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Review Article

A review on surface treatment of titanium implant

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ABSTRACT

Dental implants are fixtures that serve as replacements for the root of the missing natural tooth and in the current day dental practice. Success or failure of the dental implant treatment is mainly based on the principles of osseointegration, which is the direct and stable anchorage of an implant due to the formation of bony tissue around the implant. A number of systemic and local factors influence the production of an osseointegrated interface and therefore the stability of the implant. Present article covers various methods used for surface treatment of titanium and titanium alloy implants. They are mechanical method such asMachining,Grinding,Polishing and Grit blasting. Chemical treatment include Acid treatment,Hydrogen peroxide treatment,Alkali treatment.Sol–gel coatings include TiO2 coating,Calcium phosphate coatings, Titania/hydroxyapatite composite coatings and Silica coating.Electrochemical treatments includes Thermal spraying,Plasma spraying.Ion implantation and deposition include Oxygen implantation, Nitrogen implantation,Carbon implantation and deposition, Metal ion implantation. Surface modification methods used to improve the mechanical, chemical and biological properties of titanium and its alloys for biomedical application.

1. Introduction

The long-term success of dental implant largely depends on rapid healing with safe integration into the jaw bone. Jaw bone accepts and osseointegrates with the titanium implant.

The integration of biomaterials into bone, or any tissue, relies on healing mechanisms involving the stages of haemostasis, inflammation, regeneration, and remodelling. With new techniques and knowledge, trials to modify the mechanisms after implant installation, to speed up the process as well as having an enhanced healing and integration, are performed with many implant surfaces.

The most important steps in the peri-implant healing cascade are profoundly influenced by implant surface microtopography. Surface characteristics is the most significant factor affecting the osseointegration. This promotes the mechanism of osseointegration with faster and stronger bone formation to confer better stability during the healing process,thus allowing rapid loading of implant.[1] Surface treatment of implant improves clinical performance in areas of poor quantity or quality of bone.[2] Implant surface topography can be macro, micro level and nano level. Microtopogaphy has been regarded as the most important factor for successful implant treatment.

2. Reasons for surface modification

The bulk properties of biomaterials, such as non-toxicity, corrosion resistance or controlled degradability, modulus of elasticity, and fatigue strength have long been recognized to be highly relevant in terms of the selection of the right biomaterials for a specific biomedical application. The events after implantation include interactions between the biological environment and artificial material surfaces, onset of biological reactions, as well as the particular response paths chosen by the body. The material surface

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plays an extremely important role in the response of the biological environment to the artificial medical devices. In implants made of titanium, the normal manufacturing steps usually lead to an oxidized, contaminated surface layer that is often stressed and plastically deformed, non-uniform and rather poorly defined. Such native surfaces are clearly not appropriate for biomedical applications and some surface treatment must be performed. Another important reason for conducting surface modification to titanium medical devices is that specific surface properties that are different from those in the bulk are often required. For example, in order to accomplish biological integration, it is necessary to have good bone formability. In blood-contacting devices, such as artificial heart valves, blood compatibility is crucial. In other applications, good wear and corrosion resistance is also required. The proper surface modification techniques not only retain the excellent bulk attributes of titanium and its alloys, such as relatively low modulus, good fatigue strength, formability and machinability, but also improve specific surface properties required by different clinical applications.

3. Methods used for surface treatment

3.1. Mechanical methods

Common mechanical surface modification methods, such as machining grinding, polishing, and blasting, involve physical treatment, shaping, or removal of the materials surface. The typical objective of mechanical modification is to obtain specific surface topographies and roughness, remove surface contamination, and improve adhesion in subsequent bonding steps

3.2. Machining

Machining (lathing, milling, threading) is not really a surface treatment method, but on the other hand it can be used to produce specific surface topographies and surface compositions. The properties of machined surfaces mainly depend on the work-piece speed, tool pressure and choice of lubricant. Machined implant surface is generally characterized by grooves and valleys more or less oriented along the machining direction and the surface layers are plastically deformed.

3.3. Grinding

Grinding involves use of coarse particles as abrasive medium to remove the surface at a faster rate. Grinding creates relatively rough surface topographies.

3.4. Polishing

Polishing of the implant surface involves use of a fine abrasive material that is applied to a flexible wheel or a belt and then the implant is brought into direct contact with the abrasive surface. Polishing is always carried out in the presence of lubricant. Polishing is generally carried out using SiC, alumina or diamond to produce extremely smooth and mirror like surface with Ra values of 0.1 μm or less

3.5. Grit blasting

Grit blasting, also known as abrasive blasting, is another technique which is used to create surface topographies on the implant surfaces. In grit blasting, surface of the implant is bombarded with hard dry particle or particles suspended in a liquid at high velocity. Various types of ceramic particles such as alumina, silica, etc. of different sizes can be used for grit blasting of titanium.

3.6. Chemical methods

Chemical methods described here include chemical treatment, electrochemical treatment (anodic oxidation), sol–gel, chemical vapor deposition (CVD), and biochemical modification. During the chemical treatment, electrochemical treatment, and biochemical modification, chemical, electrochemical or biochemical reactions occur, respectively, at the interface between titanium and a solution. Chemical vapor deposition is a process involving chemical reactions between chemicals in the gas phase and the sample surface resulting in the deposition of a non-volatile compound on the substrate.

3.7. Chemical treatment

Chemical treatment of titanium and its alloy are mainly based on chemical reactions occurring at the interface between titanium and a solution. The common ones are acid, alkali, H202, heat, and passivation treatments.

3.7.1. Acid treatment

Acid treatment is often used to remove oxide and contamination to obtain clean and uniform

surface finishes. A combination of acids is frequently used to pre-treat titanium. Acid etching generally leads to a thin surface oxide layer (<10 nm). These oxide layers have been shown to grow slowly in air, from 3 to 6 nm during a 400-day period.[3] The oxide is predominantly TiO2

3.7.2. Hydrogen peroxide treatment

Titania gel coating can improve the bioactivity of titanium implants because titania gels can induce the formation of apatite when soaked in a simulated body fluid (SBF)[4] Titanium surfaces have been shown to react with H2O2 producing Ti-peroxy gels. The titania gel processed between 400 and 500^0 c possesses the anatase structure and exhibits excellent bioactivity.

3.7.3. Alkali treatment

The alkali and heat treatment can be described as follows . The materials are first immersed in a 5–10 M NaOH or KOH solution for 24 h, followed by rinsing with distilled water and ultrasonic cleaning for 5 min. The specimens are then dried in an oven at 40 0C for 24 h and finally heated to around 600–800 0C for 1 h because of the strong tendency of titanium to oxidize, the heat treatment is performed at a pressure of 10-4 to 10-5 Torr. The alkali and heat-treated (AHT) titanium possesses good bioactivity.

3.8. Sol–gel coatings

The sol–gel process can be divided into five main steps: (1) hydrolysis and polycondensation;(2) gelation; (3) aging; (4) drying; (5) densification and crystallization The sol–gel process is widely used to deposit thin (<10 mm) ceramic coatings. Compared to conventional thin film processes, it allows for better control of the chemical composition and microstructure of the coating, preparation of homogeneous films, reduction of the densification temperature and finally simple equipment and lower cost. It is especially easy to purify the precursors by distillation or crystallization or, taking the opposite approach, to introduce trace elements.

3.8.1. TiO2 coating

The standard sol can be prepared by mixing tetraisopropyl orthotitanate, ethanol, ethyleneglycol monoethylether, hydrochloric acid, and water. The sol is mixed for 1 h before titanium plates are dip coated. The sol container is kept at 0 0C in order to slow down the condensation reaction.

Valeric acid is then added to part of the sol and these containers are kept at room temperature. It is believed that the sol–gel titania rich in Ti–OH groups can induce calcium phosphate formation and may therefore be able to contribute to enhanced bonding to bones. Li et al. In vivo, the calcium phosphate was observed within the titania gel film after 12 weeks of implantation in femurs of goats by Li et al.[5]

3.8.2. Calcium phosphate coatings

The possibility of modifying the surface area, porosity, composition, adsorption capacity, and dissolution rate using the sol–gel technique is very attractive in the fields of medicine and dentistry. Calcium phosphate coatings, especially hydroxyapatite coatings, are commonly used in orthopedic applications. The sol–gel method is a relatively simple way to prepare hydroxyapatite coatings on titanium alloys because of the easy formation of the oxide coatings at a relatively low temperature.

3.8.3. Titania/hydroxyapatite composite coatings

The hydroxyapatite coatings synthesized by the sol–gel method are typically bioactive but have poor adhesion strength to the substrate. The biocompatibility of titania/hydroxyapatite coatings prepared by the sol–gel process was investigated by Ramires et al.[6] The TiO2/HA coatings are bioactive due to the presence of hydroxyl groups on the surface promoting calcium and phosphate precipitation thereby improving the interactions with osteoblastic cells.

3.8.4. Silica coating

The role of silica gel in the formation of bone-like apatite on the substrate has been investigated by many researchers. Hench et al. proposed that the combination of an alkaline interfacial pH due to the high content of soda in the glasses and repolymerizing SiO2 from surface Si–OH groups is sufficient to attract CaO and P2 O5 from the body fluids to achieve nucleation and growth of the apatite layer. Karlsson et al.

3.9. Anodic oxidation

Anodic oxidation encompasses electrode reactions in combination with electric field driven metal and oxygen ion diffusion leading to the formation of an oxide film on the anode surface. Anodic oxidation is a well-established method to produce different types of protective oxide films on metals. Yang et al.[7] indicated that anodic oxidation in H2 SO4 solution combined with subsequent heat treatment was an effective method to prepare bioactive titanium. After anodic oxidation, the surface was observed to be covered by porous titania of the anatase and/or rutile phase. In simulated body fluids, the titanium anodically oxidized during spark discharge inducing apatite formation on its surface

3.10. Chemical vapor deposition

Chemical vapor deposition is a process involving chemical reactions between chemicals in the gas phase and the sample surface resulting in the deposition of a non-volatile compound on the substrate. It is different from physical vapor deposition (PVD), which typically employs techniques, such as evaporation and sputtering involving no chemical reactions. Biochemical modification of titanium and titanium alloys Biochemical modification of biomaterials utilizes biological and biochemical knowledge on cellular function, adhesion, differentiation and remodeling. The objective of modification is to induce specific cell and tissue response by means of surface-immobilized peptides, proteins, or growth factors.

3.11. Physical method

During some surface modification processes, such as thermal spraying and physical vapor deposition, chemical reactions do not occur. In this case, the formation of surface modified layer, films or coatings on titanium and its alloys are mainly attributed to the thermal, kinetic, and electrical energy.

3.12. Turning process

The turning process of dental implants is often used to gain the macro design of the implant that may, thereafter, be modified. Turned surfaces have mainly been found smooth (average height deviation <0.5 μm) or minimally rough (average height deviation of 0.5-1 μm) and anisotropic due to the turning process.

3.13. Grit/abrasive blasting

The processing can produce isotropic surfaces with various roughnesses and chemistries depending on the blasting particle (TiO2 and Al2 O3 are commonly used) and its size, as well as the pressure and the distance of the blasting instrument.

3.14. Ultraviolet irradiation of TiO2 crystalline surfaces

By treating a crystalline surface with ultraviolet irradiation, decomposition of organic compounds occur and an extremely clean surface is achieved. Furthermore, surface oxygen vacancies appear, which interact with water molecules and forms hydroxyl-groups with hydrophilic domains on the outermost layer.[8]

3.15. Electrochemical treatments

3.15.1. Thermal spraying

Thermal spraying is a process in which materials are thermally melted into liquid droplets and introduced energetically to the surface on which the individual particles stick and condense. The coating is formed by a continuous build-up of successive layers of liquid droplets, softened material domains and hard particles. Thermal spraying requires a device that creates a high temperature flame or a plasma jet. Therefore, thermal spraying is often divided into flame spraying and plasma spraying.

3.15.2. Plasma spraying

Since its inception in Union Carbide in the mid-1950s, plasma spraying, a subset of thermal spraying, is often used to form ceramic coatings. With the advent of the space age and commercial plasma spray devices in the early 1960s, thermal-sprayed ceramic coatings have found utility in thermal barrier coatings (TBCs), some electrical conductors, and dielectrics. The materials are often used in the aerospace, printing, petrochemical, and other industries with much research being conducted in the medical, biomedical, electronic, and electrical engineering fields.

3.15.3. Plasma sprayed hydroxyapatite coating

Because of its similarity to the mineral phase of natural hard tissues, artificial hydroxyapatite is considered to be a bioactive material. Bone can be regarded as an organic matrix with inclusion of inorganic filler with a crystal size in the submicron range. About 70% of the mineral fraction of bone has a HA-like structure and the use of HA as an orthopedic biomaterial has been suggested and clinically demonstrated.

3.15.4. Plasma sprayed calcium silicate coating.

Some glasses, glass–ceramics, and ceramics consisting of CaO–SiO2have been reported to possess good bioactivity and biocompatibility. Bioactive glass was once deposited onto titanium and its alloys using plasma spraying. The bioactive glass coating retains the properties of the original glass with respect to the amorphous structure and the behavior in a hydrolytic environment.[9]

3.15.5. Plasma sprayed titanium coating

Plasma-sprayed titanium coatings with porous structure have been used in teeth root, hip, knee and shoulder implants. The porous surface improves fixation via the growth of bone into the coating forming a mechanical interlock.[10]

3.15.6. Other thermal spraying techniques

In addition to plasma spraying, some other thermal spraying techniques are used to modify the surface of titanium and its alloys in biomedical applications. A high velocity oxy-fuel torch was developed in the late 1970s and early 1980s. The principle of the HVOF process can be described as follows. The powder is injected axially into the jet as suspension in the carrier gas, burns in the combustion chamber, and flows through the nozzle out of the torch.[11]

3.15.7. Physical vapor deposition

Physical vapor deposition process can be described succinctly as follows. In vacuum, the target materials are evaporated or sputtered to form atoms, molecules or ions that are subsequently transported to the substrate surface, on which condensation and sometimes some reactions with the materials surface take place leading to film growth. The important processes and parameters inPVD are: (1) generation of particles from the target materials; (2) transport and film growth; (3)particle energy, density, substrate temperature and reactive gas properties. PVD processes are characterized by high coating density and strong adhesion, multi-component layers, low substrate temperature, and a myriad of coating and substrate materials. Physical vapor deposition processes include evaporation, sputtering, and ion plating.

3.15.8. Evaporation

The evaporation process consists of a thermal phase change from a solid to vapor similar to boiling. The difference between vacuum evaporation and boiling is that the boiling point is defined as the temperature at which the phase of a material changes from a liquid to a gas at one atmosphere of pressure. When evaporation is conducted in an ambient with reactive gases, compound films can be deposited at higher rates and lower temperature. For example, TiC and TiN coatings have been deposited by evaporating Ti in the presence of c2 H2 and N2 plasma, respectively.[12]

3.15.9. Ion plating

Ion plating is characterized by energetic bombardment by particles that alter the substrate surface and influence the film formation process. Generally, energetic particles are extracted from plasma, a compound or alloy sputtering target, vacuum or plasma arcs, or special ion sources.[13]

3.15.10. Sputtering

Sputtering is a common method to deposit thin films and its popularity stems from the simplicity of the physical processes involved, versatility, and flexibility. It is widely used in the semiconductor, photovoltaic, recording and automotive industries. Attempts have been made to deposit a thin film on titanium and titanium alloys to improve their biocompatibility, bioactivity, wear resistance and corrosion resistance.

3.15.11. Glow discharge plasma treatment

Glow discharge plasma is a low-temperature, low-pressure gas in which ionization is controlled by energetic electrons. Glow discharge plasma treatment has been well established for cleaning and surface processing in the microelectronics industry and has attracted much interest in biomaterials research in which it is used for the surface modification of bulk polymers and production of thin polymer coatings (plasma polymerization) Plasma treatments have for some time been a relatively common method to increase the surface energy and clean the surface of biomaterials before biological evaluation studies.[14]

3.16. Ion implantation and deposition

Ion beam processing is a process in which energetic ions are introduced into the surface layer of a solid substrate via bombardment. The use of energetic ions affords the possibility of introducing a wide range of atomic species independent of thermodynamic factors thus making it possible to obtain impurity concentration sand distribution of particular interest. Ion implantation includes conventional beam-line ion implantation and plasma immersion ion implantation.

3.16.1. Oxygen implantation

Oxygen is a common element introduced into metals to modify their mechanical, physical, chemical, and biological properties using either conventional beam-line ion implantation or PIII. Titanium oxide is known to have varying stoichiometries and the common compounds are Ti 3O to Ti2 O, Ti 3O2, TiO, Ti 2O3, Ti 3O5 and TiO3. This is a consequence of the facts that titanium exists in many different stable oxidation states and that that oxygen is highly soluble in titanium.

3.16.2. Nitrogen implantation

Titanium nitride is a member of the refractory transition metal nitride family, which exhibits properties characteristic of both covalent and metallic compounds. TiN also has in its high hardness and remarkable resistance to wear and corrosion and is therefore commonly used in products, such as cutting tools. Because of its intrinsic biocompatibility, TiN is also a suitable material for orthopedic implant and has been used as a coating on the heads of hip prostheses to improve their wear and fatigue resistance.[15] Moreover, TiN is the material of choice as the hard coating on dental implants resistance.

3.16.3. Carbon implantation and deposition

Carbon does not worsen the biocompatibility of titanium alloys and is widely used as coatings on metal implants. Carbon has been implanted into or deposited onto titanium using ion implantation and deposition technologies to improve the mechanical properties, corrosion resistance and biocompatibility. The implanted ions are bound either to titanium to form titanium carbides or to carbon atoms to form C–C bonds near the surface.

3.16.4. Metal ion implantation

Calcium ion implantation is a promising method to enhance the surface bioactivity of titanium and both conventional ion implantation and PIII have been used.

Hanawa et al.[16] revealed that the bone conductivity of titanium was improved by calcium ion implantation as calcium ion implantation expedited calcium phosphate precipitation on titanium. Krupa et al.[17] also investigated the effects of phosphorus ion implantation on the corrosion resistance and biocompatibility of titanium. The process led to amorphization of the surface layer and the formation of TiP.

Calcium and phosphorus have been co-implanted into titanium and titanium alloys to enhance their mechanical properties and biocompatibility.[18] Sodium has also been implanted into titanium and its alloys to improve the bone conductivity by inducing the formation of apatite on their surface in body fluid.

Fluorine has been implanted into titanium to improve the antibacterial effect.[19] F-implanted specimens were observed to significantly inhibit the growth of both P. gingivalis ATCC33277(P.g.) and A. actinomycetemcomitans ATCC 43718 (A.a.). There are two possible explanations for the antibacterial mechanism. On one hand.

3.16.5. Chemistry

Regarding surface chemistry, most studies indicate no differences in the soft-tissue response either in humans, or in animals for materials used as oral implant abutments or for soft tissue adaptation, e.g. titanium/titania and zirconia. However, lower grade of inflammatory response has been found to ziconia as compared to titanium Similar findings with generally no differences in tissue response, further apply to Al2O3 in comparison with titania in human. For hydroxyapatite coated surfaces, there are findings of similar or enhanced soft-tissue/mucosa adaptation to such surfaces compared with titanium oxide surafaces; when Ti6Al4V were coated with hydroxyapatite together with bioglass, and compared to machined/turned Ti6Al4V there were a thinner capsule formed together with appreciated improved tissue quality.[20]

4. Conclusion

Surface modification methods used to improve the mechanical, chemical and biological properties of titanium and its alloys for biomedical application. These methods are classified into mechanical, chemical and physical methods according to the formation mechanism of the modified layer on the surface of titanium and its alloys. The properties of titanium and its alloys

can be upgraded to some extent after their surfaces are modified using suitable surface modification technology. With the development of the surface engineering, more new surface modification technologies will be introduced to improve the properties of titanium and its alloys for meeting the clinical need.

Various methods of surface modification or rough surface preparation in titanium and its alloys for implants were discussed with an emphasis on the methods based on the mechanical, thermal, chemical, electrochemical and laser methods. Although mechanical methods can be used to produce roughness on the titanium implant surfaces, the properties of the surface oxide layer are more difficult to control. Chemical treatments of implant surface are mainly employed to improve the oxide layer thickness required for the passivation of the metal. Several alternative methods have been discussed which are used to produce surface films on titanium implants with varying morphology, thickness, microstructure, and chemical composition. In thermal treatments, surface roughness and amount of oxide layer formation are temperature and time dependent. Laser surface treatment, on the other hand, can used to produce desired surface roughness without any contamination of the implant surfaces. Methods discussed are well established and are the methods that are widely used by the manufacturers of current day dental implants. Although these methods have been successfully developed and employed to produce dental implants with varying surface topographies, the effect of the surface topographies on the long term biological compatibility and osseointegration has not been established very well. However, research in this area is very much active and several new technologies and methods will be introduced in near future to produce various surface topographies on the implants surfaces.

Oral implants need to perform in three biological arenas: in relation to bone, soft-tissue, and microbial biofilms. What characteristics that may make a surface less prone to accumulate large biofilms and/or that do not stimulate the bacteria to co-adhere or assume a pathogenic phenotype, cannot be completely stated. However, smooth surfaces tend to accumulate and retain less biofilm biovolume in comparison to moderately rough surfaces. The optimal surface for osseointegration has been suggested to be of moderate roughness, whereas surfaces used in relation to oral mucosa generally have a smooth surface. Regarding the roughness, the part of the implants aimed to be bone integrated provides the most precarious surface for biofilm accumulation. Anodization and calcium ion incorporation of a titanium surface could possibly compensate for a minimal surface roughness regarding the performance in bone-tissue. Furthermore, the anodized and calcium ion incorporated smooth surfaces did not seem prone for extensive biofilm formation. To have a smooth surface performing comparatively to moderately rough surfaces, through altered chemistry or other altered properties, could be a new focus for oral implants when smooth surfaces possibly reduce the risks for biofilm infections. Furthermore, although surfaces aimed for soft-tissue integration most commonly are smooth, there are surface modifications (topographical and chemical) that aim for a stimulation of the cells and biological structures within the soft-tissue and since bacteria also are cells the stimulation and/or adhesion of such may as well increase. Modification with sol-gel dip coating, resulting in a nanoporous TiO2 surface, indicates advantages for soft-tissue integration in relation to turned/polished surfaces.

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6. Conflict of Interest

The authors declare they have no conflict of interest.

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