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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 (13.3×10^{-6} K^{-1}) coating and titanium substrate (8.5×10^{-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.

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