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Advanced Surface Treatments for Improving the Biocompatibility of Prosthesis and Medical Implants

José A. García, Pedro J. Rivero, Rocío Ortiz,
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Abstract

During the last two decades, numerous surface treatments have been developed to improve the biocompatibility of different types of prosthesis and other medical implants. Some of these devices are subject to demanding loading and friction conditions (e.g., hip, knee, and spine prosthesis). However, for other implants, there are more specific requirements as it happens for coronary stents or pacemaker electrodes. The materials used for the manufacture of the aforementioned devices are subjected to very high restrictions in terms of biocompatibility, in particular on chemical composition, corrosion resistance, or ion release. As a consequence, most of prosthesis and other implants are made of a limited number of materials such as titanium alloys, stainless steels, cobalt-chromium alloys, UHMWPE, or PEEK. Unfortunately, from a strict point of view, none of these materials meet all the requirements that would be desirable in terms of durability and prevention of infections and inflammatory processes. Coatings and other surface treatments have been developed to solve these problems and to improve biocompatibility. In this chapter, we present an updated review of the most used surface engineering technologies for biomaterials, like novel PVD coatings, ion implantation, and other plasma spray treatments, as well as a critical review of the characterization techniques. This study is completed with an insight into the future of the field.

Keywords: surface engineering, biomaterials, biocompatibility, plasma spraying, PVD coatings, ion implantation

1. Introduction

Since the first prosthetics were placed in patients in 1890, the evolution of materials and superficial treatments has been in continuous evolution [1]. Currently, prostheses are used

in different areas of the body ranging from scaffolds, coronary stents, and heart valves to hip and knee prostheses [2–5]. Although there are characteristics common to all the different prostheses such as resistance to corrosion and biocompatibility (they should not "harm" the patient), the requirements of each of them are in many cases very different [6]. A replacement plate of a cranial bone or a hip prosthesis inserted into the femur should have a good capacity for osseointegration. However, a coronary stent should prevent cell growth in its internal part [7]. This differentiation occurs not only between different prostheses but also between different zones in the same prosthesis. This determines that different materials are used not only for different prostheses but also in different areas of the same prosthesis; for instance, hip prostheses have a basal titanium alloy, with a femoral head of CoCr or ceramic that rotates on a high-density polyethylene cup.

Although the development of materials and treatments has allowed the durability and performance of these devices to be very high, there are still several problems associated with the prosthesis [8]. The most known are premature wear and dislocation in hip and knee prostheses, infection and rejection in dental prostheses, restenosis and heavy metal release in coronary stents, among others. In this way, infections are frequent complications in hospitals with dramatic consequences. It has been estimated that 80% of the infections in hospitals involve bacterial biofilms that have up to 1000 times higher resistance to antimicrobials than bacteria in the planktonic form [9, 10].

In this context, advanced surface treatments are playing an essential role in improving performance and increasing the life of prostheses. The treatments of thermal projection of hydroxyapatite (HA) are an extended solution to increase the capacity of growth of the cells of the bone on alloys of titanium and stainless steels. Physical vapor deposition (PVD) treatments, both ceramic and diamond like carbon (DLC), are an effective tool for increasing wear resistance. Ionic implantation is a method used to decrease the migration of heavy ions to the body, and laser texturing is being effectively used to obtain antimicrobial surfaces in an effective strategy to interrupt infections. This work includes a review of the state of the art and industrial implementation of some of the most used surface treatment techniques for the improvement of the different types of prostheses, paying special attention to the most used solutions and the future possibilities of advanced surface treatment techniques.

2. Plasma-sprayed hydroxyapatite coating

One of the ongoing research fields in the scientific community is the design of novel materials which can stimulate the bone regenerative process because the bone regeneration is a constant and continuous process in our lives, although the resultant regeneration speed shows a decreased tendency as a function of the age [11]. In addition, several studies indicate that every year over 2 million people worldwide require bone grafting surgery in order to repair large bone defects which are a very common problem in orthopedic surgery, being the main alternatives to repair these defects the use of autologous bone grafts, allografts, or biocompatible synthetic materials [12, 13].

Bones as well as other calcified tissues are considered as natural anisotropic composites consisting of biominerals embedded in a protein matrix, other organic materials, and water [14]. More specifically, the biomineral phase can be one or more types of calcium phosphates (CP) salts which vary in the resultant chemical formula and solubility value, respectively. Among all the known CP salts, hydroxyapatite (HA) stands out because it is the main calcium phosphate phase constituent of bones, comprising around 70% in comparison with water (10%) and organic phase (collagen) which constitutes the remaining part (around 20%), providing elastic resistance [15]. Due to this, multiple works can be found in the bibliography related to a wide variety of chemical methods (dry, wet, or high-temperature processes) for the fabrication of synthetic HA for biomedical applications (bone scaffold, bone filler, implant coating, or drug delivery systems) [14, 16, 17]. It has been demonstrated that synthetic HA shows a wide number of advantages such as an excellent biocompatibility, bioactivity, noninflammatory, affinity to biopolymers, and high-osteoconductive as well as osteointegrative properties without causing any systemic toxicity, rejection, or foreign body response [18–20]. A representative example can be observed in **Figure 1** where the in vivo bone repair experiments demonstrate that a new type of porous scaffold such as poly (γ-benzyl-L-glutamate)-modified hydroxyapatite/(poly (L-lactic acid) (PBLG-g-HA/PLLA) induced higher levels of new bone formation (rat femur defect) in comparison with blank (control), poly (L-lactic acid) (PLLA), and hydroxyapatite/poly (L-lactic acid) (HA/PLLA), respectively. These results indicate the potential applications for bone tissue engineering by demonstrating favorable osteogenic properties [21].

Other aspect of great relevance is that the presence of hydroxyapatite particles can be also employed for the inhibition growth of different types of cancer cells [22–24]. In this sense, it is well documented that the use of nanosized hydroxyapatite particles can significantly increase the biocompatibility and bioactivity of man-made materials [25, 26]. A clear example can be found in [26] where a highly biocompatible hydroxyapatite nanopowder (known as GoHAP) has been successfully synthesized in a very short of period of time (range of 90 s). These GoHAP nanoparticles showed excellent biocompatibility properties (confirmed by in vitro tests) because no vacuolization or cell membrane lysis was found on the surface and the resultant cells presented a correctly flattened phenotype, maintaining morphology typical for bone cells. The experimental results clearly indicate that GoHAP could be a promising material for resorbable bone implant fabrication.

One of the most important applications is that as coatings deposited onto bioinert metallic implants can promote early bonding of bones with an increase of biological fixation. In this sense, it has to be mentioned that as coatings, they are not intended to substitute existing materials, although these HA coatings are used for an enhancement of a fully functional implant. Due to this, different deposition techniques such as sol-gel process [27–29], pulsed laser deposition [30–32], electrospinning [33, 34], sputtering [35–37], or plasma spray [38] can be found in the bibliography related to design of optimal HA coatings onto the surface of metallic implants. Among all these fabrication methodologies, it has to be mentioned that plasma spray technique is the only process which has been approved by US Food and Drug Administration (FDA) for coating implants with biocompatible materials [39]. The plasma
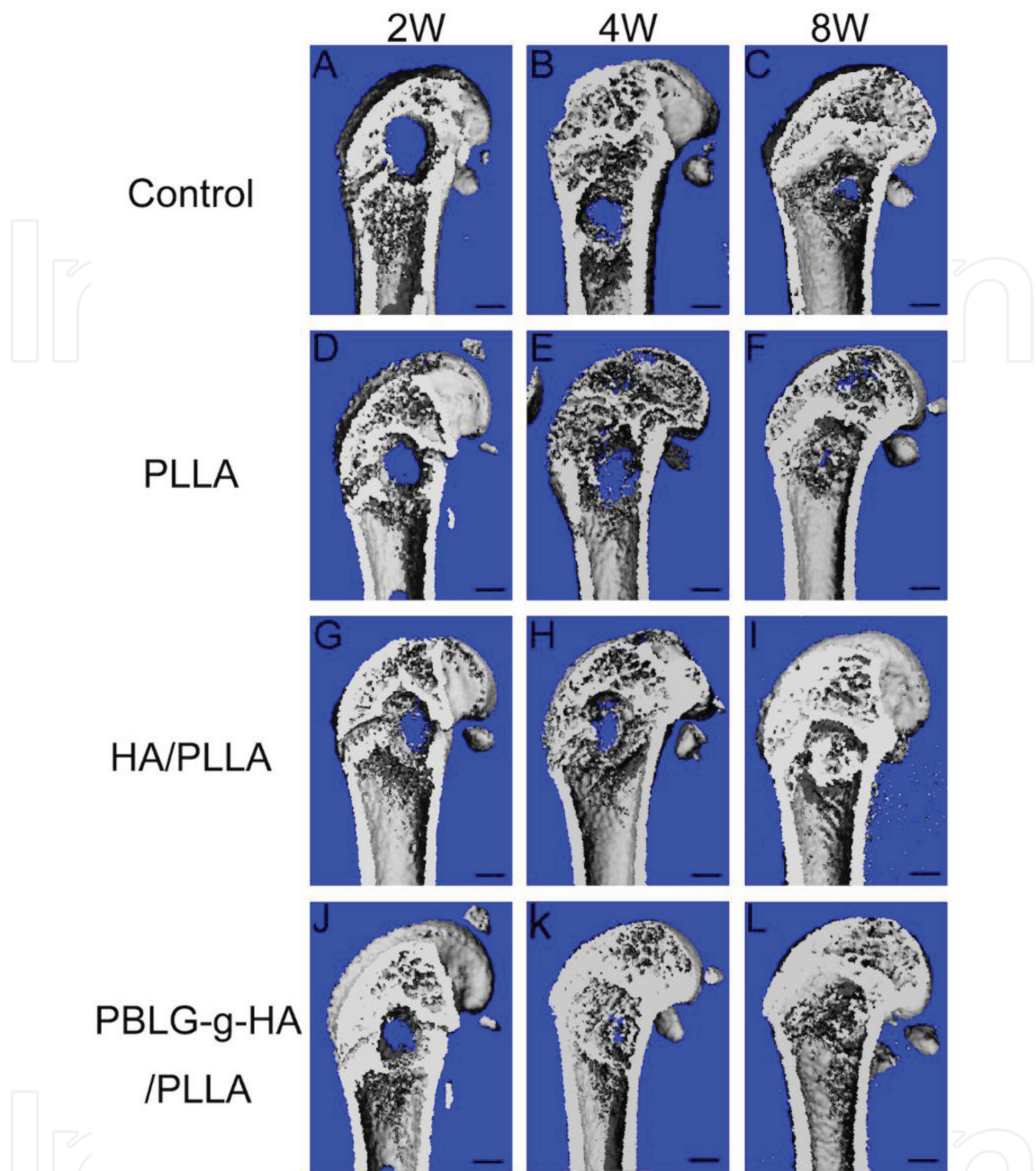
Figure 1. In vivo bone formation assessed by microcomputerized tomography (μ- CT) of control (A–C), poly (L-lactic acid) (PLLA) (D–F), HA/PLLA (G–I), and poly (γ-benzyl-L-glutamate)-modified hydroxyapatite/(poly (L-lactic acid) (PBLG-g-HA/PLLA) (J–L) scaffolds at 2, 4, and 8 weeks postimplantation. Reprinted with permission of [21].

spray process demands a control of several parameters for the design of optimal coatings (particle size range, distance between gun and substrate, arc current, power setting, particle morphology, plasma gas mixture, postspray treatment, etc.) [40]. A schematic representation of plasma spray torch is shown in **Figure 2**.

A novel study about the physical and chemical characterization of bioactive ceramic-coated plateau root form implant surface by using plasma-sprayed hydroxyapatite (PSHA) is presented in [41]. The surface characterization of the PSHA coatings has been performed by
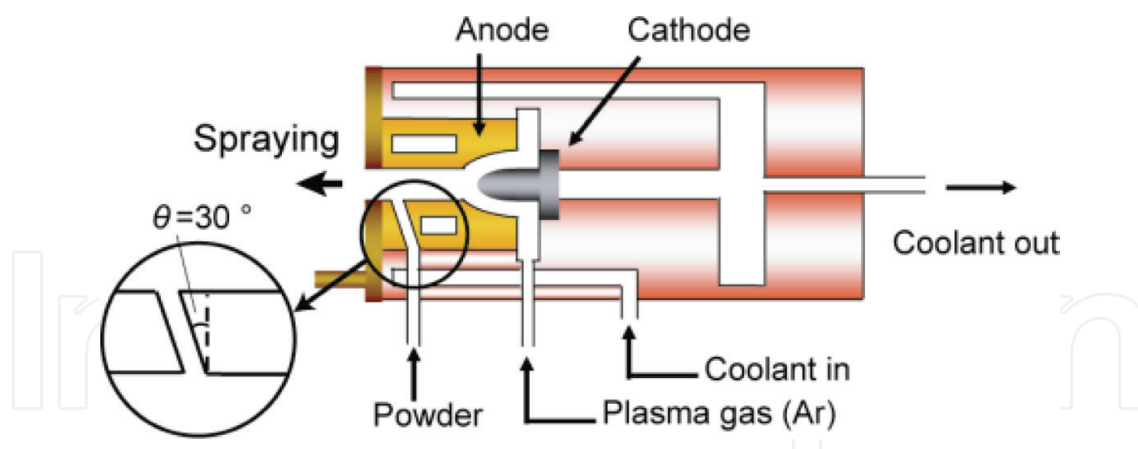
Figure 2. Schematic diagram (cross section) of plasma spray torch. Reprinted with permission of [40].

scanning electron microscopy (SEM), whereas the determination of the roughness has been performed by optical interferometry (IFM), as it can be observed in **Figure 3**. The experimental results indicate that lamellar bone formation in close contact with implant surfaces has been observed.

A consideration related to the material concerned (HA) is that it reacts strongly to rapid solidification following the plasma spray, yielding the formation of amorphous or metastable phases. According to this, the presence of an amorphous phase is undesirable because the natural bone is crystalline, being the integrity of the bone-implant compromised [42]. In this sense, an ideal HA coating for biomedical implants should have low porosity, high cohesive strength, a good adhesion to the substrate, high degree of crystallinity, high chemical purity, and phase stability [43]. According to this, the optimization of the coating properties by just varying the plasma spray parameters is a concern for obtaining a coating with the desired characteristics. An interesting work can be found in [44] where several steps are recommended in order to produce stable and adherent HA coatings.

However, mechanical tests indicate that the resultant HA coatings suffer poor mechanical properties (tensile strength, wear resistance, hardness, toughness, or fatigue), limiting its long-term application due to the relative movement between the implant and human bone, respectively. In order to overcome these mechanical limitations of HA coatings, the addition of different bioinert ceramic materials into HA matrix for reinforcement such as aluminum oxide [45, 46], zirconia [45], mixture of titania and zirconia [47], yttria-stabilized zirconium [48], or nanodiamond particles [49] have been evaluated. A representative example can be found in [45] where two reinforced HA coatings with alumina (Al_2O_3) and zirconia (ZrO_2), respectively, have been analyzed in order to investigate the microstructure, phase formation, and mechanical properties (hardness and tensile bond strength) as a function of as-sprayed coating and after postthermal treatment at 700°C for 1 h. The results indicate that after postcoating heat treatment, a dual effect has been observed such as an increase in the crystallinity and a decrease in the resultant porosity. This heat treatment enables an enhancement in cross-sectional hardness, although a decrease in bond strength has been also observed.
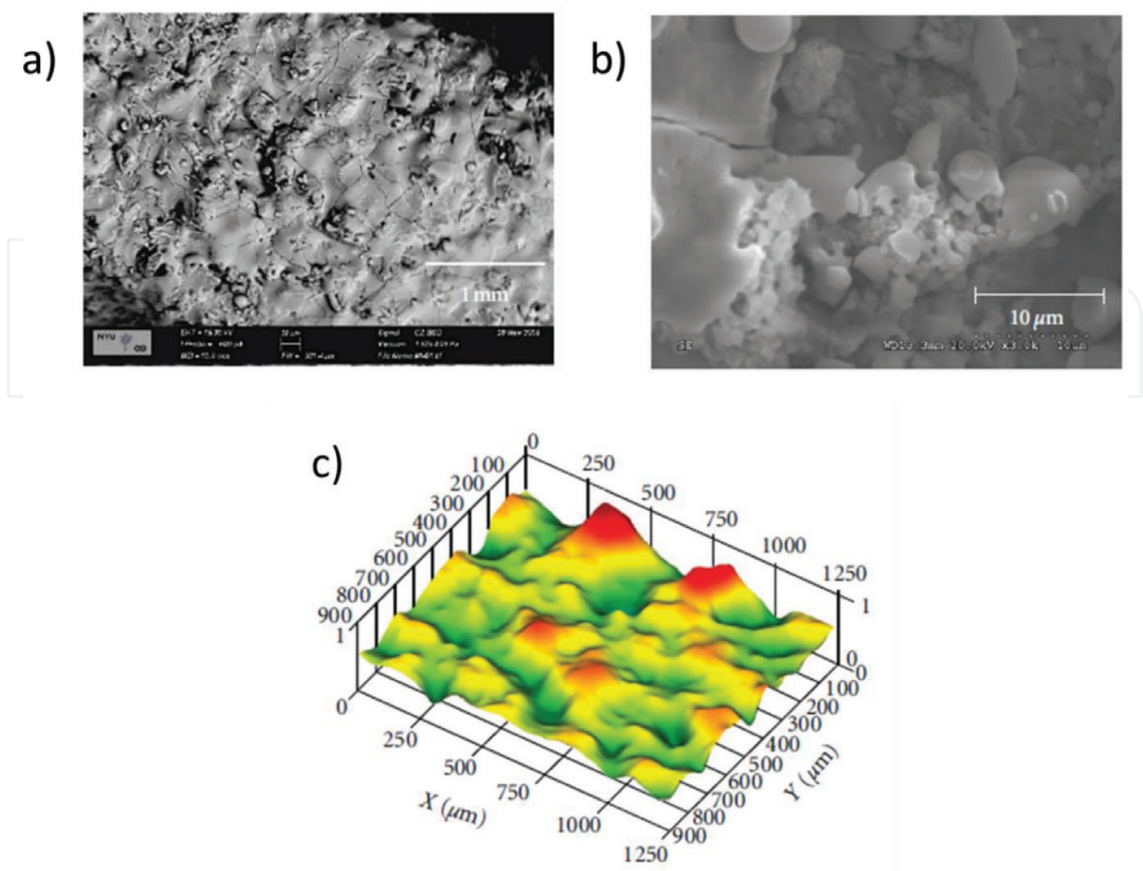
Figure 3. SEM intermediate micrograph (a) high magnification micrograph (b) and IFM three-dimensional reconstruction for PSHA coatings (c). Reprinted with permission of [41].

3. Physical vapor deposition coatings

The acronym PVD comes from the English expression Physical Vapor Deposition, knowing by this name a wide range of coating techniques that have in common the use of physical methods to obtain some of the components of the deposited layer. PVD coatings are made in high-vacuum chambers (10–50 mbar), working with average process temperatures in the range of 450°C to room temperature. By using this deposition technique, films from very thin thickness (10 nm) up to several microns with controllable composition can be perfectly obtained. In **Figure 4**, a schematic representation of PVD chamber is presented.

Basically, the PVD coatings are formed as follows. Firstly, a material is evaporated starting from a solid source (Ti, TiAl, Cr) by means of different physical methods as a function of the deposition technique employed which are electron beam evaporation or arc electric, pulverization (sputtering) by ionic bombardment, etc. The atmosphere of the treatment chamber consists of high vacuum in which there are partial pressures of controlled gases (mostly nitrogen and argon). The evaporated metal and the reactive gas of the chamber react condensing on the surface of the components to be coated. According to this process, the most known PVD coatings of typical industrial use are TiN, TiAlN, TiCN, or CrN, among others [50–55].

Concerning to the PVD processes, there are three main methods that are more widespread such as the electron beam (EB), the cathodic arc (CA), and the magnetron sputtering (MS), respectively. On the other hand, new concept in magnetron sputtering systems has been developed using high-power pulses (HIPIMS), making possible a significant increase in plasma ionization, and as a result, a considerable enhancement in the resultant adhesion of the coatings has been obtained [56, 57]. In **Figure 5**, a comparison between high-power impulse magnetron sputtering (HIPIMS), direct current magnetron sputtering (DCMS), and modulated pulsed power magnetron sputtering (MPPMS) is presented as function of power and time, respectively.

One of the research lines where PVD coatings have shown a high degree of novelty is in the protection against joint wear. The first experiences date back to the decade of the 1980s of the last century where TiN in total join arthroplasty was used as well as clinical trials were started in the 1990s in knee and hip arthroplasty [58, 59].
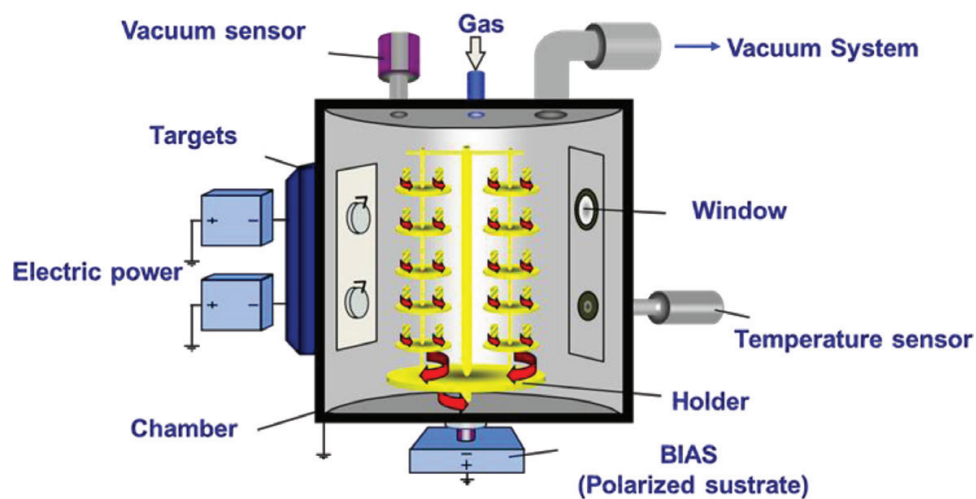
Figure 4. Scheme of the Metaplas Ionon MZR 323 arc evaporation PVD system. Courtesy of AIN.
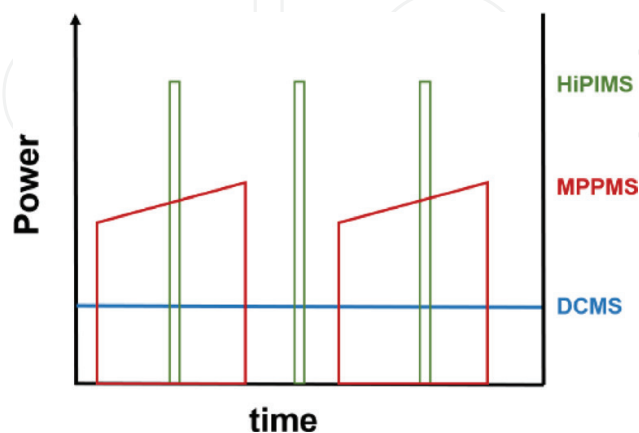
Figure 5. Power versus time in direct current magnetron sputtering (DCMS), high-power impulse magnetron sputtering (HIPIMS), and modulated pulsed power magnetron sputtering (MPPMS), respectively.

Subsequently, diamond-like carbon (DLC) coatings were introduced, following the strategy of favoring sliding with very low coefficients of friction (0.1), maintaining relatively high hardness (H > 15 GPa). Although these specific coatings showed high efficacy in laboratory tests, the clinical tests performed to date for hip and knee prostheses showed undesirable results, being the decohesion of the layers and the subsequent localized corrosion the main cause of the failure.

On the other hand, TiN and DLC coatings showed very good biocompatibility so they are being marketed in other types of prostheses such as dental implants and heart valves. For these specific purposes, the absence of high loads which can delaminate the coating as it happened in the case of hip and knee prosthesis enables its introduction into the market. In **Figure 6**, two representative examples of Ti dental implants obtained which are coated by TiN (left) or DLC (right) magnetron sputtering can be clearly appreciated.

However, one of the main problems concerned to this type of coatings is the adhesion and corrosion behavior, being one of the hot topics in the community scientific their implementation and introduction of them in a massive way in the market of hip and knee prostheses. One of the most promising approaches is the use of the aforementioned HIPIMS. This PVD technology allows obtaining layers of much greater adhesion and density, giving excellent results in terms of corrosion and wear resistance. A representative example is shown in **Figures 7** and **8**, respectively. In **Figure 7** is shown a cross section of a sample coated with TaN DC magnetron sputtering (left), where a columnar growth with micron-sized grains can be appreciated. On the other hand, the photograph on the right shows a layer of TaN coating by HIPIMS where a greater density and compactness can be observed. The corrosion resistance in terms of polarization resistance as a function of time (4, 24, and 168 h, respectively) is shown in **Figure 8**.

Another research line which is showing promoting results is ceramic coatings doped with bactericidal elements (mostly Ag or Cu) in the form of nanoparticles embedded in the TiN or CrN. The controlled release of Cu or Ag ions provides a bactericidal effect which makes possible the prevention of infections due to bacterial proliferation on the surfaces of the prostheses. Doped metal nitrides and carbonitrides deposited by pulsed magnetron sputtering are widely tested [60, 61]. In addition, Cu and Ag concentrations between 5 and 25% have been shown to be highly efficient, avoiding the proliferation of different contagious types of bacteria such as *S. aureus*, *P. aeruginosa*, and *S. epidermis*, increasing bactericidal efficacy with increased concentration of Ag and Cu, respectively. Finally, another extended solution is the coatings of diamond-like carbon(DLC) doped with Ag because the experimental results of depositing these layers by means of magnetron sputtering point to the fact that silver segregates in the form of nanoparticles (order of 3 nm), and in high concentrations appear nanofibers of Ag on the surface, showing very good antibacterial behavior [62].

Figure 6. TiN magnetron sputtering coating (left) and diamond-like carbon (DLC) magnetron sputtering coating (right) on Ti dental implant. Courtesy of the commercial company Flubetech.
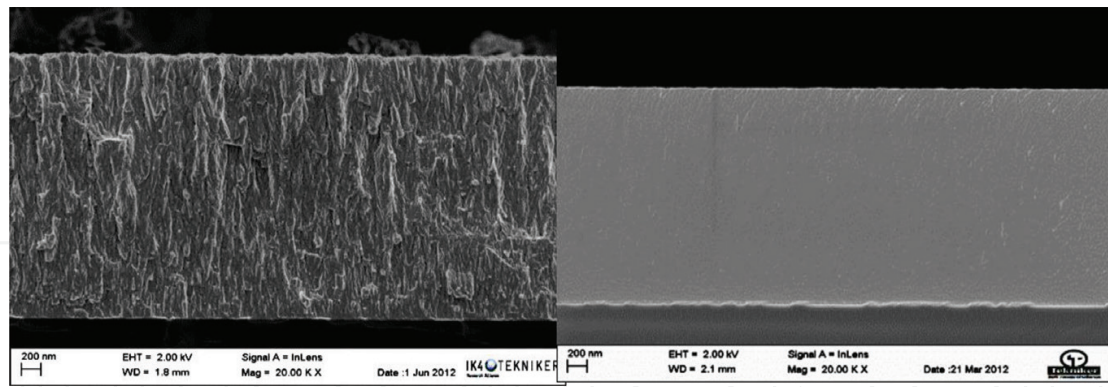
Figure 7. Cross-sectional SEM images of TaN DC magnetron sputtering (left) and TaN HIPIMS coating (right), respectively. Courtesy of IK4-TEKNIKER.
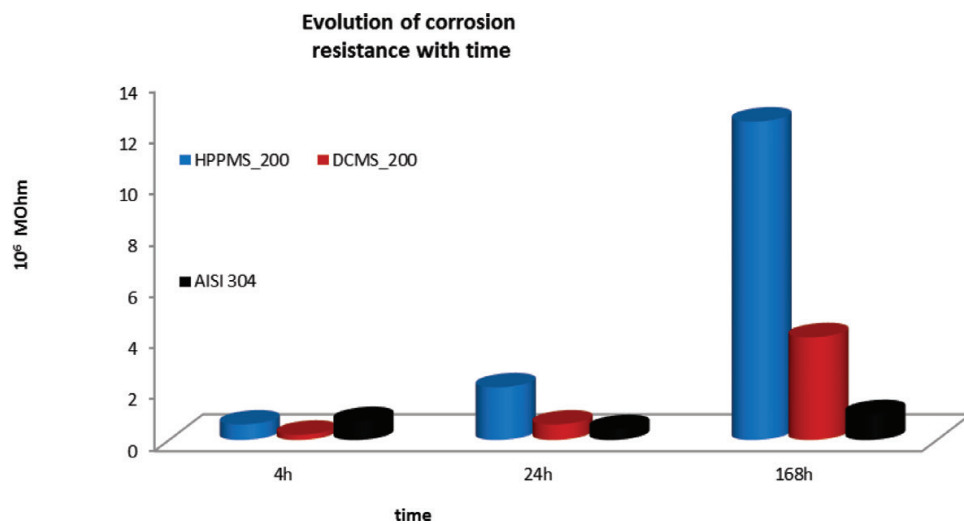
Figure 8. Evolution of corrosion resistance for TaN HIPIMS sample (blue color), TaN DCMS (red color), and pristine sample (AISI 304, black color), respectively. Courtesy of IK4-TEKNIKER.

## 4. Ion implantation techniques

Ion implantation techniques consist in the superficial modification of materials by ion bombardment. By means of these techniques is possible to improve surface properties of different materials [63, 64]. Although these techniques have their origin in the nuclear industry [65, 66], the first works on semiconductor applications appeared in Bell Laboratories in 1948 when Kingsbury and Ohl carried out studies of implantation of light ions on wafers of Si [67, 68]. Metallurgical application of ion implantation was firstly reported simultaneity in the 1970s by Harwell laboratory (UK), and Naval Research Laboratory (USA). These early works were mainly focused on nitrogen implantation of steels. From these first results up to today ion implantation techniques have been introduced in many different industrial applications (mostly in aeronautical or biomedical sector).

Ion implanters equipment consists of a series of characteristic elements (see **Figure 9**) such as a source of ions (capable of producing sufficient quantities of certain types of ions), one

or two acceleration stages (potential differences of the order of 100,000 V), a mass separator magnet, and a thermal chamber (high-vacuum chamber where the samples whose surface is to be treated) are placed. The whole process of generation, acceleration, and implantation is carried out in high vacuum, of the order of 10^{-5}–10^{-6} mbar to ensure that the average travels of the ions far surpass the distance that separates the source of the whites to implant. In addition, ion implantation process is performed in an approximate range of energies of 25–300 KeV, although most of the studies are carried out to energies between 50 and 200 keV. The relevant parameters of these treatments are the type of ion, the implanted dose, the implantation energy, and the temperature of the process, which in the most cases is kept deliberately below a certain level (being able to talk about temperature environment), as it can be observed in **Figure 9**. By a properly selection of all these parameters, physical-chemical properties of the surface of the implanted samples can be perfectly controlled [69].

In **Figure 10**, a schematic diagram of the used plasma immersion ion implantation-enhanced deposition (PIIIeD) processing system is shown. For this figure, the process chamber is similar to a conventional plasma immersion ion implantation (PIII) combined with an RF magnetron sputtering and a glow discharge (GD) plasma source. In this system, thin films are deposited simultaneously with 3-D implantation of argon ions, improving film adhesion and relaxing film stress. As metal ions are rare in a magnetron discharge, the auxiliary electrode for glow discharge plasma helps to ionize some metal neutrals which are also implanted into the substrate during the high-voltage pulses.

The basic difference between ion beam implantation (II) and plasma immersion ion implantation (PIII) consist in PIII the target is an active part of the system, and it is biased at pulsed high voltage. On the other hand, in II, the target is isolated from the ion beam generation (it is not active part of electric circuit), and both treatments have relevant differences as it can be shown in **Table 1** [71].
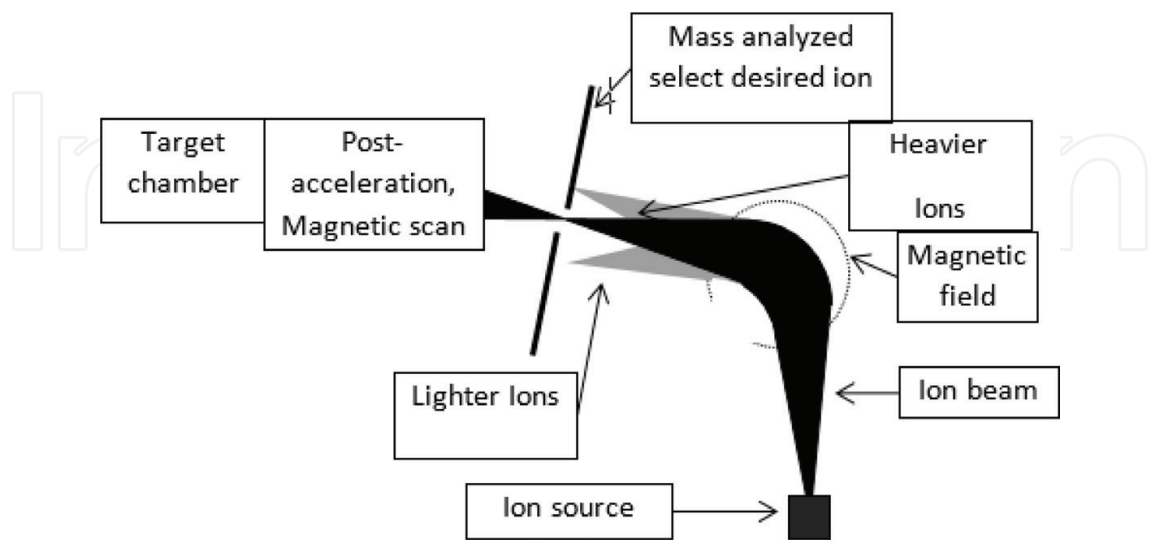
Figure 9. Scheme of a mass separation ion implanter. Ion implantation, the invisible shield. Courtesy of R. Rodríguez, T. Tate & N. Mikkelsen, SPRINT RA372 project.
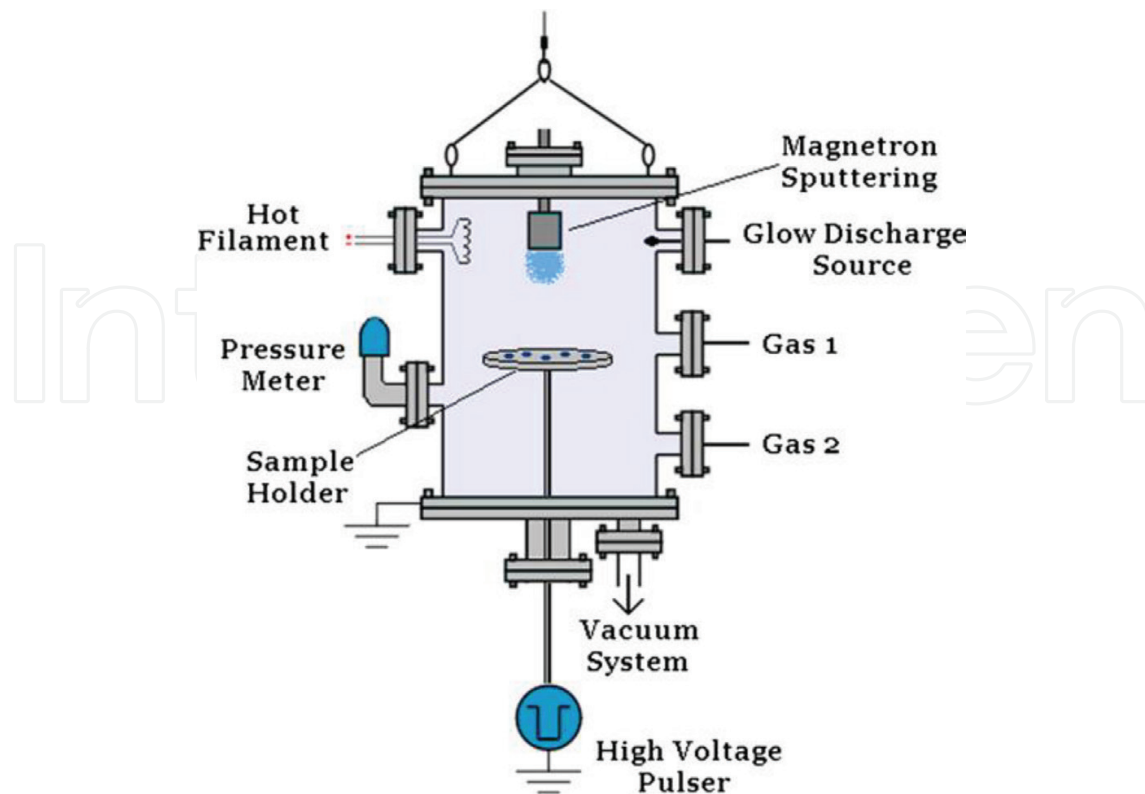
Figure 10. Schematic diagram of the used plasma immersion ion implantation-enhanced deposition (PIIIeD) processing system. The process chamber is similar to a conventional PIII combined with an RF magnetron sputtering and a glow discharge (GD) plasma source. Reprinted with permission of [70].

Conventional ion implantation is a ballistic process where kinetic energy from ions promotes ion implantation in the target. Plasma immersion ion implantation (PIII) is a combined process where temperature and voltage were defined to obtain an implantation profile. According to this, the temperature is an important parameter in PIII, dominating in many cases the final implantation characteristics. In addition, ion energy is the other key parameter in ion implantation, much more important in II where is the most relevant parameter affecting implantation profile. However, the temperature is not considered a key factor in plasma immersion ion implantation, being the typical implantation energies from a few KV up to no more of 30 kV.

The most extended applications of ion implantation technologies have been in biomedical devices. There are different functionalities that ion implantation can achieve in hip, knee, and other prosthesis. One of the first applications was the implantation of Ca and P to obtain a surface with characteristics similar to hydroxyapatite [72]. As in the case of PVD, this solution has not been incorporated into the market due to the good performance of the hydroxyapatite grown by plasma spraying. In this way, ion implantation has been more relevant in the strategies aimed at increasing the hardness and wear resistance of the prostheses. Conventional ion implantation was the first attempt to apply on different alloys of titanium and CoCr in order to reduce the wear of the prosthesis. The results obtained were not satisfactory due mainly to the low thickness of the modified layer (typically around 0.1 microns) [71]. In order to overcome the problem of the low thickness of the conventional ionic implantation, low

energy-high temperature implantation techniques [73], and plasma immersion ion implantation techniques have been performed [74]. By using these techniques, the resultant implantation profiles of more than 1 micron have been achieved (see figure GDOS profile of **Figure 11**), increasing the hardness and wear resistance.

Although the experimental results indicate an enhancement in the wear resistance, it has been also observed the precipitation of part of the chromium of the stainless steels, or of the alloys of CoCr, due to an increase in the temperature produced a decrease in the corrosion resistance, even at temperatures where carbides are not appreciated [74], as it can be appreciated

|	Ion implantation	Plasma immersion
Geometry	Line of sight	Conformal
Temperature	Room temperature	400°C
Thickness	0.1 micron	0.05–10 microns
Batch time	10–100 h	0.1–2 h
Ion energy	10–1000 kV	0.1–100 kV
Ion current	1–100 mA	100–1000 mA
Industrial scaling	Low	Medium

Table 1. A comparative scheme of the different parameters (geometry, temperature, thickness, batch time, ion energy, ion current, or industrial scaling) between plasma immersion ion implantation and ion beam implantation, respectively. Reprinted with permission of [71].
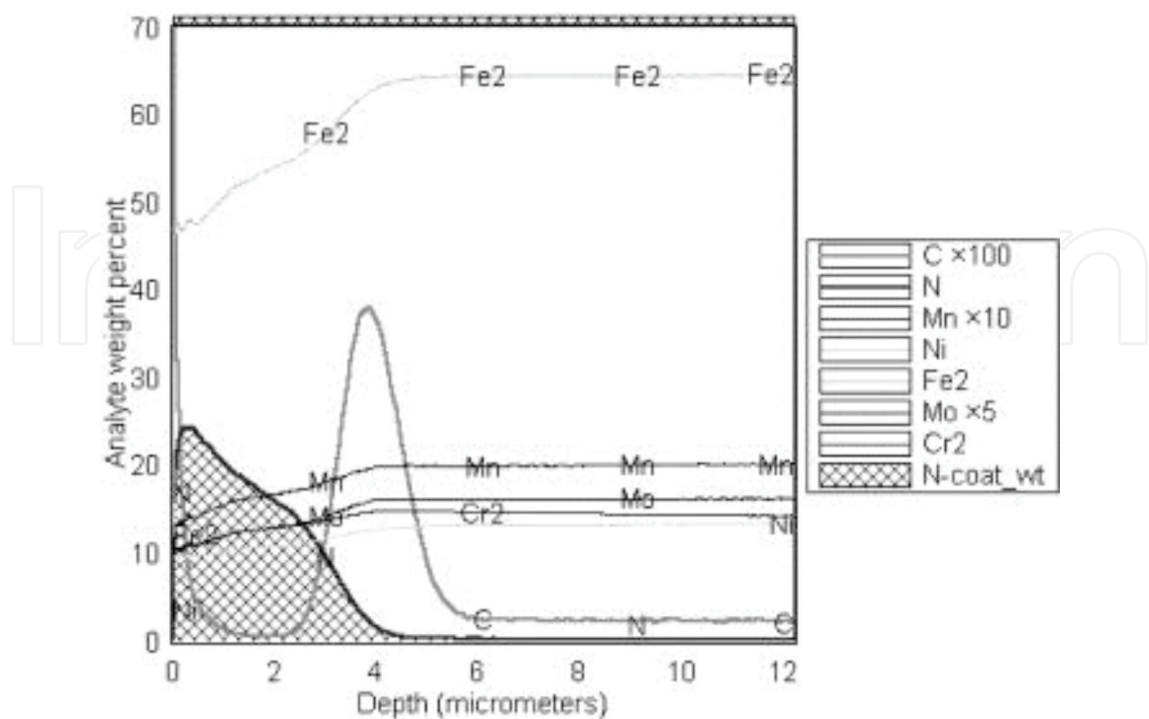

Figure 11. Glow discharge optical spectroscopy (GDOS) depth profiles of nitrogen after implantation at 400°C (ion energy 1.2 keV, current density 1 mA/cm^2 and fluence 3.5×10^{19} cm^{-2}) for AISI 316. Reprinted with permission of [73].

in the polarization curves (Tafel plots) of **Figure 12**. However, this problem can be solved through the implantation of oxygen, obtaining for these specific cases an important increases of the corrosion resistance [75], as it can be observed in **Figure 13**.

Another application of interest for implantation by immersion in oxygen plasma is the reduction of the release of heavy ions to the blood flow observed in cardiovascular devices. The implantation of oxygen in stainless steels "pushes" the ions such as Ni and Cr into the surface, and as a promoting result, a significant decrease in the release of these ions have been obtained with an improvement in biocompatibility [71]. By means of oxygen implantation, heavy ions (Ni, Mo, and Cr) go deeper into the material as shown in **Figure 14**, where it is
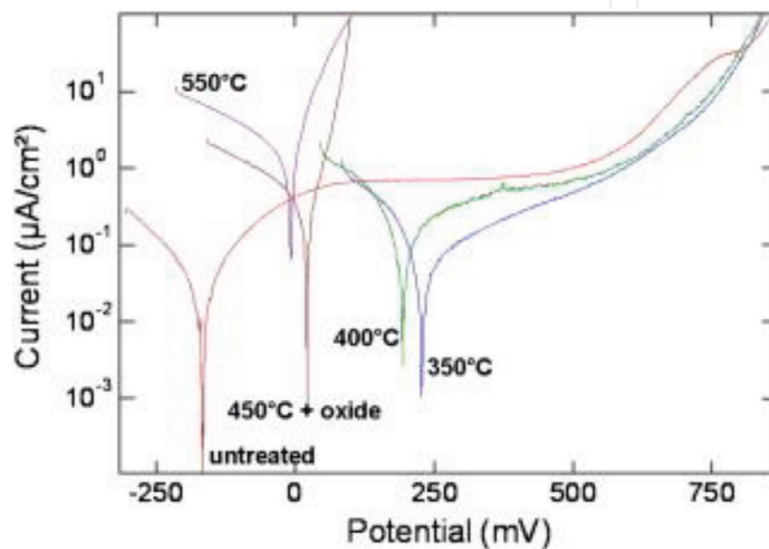
Figure 12. Polarization curves for different samples in Ringer solution at 37.2°C. Reprinted with permission of [74].
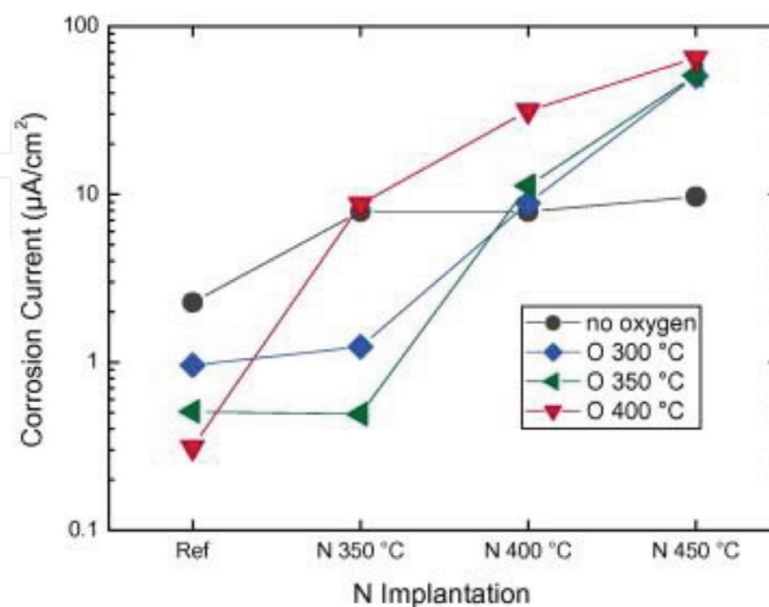
Figure 13. Corrosion rates calculated from the polarization curves as function of nitrogen and oxygen implantation temperature. The samples labeled as "ref" are either only implanted with oxygen (with indicated temperature) or a sample from untreated base material (circle). Reprinted with permission of [75].
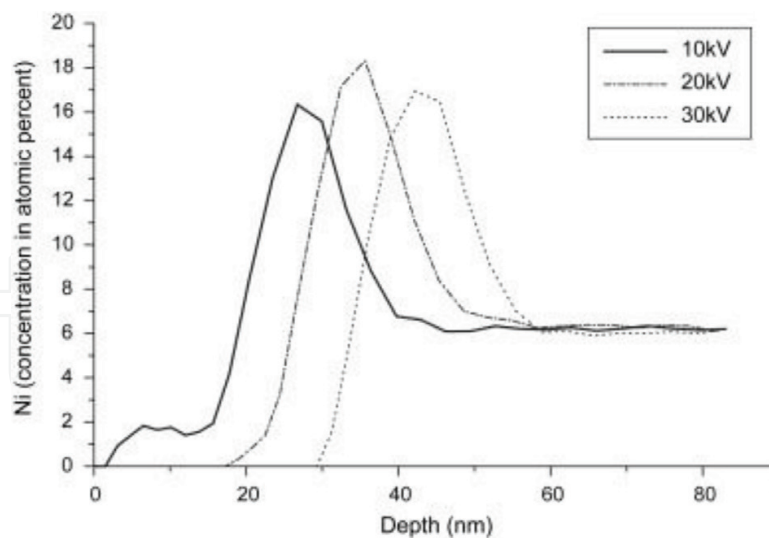
Figure 14. Compositional profiles for oxygen implanted into stainless steel at energies of 10, 20, and 30 keV. Reprinted with permission of [71].

possible to observe atomic concentration of Ni after oxygen implantation. As a consequence of this, migration tests show a reduction of the concentration of these ions in blood of more than 50%.

Finally, interesting approaches for the design and implementation of multifunctional layers (bactericides, wear resistance, and anticorrosion) have been tested by using combined treatment techniques. As a representative example, ionic implantation of Ag on ceramic layers previously deposited by PVD is a novel approach that allows to have a better control of the distribution of the Ag, solving potential problems of cytotoxicity by the excessive release of silver cations [76].

5. Summary

Since the first implant was made in the nineteenth century, different prostheses have achieved significant improvements in terms of durability and performance. In addition to the improvements in the design, result of the better knowledge of the biomechanical processes, the development of new materials, and the superficial treatments have been decisive. Hundreds of different materials and dozens of surface treatments which have been studied in a rigorous and systematic way to be used as part of the different types of prostheses. Among all these vast set of materials and treatments, the solutions applied in each type of prosthesis are considerably reduced, as a result of all the research carried out.

In this work, we have reviewed some of the most widespread solutions and have the best results and perspectives of implantation. The thermal injection of HA is currently an extended solution that is applied in different types of implants to significantly increase the osseointegration capacity. PVD coatings by conventional magnetron sputtering techniques are being used

to increase corrosion and wear resistance in heart valves and dental implants. In this line, the appearance of improved PVD techniques (HIPIMS) has achieved levels of adhesion and layer density that augur a wide use in other types of implants. Ion implantation and fundamentally the immersion in plasma are very effective tools to increase the wear resistance, maintaining the corrosion resistance of stainless steels and titanium and CoCr alloys.

Although all these techniques, and some more like plasma electrooxidation (PEO), have allowed significant advances already introduced in the market, there are still problems to be solved and challenges to be addressed within the surface treatments and design of novel materials. New manufacturing techniques such as additive manufacturing and social aspects such as the increase in life expectancy, determine that a continuous research is necessary to develop new materials and treatments compatible with this new framework. Probably one of the most promising ways of research is the use of combined treatment techniques within materials and customized designs for each patient.

Nomenclature

HA	hydroxyapatite
PVD	physical vapor deposition
DLC	diamond-like carbon
CP	calcium phosphates
PBLG-g-HA	poly (γ-benzyl-L-glutamate) modified hydroxyapatite
PLLA	poly (L-lactic acid)
FDA	food and drug administration
PSHA	plasma sprayed hydroxyapatite
SEM	scanning electron microscopy
IFM	interferometry
EB	electron beam (EB)
CA	cathodic arc
MS	magnetron sputtering
HIPIMS	high power impulse magnetron sputtering
DCMS	direct current magnetron sputtering
MPPMS	modulated pulsed power magnetron sputtering
PIII	plasma immersion ion implantation

GDOS	glow discharge optical spectroscopy
II	ion beam implantation (II)
PIIIeD	plasma immersion ion implantation-enhanced deposition

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