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Hydroxyapatite coating techniques for Titanium Dental Implants — an overview

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Abstract

Titanium and its alloys are the most commonly used materials for dental implants and hydroxyapatite is the most common bioactive material coated on titanium dental implants. Hydroxyapatite is from the ceramic class of biomaterials which has chemical and structural similarity with the biological apatite which forms the major inorganic portion of bone and tooth. It is not only bioactive, but also osteoconductive and non-toxic. The most interesting property of hydroxyapatite is its ability to interact with living bone tissue, forming strong bonds with the bone. Since the introduction of dental implants by Branemark in 1981, hydroxyapatite has gained attention as a preferred bioactive coating material for titanium dental implants and is still a hot topic of discussion. So, in this article an attempt has been made to give an overview of present techniques of hydroxyapatite coatings on titanium dental implants, including their advantages, disadvantages and limitations.

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Introduction

Titanium and its alloys are the most commonly used materials for dental implants because of their excellent biocompatibility, superior mechanical strength, and high corrosion resistance. However, they are bio-inert and do not bond or integrate with tissues (bone). A direct structural and functional connection between bone and the surface of an implant is critical for success of implant therapy. Therefore, to facilitate implant fixation and bone growth, bioactive agents are being applied on the surface of dental implants. ^{[1][2][3]}.

Bioceramic coatings are classified into two main categories- bioinert (such as alumina and zirconia) and bioactive (such

as calcium phosphate/hydroxyapatite and bioglass) coatings ^{[2][3][4]}. The bioinert ceramic coatings have the advantage of good biocompatibility and higher mechanical properties compared to the other. However, the high brittleness, high elastic modulus and the poor interaction ability with the surrounding tissues limit the use of bioinert ceramics in this field. On the other hand, calcium phosphate and bioglass, are more extensively used to treat the Ti implant due to their abilities to enhance the adhesion between the implant and the bone by interacting with the tissues ^{[2][5][6]}.

Since the introduction of dental implants by Branemark in 1981, efforts have been made to improve osseointegration and osteogenesis by coating the implant surface with hydroxyapatite ^{[1][2]}. Hydroxyapatite comes under the ceramic class of biomaterials which has chemical and structural similarity with biological apatite present in bone and tooth. It is the major inorganic constituent in bone and tooth. Titanium implants are commonly coated with it, infact hydroxyapatite has become an ultimate candidate for coating titanium dental implants. It is not only bioactive, but also osteoconductive and non-toxic ^{[2][3][4][5]}. The bonds they make with the bone are of a physico-chemical nature^[4]. The bone cells interact with the hydroxyapatite forming ionic, hydrogen and Vander walls bonds. Hydroxyapatite can crystallize as a fine salt depending on the Ca/P ratio, the formation temperature, the presence of water or impurities and, depending on the preparation medium, in a humid environment at relatively low temperatures^{[4][5]}.

Hydroxyapatite was the material of choice in the past for coating titanium dental implants and is still a hot topic of interest. But, in between there was a period when its use was questioned and it was about to disappear from the market because of its vulnerability to periimplantitis, dissolution, and failed interfacial adhesion between implant and hydroxyapatite ^{[6][7]}. However, advancements in coating methods have brought back the interest in hydroxyapatite coating. It is now known that the properties of hydroxyapatite, including bioactivity, biocompatibility, solubility, mechanical and adsorption properties can be adapted to a wide range of applications by controlling particle composition, size and morphology. The most interesting property of hydroxyapatite is its ability to interact with living bone tissue, forming strong bonds with the bone. The clinical concern with its use regarding the bonding strength between coating and the alloy/ Ti substrate can be increased by thermal spraying technology such as hot dip method, chemical vapour deposition method, slurry method etc. Thermal spray coating is the most efficient and commonly applied method now-a-days on metallic implants due to its uniform coating layer on the metal surfaces.

