconnected network (3D) to the cellular structure.

The compressive strength was 61.5±4.5MPa and the elastic modulus of the scaffolds was 2.21±0.16 GPa. The biocompatibility results show that porous Tantalum foam scaffolds can significantly promote the proliferation of rat osteoblasts and that the material was not toxic [78].

Porous Magnesium scaffold or foam for tissue engineering or drug deliver application can be obtained by various techniques such as powder metallurgy, laser perforation and unidirectional metal / gas eutectic solidification method (called GASAR process), and negative salt-pattern molding process [79]. The most common solid processing technique for the synthesis of magnesium materials is the powder metallurgy technique [2, 80]. The Mg-Zn alloy was prepared by powder metallurgy of Mg, Zn and Y powders [80]. The powders were mixed manually and compacted uniaxally at 530 MPa to form cylindrical green compacts and then sintered in a tubular furnace under an argon atmosphere.

The sintering temperature was chosen according to the phase diagrams of the individual alloys (MgZn5: 575 °C, MgZn10: 405 °C, MgY5: 600 °C) and the sintering time was 2 hours. For MgZn5 and MgZn10 samples, sintering was prolonged up to 4 hours or 24 hours to observe the influence of sintering time on porosity and mechanical properties. The pore forming agent (NH4)2CO3, which was used in some experiments, was removed prior to sintering by thermal decomposition [80]. Magnesium alloys prepared with P / M without a pore forming agent have an adequate elastic modulus and an ultimate compressive strength superior to the natural bones (Figure 8).

Figure 8. Compressive strength and modulus of elasticity of prepared Mg-Zn samples [79]
The porosity of the samples without the pore forming agent is up to 10% of the volume fractions. About 90% of pores have less than 10 μm diameter.

The number of pores with an equivalent diameter of 200 μm and a pore area fraction increases (18–48 % of the volume fractions) by addition of (NH4)2CO3 pore forming agent to the MgZn5 and MgAl3Zn1 alloys. The ultimate compressive strength reached ranging 203 to 236 MPa. With the increase in porosity after addition of (NH4)2CO3, the compressive strength decreased to 61 MPa [80].

4. CONCLUSIONS

The first section of the paper presents various types of metallic biomaterials (both in porous or dense state), used over time or in a laboratory testing stage, emphasizing their characteristics according to a definite medical field of use. The Conventional and Advanced Powder Metallurgy techniques used to make biocompatible and/or biodegradable materials and the advantages of using P/M techniques in comparison with other conventional techniques (i.e. casting methods) have been also concisely presented.

The advantages shown by PM techniques over the conventional methods deals with the control of porosity, pore size and pore distribution. The importance of porous structures of metallic materials is that they provide a better anchoring effect of the artificial implant in the bone by growing a new bone tissue into the pore spaces of the materials. The existence of porosity decreases the elasticity of the implant material closer to those of the human bone, thus preventing the stress-shielding effect and, consequently, improving the mechanical biocompatibility (binding) of the two dissimilar materials.

Studies of the compaction-sintering behavior of porous metallic biomaterials for use as permanent or temporary implants in reconstructive surgery have also been reviewed, focusing on the effects of processing parameters on physical-mechanical characteristics, wear resistance, corrosion and biocompatibility behavior.

REFERENCES

Journals:


[77] M. Walter, Benefits of PM Processed Cobalt-Based Alloy for Orthopaedic Medical Implants, Carpenter Technology Corp., Wyomissing, PA, USA 2006.


Books:


