DOI: 10.2478/v10077-010-0003-3

Sylwia Sobieszczyk
Gdansk University of Technology, Faculty of Mechanical Engineering, Department of Mechanical Engineering and Materials Strength, 80-952 Gdansk, Poland

SURFACE MODIFICATIONS OF Ti AND ITS ALLOYS

ABSTRACT

This article reviews the various surface modification techniques pertaining to titanium and titanium alloys including physical treatment, mechanical treatment, and chemical and electrochemical treatment. The proper surface modification expands the use of titanium and its alloys in the biomedical field for long-term implants retaining the excellent properties of substrate material and improving the specific surface properties required by clinical applications.

Key words: *bioactivity, osteoconductivity, osseointegration, surface modifications, titanium*

INTRODUCTION

Titanium and its alloys are widely used in biomedical field for hard tissue replacements because of their desirable properties, such as relatively low elastic modulus, good fatigue strength, formability, and corrosion resistance. However, titanium and its alloys are still not sufficient for long-term clinical usage because the biocompatibility and bioactivity of these materials must be improved. Titanium and its alloys are being bioinert metallic materials and they cannot bond to living bone directly at the early stage after implantation into a human body. Their surfaces play an important role in the response of the artificial devices in a biological environment and in order of titanium and its alloys to meet the clinical demands, it is necessary to modify the surface of the titanium materials. Different surface modifications have been developed to improve the biocompatibility, bioactivity, osteoconductivity, and osseointegration of titanium implants. In general, the term bioactivity is related to the ability of the material to trigger a biological action, the cell response or more commonly to formation of an apatite layer from simulated body fluid. Several physical, chemical and heat treatments have been used for purpose of enhancing the precipitation of calcium phosphates, and hence the bioactivity of the implants.

SURFACE MODIFICATION METHODS

Surface of titanium and its alloys plays a significant role in implant integration in human body. As a result of different surface modifications, following features could be achieved:

- better mechanical anchoring of the implant to the bone tissue (improved implant/bone bonding);
- improvement of bone conductivity and inductivity;
- improvement of wear resistance;
- improvement of corrosion resistance;
- improvement of biocompatibility and bioactivity;
- shortening of the healing time after the implantation.

Various surface modification techniques have been developed to improve the osseointegration of titanium and its alloys as have been presented in *Table 1* [1].

Table. 1. *Surface modification methods for titanium and its alloys implants*

Surface modification methods	Objective	Reference
Mechanical methods	Improvement of adhesion by producing the specific surface topographies	[1]
Machining		[2]
Grinding		[3,4,5]
Polishing		[6]
Blasting		[3,4,7,8]
Chemical methods	Improvement of biocompatibility, bioactivity and bone conductivity. Improvement of corrosion resistance. Removal of contamination.	[1]
Acidic treatment		[9.10]
Alkaline treatment		[10,11]
Hydrogen peroxide treatment		[12]
Sol-gel treatment		[13,14,15]
Anodic oxidation		[16-19]
Chemical vapor deposition methods (CVD)		[20-22]
Biochemical methods		[15,23,24]
Physical methods	Improvement of wear resistance, corrosion resistance and biocompatibility.	[1,15]
Thermal spray: flame spray, plasma spray, high velocity oxygen fuel (HVOF), detonation gun spraying (DGUN)		[25-29]
Physical Vapor Deposition methods (PVD)		[15,30,31]
Ion implantation		[15,32,33]
Glow discharge plasma treat.		[34,35]

MECHANICAL METHODS

Mechanical surface treatments include machining, grinding, and blasting as have been explained in detail by Lausmaa [36], and lead to rough structures which are more favourable for biomineralization due to their greater surface area.

Some researchers suggest that the surface roughness (Ra, mean roughness) in the interval 0.5-1.5 µm shows stronger bone response after the implantation than the smoother or rougher implants [3,37-39]. Those observations are in contrast with the results obtained by Fini *et al.* [40], where positive results were obtained with the surface roughness as high as 21.4 µm. Their results were confirmed during in vivo experiments using titanium implants with various different roughness 16.5 – 21.4 µm inserted in the cortical and trabecular bone of goats. They suggest that the rougher surfaces exhibit a more prolonged effect over time. Surface roughness enhances cell attachment, proliferation and differentiation of osteogenic cells and is the key factor for the osseous integration of metallic implants. One of the most popular method of achieving desirable surface roughness is blasting titanium surface with the SiC particles (SiC), alumina particles (Al_2O_3) and biphasic calcium phosphates particles (BCP), hydroxyapatite and ß-Tricalcium phosphate) [3], although there have been some reports that blasting with SiC and Al_2O_3 may lead to surface contamination and local inflammatory reactions of surrounding tissues by dissolution of Al_2O_3 into host bone [5].

CHEMICAL METHODS

Chemical methods provide titanium with bioactive surface characteristics. They include soaking in NaOH followed by heat treatment [41] or etching in HCl and subsequent NaOH treatment [42], anodic oxidation [16], chemical vapor deposition (CVD) and biochemical modification as shown in *Table 1.*

Chemical treatment

Chemical treatment methods of titanium and its alloys are based on chemical reactions occurring at the interface between titanium and a solution. Those methods induce the growth of a bioactive, nanostructured sodium titanate layer on the surface of the titanium substrate. Hence, the surface acts as a site for the subsequent in vitro nucleation of calcium phosphates from SBF, mimicking the earliest surface reaction stages after implantation. Ho *et al.* [43] have noticed, that titanium and its alloys with untreated surfaces do not induce calcium phosphates precipitation after soaking in SBF. The possible mechanism of nucleation and growth of apatite on alkaline treated titanium has been first explained by Kim *et al.* [44]. After alkaline treatment, the created sodium titanate layer releases its Na^+ ions into the surrounding fluid via an ion exchange with H_3O^+ in the fluid to form Ti-OH groups (as early as 0.5 h after the immersion). The Ti-OH groups then immediately interact with the calcium ions from the fluid and calcium titanate is formed. The calcium titanate incorporates the phosphate ions, as well as calcium ions. Therefore, the apatite nuclei in SBF is formed. Once formed, the apatite nuclei grows by consuming the calcium and phosphate ions from the SBF solution. Also, it has been proved during in vitro and in vivo experiments by Lu X *et al.* [45] that bone growth on the alkali treated titanium surface can further be enhanced by topographic patterning.
Another common method of chemical treatment of titanium is the acid pre-treatment which is used to remove native oxide and contamination to obtain clean and uniform surface finishes [46]. The frequently used combination of acids is the solution of 10-

30% HNO_3 and 1-3% HF in distilled water [9]. Takeuchi *et al.* [47] have investigated other three substances, like $Na_2S_2O_8$, H_2SO_4, and HCl. During acid etching there has been a transformation of the Ti substrate surface into soluble titanium fluorides and hydrogen.

The next chemical method is hydrogen peroxide (H_2O_2) treatment, which leads to chemical dissolution and oxidation of titanium surface as well as is a good pre-treatment for apatite precipitation [48]. Titania surface reacts with H_2O_2 and as a result the Ti-peroxy gels are produced [49]. Amorphous titania gels could be also provided with chemical treatment in a H_2O_2/0.1 M HCl and in a $H_2O_2/TaCl_2$ [1]. Subsequent heat treatment above 300^{o}C gradually changes the amorphous gel into crystalline one. The best results have been achieved using heat treatment between 400 and 500^{o}C as the titania gel would have natase structure exhibiting excellent bioactivity [50].

Sol-gel method

The sol-gel process is widely used to deposit thin ceramics coatings (less than 10 μm) and allows for better control of the chemical composition and microstructure of the coating, preparation of homogeneous films, reduction of the densification temperature, and finally simpler equipment and lower cost [51]. The sol-gel method could be successfully used to deposit calcium phosphate coatings, especially hydroxyapatite coatings [1,53-54]. Also, one of the most promising method of improving bioactivity of titanium and its alloys is titania (TiO_2) coating synthesized by sol-gel method [55]. It is believed that sol-gel titania coatings can induce calcium phosphate formation and may therefore be able to contribute to enhanced bonding to bone, as has been proved by Li *at al.* [52]. The most common sol can be prepared by mixing tetraisopropyl orthotitanate, ethanol, ethyleneglycol monoethylether, hydrochloric acid, and water [1]. Also, it have been noticed that the synthesized by the sol-gel method a composite titania/hydroxyapatite coating is a very promising method of achieving high adhesion to the substrate with a very good bioactivity [56]. There is a significant improvement of bond strength (up to 55 MPa) with the insertion of TiO_2 buffer layer in the HA/TiO_2 coating through the enhanced chemical affinity of TiO_2 towards HA layer as well as Ti substrate.

Anodic oxidation

Anodic oxidation is commonly used for surface treatments of titanium and its alloys, especially to obtain uniform, microporous structure at the surface [11,57]. Also, the regular arrays of oxide nanotubes can be grown by anodic oxidation, which can be beneficial for tight adhesion of HA coating to titanium substrate as well as providing the high specific area for reactive nucleation of calcium phosphates [50]. The nano-scale HA on TiO_2 nanotubes forms much stronger bonded and stable nanoporous layer which enhances bond strength and reduces interfacial failure, improving the most important parameters – the stability of the implant coating and prolonged lifetime of the implant [59].

Very promising method of producing the orous oxide surface with bioactive composition is anodic spark oxidation, also called micro-arc oxidation (MAO) or plasma electrolytic oxidation [60-62]. Spark oxidation can be performed with a pulsed voltage higher than the breakdown voltage 200-500V [56] which results in the formation of micropores in diameter ranged from several nm to 4-5 μm [63].

Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD), as a process involving chemical reactions between chemicals in the gas phase and the surface of the substrate resulting in the deposition of a non-volatile compound on the substrate, is quite widely used as a chemical surface modification method [20,22]. There are different CVD processes so far developed (*Table 2*):

Table. 2. *Chemical vapor deposition process*

CVD process	Objective	Reference
Atmospheric-pressure chemical vapor deposition (APCVD)	Self-cleaning, good uniformity of the coating	[64]
Low-pressure chemical vapor deposition (LPCVD)	Increased hardness and corrosion resistance	[65]
Laser-enhanced chemical vapor deposition (LECVD)	Improved wear and corrosion resistance	[1]
Plasma-enhanced echmical vapor deposition (PECVD)	Improved wear and corrosion resistance	[66]
Plasma-assisted chemical vapor deposition (PACVD)	Improved biocompatibility, chemical stability, corrosion resistance	[67,68]

Biochemical methods

Biochemical modifications of titanium surface can influence cellular function, adhesion, differentiation and remodeling of bone tissue. One of the major objective of biochemical modification is to induce specific cell and tissue response by means of surface-immobilized proteins, or growth factors. One of the important techniques of biomechanical modification of titanium substrate are self-assembled monolayers (SAMs) of alkane phosphates or phosphonates which results in a very well defined chemical composition with controlled wettability and electrical charge [69]. Another modification method is protein immobilization technology which allows the adsorption of cell-adhesive proteins or bioactive proteins (bone morphogenetic proteins) to be immobilized on the surface of Ti and its alloys by e.g. plasma polymerization of allyl amine to provide functional groups for immobilization of biomolecules on Ti6Al4V [70].

PHYSICAL METHODS

Physical surface modification methods include processes, such as thermal spraying, physical vapor deposition, ion implantation, and glow discharge plasma treatment, where chemical reactions do not occur. Using those methods, the surface modified layer, film or coating on titanium substrate are mainly attributed to the thermal, kinetic, and electrical energy.

Thermal spraying

Thermal spraying, in which materials of coating are thermally melted into liquid droplets and introduced energetically to the titanium surface where subsequently condensate, can be divided into flame spraying [71], plasma spraying [72], arc spraying [73], detonation gun spraying [74], laser spraying [75] and high velocity oxy-fuel (HVOF) spraying [28]. Those methods of surface modification of titanium and its alloys are quite widely used in industry for preparing biomedical coatings, e.g. to produce hydroxyapatite (HA) coatings on endoprosthesis. Unfortunately, one of the main disadvantage of those methods is the relatively poor bonding between a plasma sprayed HA coating and titanium because of the mismatch of the thermal expansion coefficient of HA ($13.3 \times 10^{-6}\ K^{-1}$) coating and titanium substrate ($8.5 \times 10^{-6}\ K^{-1}$) resulting in high residual stress leading to delamination of the coating [72]. An improving the bonding strength of HA coatings on titanium substrates can be achieved by attrition of titania or zirconia as secondary phase to the coating as have been showed by Chiu *et al.* [76].

Physical vapor deposition (PVD)

Physical vapor deposition processes of titanium surface modifications include evaporation, sputtering and ion plating allowing to deposit thin films in order to improve the implant biocompatibility, bioactivity, wear resistance and corrosion resistance [77,78]

Glow discharge plasma treatment

During the glow discharge plasma treatment, the surface exposed to the plasma is bombarded by electrons and ions. Sobiecki *et al.* [79] examined the influence of glow discharge nitriding, oxynitriding and carbonitriding on the surface modification of Ti-1Al-1Mn alloy. As a result of those treatments they produced the surface layer with a diffusion character exhibiting high hardness, good wear and corrosion resistance as well as increased fatigue limit.

Ion implantation and deposition

Ion implantation includes conventional beam-line ion implantation [80] and plasma immersion ion implantation (PIII) [81] producing in result the surface-modified layer with graded composition. It has been proved that oxygen implantation can improve wear and corrosion resistance, and biocompatibility of titanium and its alloys. There are different elements which are implanted into the surface of titanium and its alloys as listed in the *table 3.*

Table.3. *Elements implanted into titanium and its alloys.*

Implanted element	Objective	Reference
Oxygen (O)	Good biocompatibility	[82]
Nitrogen (N)	High hardness, wear, corrosion and fatigue resistance, good biocompatibility	[83-85]
Calcium (Ca)	Bioactivity, good corrosion resistance	[32,52]
Sodium (Na)	Increased surface roughness, improvement of corrosion resistance, bioactivity, cytocompatibility	[86,87]
Titanium (Ti)	Increased bond strength of the coating, higher hardness.	[88,89]
Magnesium (Mg)	Corrosion resistance	[90]
Phosphorus (P)	Biocompatibility	[91, 92]
Helium (He)	Good blood biocompatibility, good cell adhesion	[93]
Carbon (C)	Improvement of mechanical properties, corrosion resistance and biocompatibility	[94]

CONCLUSIONS

Osseointegration of the titanium implants to the bone tissue is a very important issue for the long-term usage of artificial implant. Surface modifications are widely used to adjust the properties of the titanium surface to the specific needs of the particular medical applications. Surface treatments, such as oxidation, nitriding, different types of coating, chemical etching, polishing and electrochemical methods etc. can lead to different degrees of bioactivation or conversely passivation improving the mechanical, chemical and biological properties of titanium and its implants.

REFERENCES

1. Liu X., Chu P.K., Ding Ch.: Surface modification of titanium, titanium alloys, and related materials for biomedical applications. Materials Science and Engineering, vol.47 (2004) 49-121.
2. Molitor P., Barron V., Young T.: Surface treatment of titanium for adhesive and adhesives. Vol. 21 (2) (2001) 129-136.
3. Citeau A., Guicheux J., Vinatier C., Layrolle P., Nguyen T.P., Pilet P., Daculsi G.:

In vitro biological effects of titanium rough surface obtained by calcium phosphate grid blasting. Biomaterials 26 (2005) 157-165.

4. Liang C.Y., Yang X.J., Wei Q., Cui Z.D.: Comparison of calcium phosphate coatings formed on femtosecond laser-induced and sand-blasted titanium. Applied Surface Science 255 (2008) 515-518.
5. Gbureck U., Masten A., Probst J., Thull R.: Tribochemical structuring and coating of implant metal surfaces with titanium oxide and hydroxyapatite layers. Materials Science and Engineering C 23 (2003) 461-465.
6. Hryniewicz T., Rokicki R., Rokosz K.: Corrosion and surface characterization of titanium biomaterial after magnetoelectropolishing. Surface & Coatings Technology 203 (2009) 1508-1515.
7. Strnad J., Strnad Z., Sestak J.: Physico-chemical properties and healing capacity of potentially bioactive titanium surface. Journal of Thermal Analysis and Calorimetry, vol. 88 (3) (2007) 775-779.
8. Mohammadi Z., Ziaei-Moayyed A.A., Sheikh-Mehdi Mesgar A.: Grit blasting of Ti-6Al-4V alloy: Optimization and its effect on adhesion strength of plasma-sprayed hydroxyapatite coatings. Journal of Materials Processing Technology 194 (2007) 15-23.
9. Lu X., Zhao Z., Leng Y.: Biomimetic calcium phosphate coatings on nitric-acid-treated titanium surfaces. Materials Science and Engineering C 27 (2007) 700-708.
10. Yousefpour M., Afshar A., Chen J., Xingdong Z.: Bioactive layer formation on alkaline-acid treated titanium in simulated body fluid. Materials and Design 28 (2007) 2154-2159.
11. Pattanayak D.K., Kawai T., Matsushita T., Takadama H., Nakamura T., Kokubo T.: Effect of HCl concentrations on apatie-forming ability of NaOH-HCl – and heat-treated titanium metal. J Materials Science: Materials in Medicine (2009) *published on-line:* *http://www.springerlink.com/content/m7l108m885m83056/*
12. Assis S.L., Costa I.: The Effect of Hydrogen Peroxide on the Electrochemical Behaviour of Ti-13Nb-13Zr Alloy in Hanks' Solution. Materials Research 9 (4) (2006) 425-429.
13. Han J.Y., Zu Z.T., Zhou L.: Hydroxyapatite/titania composite bioactivity coating processed by sol-gel method. Applied Surface Science 255 (2008) 455-458.
14. Nguyen H.Q., Deporter D.A., Pilliar R.M., Valiquette N., Yakubovich R.: The effect of sol-gel formed calcium phosphate coatings on bone ingrowth and osteoconductivity of porous-surfaced Ti alloy implants. Biomaterials 25(5) (2004) 865-876.
15. Wierzchoń T., Czarnowska E., Krupa D.: Inżynieria powierzchni w wytwarzaniu biomateriałów tytanowych. Oficyna Wyd. Politechniki Warszawskiej. Warszawa 2004.
16. Wilks R.G., Santos E., Kurmaev E.Z., Yablonskikh M.V., Moewes A., Kuromoto N.K., Soares G.A.: Characterization of oxide layers fordem on electrochemically treated Ti by Rusing soft X-ray absorption measurements. J Electron Spectroscopy and Related Phenomena 169 (2009) 46-50.

17. Diamanti M.V., Pedeferri M.P.: Effect of anodic oxidation parameters on the titanium oxides formation. Corrosion Science 49 (2007) 939-948.
18. Cui X., Kim H.-M., Kawashita M., Wang L., Xiong T., Kokubo T., Nakamura T.: Preparation of bioactive titania films on titanium metal via anodic oxidation. Dental materials 25 (2009) 80-86.
19. Bauer S., Park J., Mark K., Schmuki P.: Improved attachment of mesenchymal stem cells on super-hydrophobic TiO_2 nanotubes. Acta Biomaterialia 4 (2008) 1576-1582.
20. Goto T.: Surface coating technology for biomaterials – morphology and nono-structure control. International Congress Series 1284 (2005) 248-256.
21. Sevilla P., Aparicio C., Planell J.A., Gil F.J.: Comparison of the mechanical properties between tantalum and nickel-titanium foams implant materials for bone ingrowth applications. J Alloys and Compounds 439 (2007) 67-73.
22. Trommer R.M., Santos L.A., Bergmann C.P.: Alternative technique for hydroxyapatite coatings. Surface & Coatings Technology 201 (2007) 9587-9593.
23. Kim D.S., Han S.J., Kwak S.-Y.: Synthesis and photocatalytic activity of mesoporous TiO_2 with the surface area, crystallite size, and pore size. J Colloid and Interface Science 316 (2007) 85-91.
24. Baram N., Starosvetsky D., Starosvetsky J., Epshtein M., Armon R., Ein-Eli Y.: Enhanced inactivation of *E.coli* bacteria using immobilized porous TiO_2 photoelectrocatalysis. Electrochimica Acta 54 (2009) 3381-3386.
25. Lewis G., McVay B.: Effect of Thermal Spray Process for Deposition Hydroxyapatite Coating on a Titanium Alloy on its Fatigue Performance. 17th Southern Biomedical Engineering Conf (1998) 119.
26. Gledhill H.C., Turner I.G., Doyle C.: In vitro dissolution behavior of two morphologically different thermally sprayed hydroxyapatite coatings. Biomaterials 22 (2001) 695-700.
27. Li H., Khor K.A.: Characteristics of the nanostructures in thermal sprayed hydroxyapatite coatings and their influence on coating properties. Surface & Coatings Technology 201 (2006) 2147-2154.
28. Lima R.S., Khor K.A., Li H., Cheang P., Marple B.R.: HVOF spraying on nanostructured hydroxyapatite for biomedical applications. Materials Science and Engineering A 396 (2005) 181-187.
29. Goana M., Lima R.S., Marple B.R.: Influence of particle temperature and velocity on the microstructure and mechanical behavior of high velocity oxy-fuel (HVOF) – sprayed nanostructured titania coatings. J Materials Processing Technology 198 (2008) 426-435.
30. Hoseini M., Jedenmalm A., Boldizar A.: Tribological investigation of coatings for artificial joints. Wear 264 (2008) 958-966.
31. Chiu S-M., Chen Z-S., Yang K-Y., Hsu Y-L., Gan D.: Photocatalytic activity of moped TiO2 coatings prepared by sputtering deposition. J Materials Processing Technology 192-193 (2007) 60-67.
32. Krupa D., Baszkiewicz J., Rajchel B., Barcz A., Sobczak J.W., Biliński A.,

Borowski T.: Effect of calcium-ion implantation on the corrosion resistance and bioactivity of the Ti6Al4V Allom. Vacuum 81 (2007) 1310-1313.

33. Xie Y., Liu X., Huang A., Ding Ch., Chu P.K.: Improvement of surface bioactivity on titanium by water and hydrogen plasma immersion ion implantation. Biomaterials 26 (2005) 6129-6135.

34. Jo Y.J., Lee C.M., Jang H.S., Lee N.S., Suk J.-H., Lee W.H.: Mechanical properties of fully porous and porous-surfaced Ti-6Al-4V implants fabricated by electro-discharge-sintering. J Materials Processing Technology 194 (2007) 121-125.

35. An Y.B., Lee W.H.: Synthesis of porous titanium implants by environmental-electro-discharge-sintering process. Materials Chemistry and Physics 95 (2006) 242-247.

36. Lausmaa J. in Brunette D.M., Tengvall P., Textor M., Thomsen P. (Eds.): Titanium in Medicine, Springer, Berlin (2001) 231-266.

37. Albrektsson T., Wennerberg A.: Part 1 – review focusing on topographic and chemical properties of different surfaces and in vivo responses to them. International J Prosthodontosis. 17(5) (2004) 536-543.

38. Cook S.D., Thomas K.A., Kay J.F., Jarcho M.: Hydroxyapatite-coated titanium for orthopedic implant applications. Clinical Orthopaedic and Related Research (1988) 225-243.

39. Ronald H.J., Ellingsen J.E.: Effect of micro-roughness produced by TiO_2 blasting-tensile testing of bone attachment by using coin-shaped implants. Biomaterials 23 (2002) 4211-4219.

40. Fini M., Savarino L., Aldini N.N., Martini L., Giaveresi G., Rizzi G., Martini D., Ruggeri A., Giunti A., Giardino R.: Biomechanical and histomorphometric investigation on two morphologically differing titanium surfaces with and without frluorohydroxyapatite coating: an experimental study in sheep tibiae. Biomaterials 24 (2003) 3183-3192.

41. Andrade M.C., Bastos I.N., Filgueiras M.R.T., Ogasawara T.: Behavior of hydroxyapatite coated titanium as a function of NaOH pretreatment. Revista Cientifica Internacional, 1(3) (2008) 1-16.

42. Conforto E., Caillard D., Muller L., Muller F.A.: The structure of titanate nanobelts used as seeds for the nucleation of hydroxyapatite at the surface of titanium implants. Acta Biomaterialia 4 (2008) 1934-1943.

43. Ho W-F., Lai Ch-H., Hsu H-Ch., Wu S-Ch.: Surface modification of low-modulus Ti-7.5Mo Allom treated with aqueous NaOH. Surface & Coatings Technology 203 (2009) 3142-3150.

44. Kim H.M., Miyaji F., Kokubo T., Nakamura T.: Preparation of bioactive Ti and its alloys via Simple chemical surface treatment. J Biomedical Materials Research, 32 (3) (1996) 409-417.

45. Lu X., Leng Y., Zhang X., Xu J., Qin L., Chan Ch-W.: Comparative study of osteoconduction on micromachined and alkali-treated titanium alloy surfaces in vitro and in vivo. Biomaterials 26 (2005) 1793-1801.

46. Nebe J.B., Muller L., Luthen F., Ewald A., Bergemann C., Conforto E., Muller

F.A.: Osteoblast response to biomimetically altered titanium surfaces. Acta Biomaterialia 4 (2008) 1985-1995.

47. Takeuchi M., Abe Y., Yoshida Y., Nakayama Y., Okazaki M., Akagawa Y.: Acid pretreatment of titanium implants. Biomaterials 24 (10) (2003) 1821-1827.
48. Tas A.C.: Formation of calcium phosphate whiskers in hydrogen peroxide (H_2O_2) solutions AT 90^{o}C. J Americal Ceramics Society 90(8) (2007) 2358-2362.
49. Shukla A.K., Balasubramaniam R.: Effect of surface treatment on electrochemical behavior of CP Ti, Ti-6Al-4V and Ti-13Nb-13Zr alloys in simulated human body fluid. Corrosion Science 48 (2006) 1696-1720.
50. Oh S-H., Finones R.R., Daraio C., Chen L-H., Jin S.: Growth of nano-scale hydroxyapatite using chemically treated titanium oxide nanotubes. Biomaterials 26 (2005) 4938-4943.
51. Sobieszczyk S., Zieliński A.: Coatings in Arthroplasty. Advances in Materials Science, vol. 8, no 4 (2008) 35-54.
52. Li P., Groot K.: A calcium phosphate formation within sol-gel-prepared titania in vitro and in vivo. J Biomedical Science Research 27 (1993) 1495-1500.
53. Wen C.E., Xu W., Hu W.Y., Hodgson P.D.: Hydroxyapatite/titania sol-gel coatings on titanium-zirconium alloy for biomedical applications. Acta Biomaterialia 3 (2007) 403-410.
54. Ben-Nissan B., Milev A., Vago R.: Morphology of sol-gel derived nano-coated coralline hydroxyapatite. Biomaterials 25 (2004) 4971-4975.
55. Maiyalagan T., Viswanathan B., Varadaraju U.V.: Fabrication and characterization of uniform TiO_2 nanotube arrays by sol-gel template method. Bull. Mater. Sci., vol.29 (7) (2006) 705-708.
56. Kim H-W., Koh Y-H., Li L-H., Lee S., Kim H-E.: Hydroxyapatite coating on titanium substrate with titania Buffet layer processed by sol-gel method Biomaterials 25 (2004) 2533-2538.
57. Feng B., Chu X., Chen J., Wang J., Lu X., Weng J.: Hydroxyapatite coating on titanium surface with titania nanotube layer and its bond strength to substrate. J Porous Materials (2009) *published on-line:* http://www.springerlink.com/content/793488162u28q61t/
58. Narayanan R., Seshadri S.K.: Phosphoric acid anodization of Ti-6Al-4V – Structural and corrosion aspects. Corrosion Science 49 (2007) 542-558.
59. Oh S., Jin S.: Titanium oxide nanotubes with controlled morphology for enhanced bone growth. Materials Science and Engineering C 26 (2006) 1301-1306.
60. Wei D., Zhou Y., Yang Ch.: Characteristic, cell response and apatite-induction ability of microarc oxidized TiO_2-based coating containing P on Ti6Al4V before and after chemical-treatment and dehydration. Ceramics International 35 (2009) 2545-2554.
61. Sun J., Han Y., Huang X.: Hydroxyaptite coatings prepared by micro-arc oxidation in Ca- an P-containing electrolyte. Surface & Coatings Technology 201 (2007) 5655-5658.

62. Wei D., Zhou Y., Jia D., Wang J.: Effect of heat treatment on the structure and in vitro bioactivity of microarc-oxidized (MAO) titania coatings containing Ca P ions. Surface & Coatings Technology 201 (2007) 8723-8729.

63. Park I.S., Woo T.G., Jeon W.Y., Park H.H., Lee M.H., Bae T.S., Seol K.W.: Surface characteristics of titanium anodized in the four different types of electrolyte. Electrochimica Acta 53 (2007) 863-870.

64. Nolan M.G.: Design and commissioning of an off-line APCVD coater to deposit titanium dioxide self-cleaning films. SIMTech technical reports, 9 (2) (2008) 75-80.

65. Romanuja N., Levy R.A., Dharmadhikari S.N., Ramos E., Pearce W., Menasian S.C., Schamberger P.C., Collins C.C.: Synthesis and characterization of low pressure chemically vapor deposited titanium nitride films using $TiCl_4$ and NH_3. Materials Letters 57(2) (2002) 261-269.

66. Cruz N.C., Rangel E.C., Wang J., Trasferetti B.C., Daranzo C.U., Castro S.G., Morges M.A.B.: Properties of titanium oxide films obtained by PECVD. Surface & Coating Technology 126 (2-3) (2000) 123-130.

67. Jóźwik K., Karczemska A.: The new generation Ti6Al4V artificial heart valve with nanocrystalline diamond coating on the ring and with Derlin disc after long-term mechanical fatigue examination. Diamond & Related Materials 16 (2007) 1004-1009.

68. Kugler C., Fink M., Laimer J., Stori H.: Dynamics of pulsed d.c. discharges used for PACVD – effect of additional high voltage pulses. Surface & Coatings Technology 142-144 (2001) 424-428.

69. Tosatti S., Michel R., Textor M., Spencer N.D.: Self-assembled monolayers of dodecyl and hydroxyl-dodecyl phosphates on both smooth and rough titanium and titanium oxide surfaces. Langmuir 18(9) (2002) 3537-3548.

70. Zhang Z.H., Feng Ch.L.: Immobilization/hybridization of amino-modified DNA on plasma-polymerized allyl chloride. Applied Surface Science 253 (22) (2007) 8915-8922.

71. Ishikawa K., Suzuki T., Kitamura Y., Tobe S.: Corrosion resistance of thermal sprayed titanium coatings in chloride solution. J Thermal Spray Technology 8(2) (2007) 273-278.

72. Liu X., Poon R.W.Y., Kwok S.C.H., Chu P.K., Ding Ch.: Plasma surface modification of titanium for hard tissue replacements. Surface & Coatings Technology 186 (2004) 227-233.

73. Nakashima Y., Hayashi K., Inadome T., Uenoyama K., Hara T., Kanemaru T., Sugioka Y., Noda I.: Hydroxyapatite-coating on titanium arc sprayed titanium implants. J Biomedical Materials Research Part A 35(3) (1998) 287-298.

74. Rajesekaran B., Ganesh S.R.S., Joshi S., Sundararajan G.: Performance of plasma sprayed and detonation gun sprayed Cu-Ni-In coatings on Ti-6Al-4V under plain fatigue and fretting fatigue loading. Materials Science & Engineering 479 (1-2) (2008) 83-92.

75. Bray M., Cockburn A., O'Neill W.: The Laser-assisted Cold Spray process and deposition charactrisation. Surface & Coatings Technology 203 (19) (2009) 2851-2857.

76. Chiu Ch-Y., Hsu H-Ch., Tuan W-H.: Effect of zirconia addition on the microstructural evolution of Poros hydroxyapatite. Ceramics International 33 (2007) 715-718.

77. Wiklund U., Larsson M.: Low friction PVD titanium-carbon coatings. Wear 241 (2) 234-238.

78. Giolli C., Borgioli F., Credi A., et.al.: Characterization of TiO_2 coatings prepared by a modified electric arc-physical vapor deposition system. Surface & Coatings Technology 202 (2007) 13-22.

79. Sobiecki J.R., Wierzchoń T.: Structure and properties of plasma carbonitrided Ti-6Al-2Cr-2Mo Alloy. Surface & Coatings Technology 200 (14-15) 4363-4367.

80. Moller W., Mukherjee S.: Plasma-based ion implantation. Current Science 83 (3) (2002) 237-253.

81. Zhao X., Liu X., Ding Ch., Chu P.K.: Effects of plasma treatment on bioactivity of TiO_2 coatings. Surface & Coatings Technology 201 (2007) 6878-6881.

82. Valencia-Alvarado R., Piedad-Beneitez A., Lopez-Callejas R., Barocio S.R., Mercado-Cabrera A., Pena-Equiluz R., Munoz-Castro A.E., Rosa-Vazquez J.: Oxygen implantation and diffusion in pure titanium by an rf inductively coupled plasma. Vacuum 83 (Supp 1) (2009) 264-267.

83. Gurrappa I., Monara D., Gerlach J.W., Mandl S., Rauschenbach B.: Influence of nitrogen implantation on the high temperature oxidation of titanium-based alloys. Surface & Coatings Technology 201 (6) (2006) 3536-3546.

84. Johansson C.B., Lausmaa J., Rastlund T., Thomsen P.: Commercially pure titanium and Ti6Al4V implants with an without nitrogen-ion-implantation: surface characterization and quantitative studies in rabbit cortical bone. J Materials Science in Medicine 4 (2) (1993) 132-141.

85. Varela M., Garcia J.A., Rodriquez R., Caceres D., Ballesteros C.: Microstructure changes induced by low-energy high-temperature nitrogen ion implantation on vanadium-titanium alloys. Nanotechnology 3 (2003) 207-210.

86. Pham M.T., Matz W., Reuther H., Richter E., Steiner G.: Hydroxyapatite nucleation on Na ion implanted Ti surfaces. J Materials Science Letters 19 (2000) 1029-1031.

87. Cai K.Y.: Surface modification of titanium films with sodium ion implantation: surface properties and protein adsorption. Acta Metallurgica Sinica 20 (2) (2007) 148-156.

88. Asami K., Ohtsu N., Saito K., Hanawa T.: $CaTiO_3$ films sputter-deposited under simultaneous Ti-ion implantation on Ti-substrate. Surface & Coatings Technology 200 (2005) 1005-1008.

89. Krupa D., Baszkiewicz J., Sobczak J.W., Biliński A., Barcz A., Rajchel B.: Influence of anodic oxidation on the bioactivity and corrosion resistance of phosphorous-ion implanted titanium. Vacuum 70 (2003) 109-113.

90. Wan Y.Z., Huang Y., He F., Wang Y.L., Zhao Z.G., Ding H.F.: Effect of Mg ion implantation on calcium phosphate formation on titanium. Surface & Coatings Technology 201 (2006) 2904-2909.

91. Krupa D., Baszkiewicz J., Kozubowski J.A., Barcz A., Sobczak J.W., Biliński A., Lewandowska-Szumiel M., Rajchel B.: Effect of dual Ion implantation of calcium and phosphorus on the properties of titanium. Biomaterials 26 (2005) 2847-2856.

92. Krupa D., Baszkiewicz J., Kozubowski J., Barcz A., Sobczak J., Biliński A., Rajchel B.: The influence of calcium and/Or phosphorous ion implantation on the structure and corrosion resistance of titanium. Vacuum 63 (2001) 715-719.

93. Hanawa T., Nakajima S., Yamamoto A., Suzuki Y., Iwaki M.: Control of platelet and cell adhesion to titanium with helium ion implantation. European Cells and Materials 6 (Supp 1) (2003) 36.

94. Ma X., Sun Y., Wu P., Xia L., Yukimura K.: Structure of titanium films implanted with carbon by plasma-based ion implantation. Surface & Coatings Technology 169-170 (2003) 375-378.