Each Implant manufacturer has its own proprietary coating process. There are many methods reported in the literature for forming hydroxyapatite coatings on Titanium implant surfaces which can be broadly classified under two categories – Pyroprocessing methods (e.g. Plasma spraying, sol- gel method, electron beam sputtering, ion beam sputtering etc.), and Hydroprocessing methods (e.g. Cathodic electrolysis method, thermal substrate method etc.) ^[8].

Some of the commonly used hydroxyapatite coating techniques are briefly discussed in this article. Among those techniques, only plasma spraying is commercially approved by the Food and Drug Administration (FDA), USA for biomedical coatings on implants due to its excellent coating properties over other coating methods^[9]. However, this technique is limited now-a-days because of some limitations mentioned below under the heading 'Plasma spraying.' So, alternative coating approaches have been extensively developed and tested like the sol–gel dip coating and electrochemical deposition techniques have relative ease of production, ability to apply a uniform coating over complex

geometric shapes, easy set up at room temperature, the potential to deliver exceptional mechanical properties, corrosion resistance, and adhesion strength due to their nanocrystalline structure.

Active ingredients Entrapment methods of nano- and micro-encapsulation to achieve the desired controlled release of the ingredients are being actively researched. Conventionally it was done by binding them to the substrate or coatings or mixing them into the coating material and applying the mixture to the implant surface. However, recently interest has shifted to a new method of entrapment of the active ingredient within another substance by microencapsulation or nanoencapsulation. Recently, coating with a bioactive growth factor (hydroxyapatite-BMP-2 coating) has been determined to enhance the relationship between an implant and the bone to which it is attached. BMP-2 enhances the osteogenic activity of osteocytes, accelerates osteoblast differentiation, and further promotes bone formation. It can also induce dentin and post-implant healing. Bacteriostatic and bactericidal agents like zinc are also being incorporated in the hydroxyapatite coating^{[10][11]}. Another hot topic which has received increased biomedical research attention in recent years is the influence of pore size and porosity of HA coatings on 3D-printed Ti scaffolds which have inherent porous structures^{[12][13]}. Besides the implementation of coatings, titania nanotube formation using anodization has gained interest nowadays^[14].

Sol- Gel Dip- coating Technique

The process starts with dispersion of the precursor particles (fine nano-sized particles) in an aqueous or alcohol solution forming a colloidal suspension (the sol). Then the addition of catalysts to the sol promotes polymerization reactions involving hydrolysis and polycondensation forming a gel ^{[15][16]}.

The dip-coating method (DCM) consist of a wellcontrolled immersion process. The speed and time of immersion are determinant factors of film thickness ^[17]. Generally, it allows for the attainment of very thin films, and thus maintains the original surface roughness of implants. Thick or irregular coating layers are not desirable because it might modify the surface roughness and could negatively interfere with cell adherence, differentiation, and consequently affecting osseointegration.

DCM consists of five sequential steps: (1) immersion of the pretreated titanium implant in the coating mixture at a specified rate; (2) keeping the implant immersed in the mixture for a specific amount of time; (3) lifting the implant out of the mixture or lowering the mixture container, which results in the formation of a wet liquid film of the coating on the surface of the implant; (4) draining off the excess liquid for the coating application from the implant surface; and (5) drying the coating layer by evaporation of the solvent under ambient conditions, thus forming a thin film on the substrate which can eventually be hardened by conventional or laser sintering ^{[17][18][19][20][21]}.

Various methods are used to synthesize nanocrystalline hydroxyapatite, such as hydrothermal, mechanochemical, precipitation, hydrolysis, and sol–gel methods. The sol–gel method can improve the chemical homogeneity of hydroxyapatite in comparison with other techniques, as it involves a mixing at the molecular level of calcium and phosphorus precursors^{[15][14]}.

But, in the dip coating-sintering technique the high-temperature sintering cycle has been judged to be unsatisfactory because of its adverse effect on the mechanical properties of the titanium implant like the excessive grain growth and loss of the wrought structure of both the commercially pure Ti and Ti-6AI-4V substrates^[17]. Another area of concern is the bond strength between the HA coating and the substrate which is not high enough to insure that interfacial failure will not occur during the lifetime of the implant^[16].

Electro-chemical Deposition (ECD)

"Electrochemical deposition is a process by which a thin and tightly adherent desired coating of metal, oxide, or salt can be deposited onto the surface of a conductor substrate by simple electrolysis of a solution containing the desired metal ion or its chemical complex"^[22].

It is the conventional well-known process based on the principle of electrolysis, that uses electrical current to reduce the cations of a desired material from an electrolyte and coat those materials as a thin film onto a conductive substrate surface^[23]. In other words it is a well-known method to produce in situ thin, metallic, inorganic or organic coating by the action of an electric current on a conductive material immersed in a solution containing a salt of the metal to be deposited. Other terms like electrodeposition and electroplating are also used for this method^[24].

Advantages of ECD are that it is performed at room temperature, is a rapid, straightforward and versatile method capable of delivering an HA coating on titanium implants with satisfactory homogeneity, thickness, and bonding strength as it has good control of the coating material's thickness, uniformity, crystallinity, and stoichiometry ^{[24][25][26]}. This technique can overcome the phase transition problems of PS-fabricated HA coatings and also the morphology of the HA coating can be modified by adjusting the electrochemical deposition parameters like the pH, temperature, and the deposition voltage and immersion time during the coating process. Other advantages of this technique are that anodic oxidation of Ti can improve the tear strength between HA coatings and Ti substrates and HA coatings can be doped with Mg to change the properties and facilitate the control of the dissolution rate of the HA coatings ^{[27][28]}.

Electro- phoretic Deposition

In this method, electrodes are immersed in a colloidal suspension, and a potential is applied between the two electrodes which results in movement of the charged suspended particles from the solution to the oppositely charged electrode (substrate), followed by the deposition of these particles on the electrode and the formation of a uniform coating up to 2.00 mm thick ^{[29][30][31]}.

Benefits are improved anti-corrosion property, improved adhesion, bioactivity, suitable cell viability, increased adhesion strength, thickness and roughness of coatings, improved corrosion resistance, and apatite formation by raising the BG concentration^{[29][30]}.

This technique has limited use as it applies a high voltage of 90V to deposit coating, followed by high sintering

temperatures and the crystal structures and coating compositions are changed after the deposition^{[30][31]}.

Biomimetic coating

Biomimetic means it mimicks nature or biology as near physiological conditions are employed for deposition of the apatites. This is a relatively new method in which heterogeneous nucleation and crystal growth of the coating occurs, which has bonelike properties. For this, pretreatment of implant surface is done by using either alkaline (NaOH) or acidic (HF or HCl) solutions or heat treatment. Then, the substrate is immersed in simulated body fluid (SBF) at body temperature (37 C) and physiological pH (7.4). It is important that the SBF contains an ion concentration similar to human blood plasma. The obtained results after several weeks in SBF are CaP-based coatings deposited on the Implant surface [³²][³³][³⁴][³⁵].

The advantages of this method are that it allows for the production of homogeneous HA coatings on porous implants, and functional and biological agents, such as growth factors, could be incorporated in HA coatings because of the near physiological conditions employed^[33]. However, the thickness, the formation rate, and the quality of the coating are difficult to control using this method, and the bonding strength of the coating is also unacceptable^[34].

Plasma spraying (PS)

Plasma spraying is a type of thermal spraying. It has been established as the most commonly used commercial coating technique for the fabrication of CaP/ HAP coatings on Ti–6Al–4V implant surface due to its time convenience, high repeatability, efficiency, and simplicity^[36]. In this method, generation of a direct current arc in the plasma torch, which consists of a cone-shaped cathode and a cylindrical anode is done. Then, HA material in the form of powder is fed into the spray gun, heated to a semi-molten or molten state (the plasma flame temperature being in the range of 6,000 -16000 degree centigrade) and then propelled to the implant surface with a high impact velocity (up to 400 m/s) which results in the coating material particles get flattened on the implant surface in the form of splats/lamellae with a large surface area and a thickness in the micrometre range ^{[37][38][39][40]}.

Based on the differences in the pressure conditions, there are variants of plasma spraying technique like atmospheric plasma spraying (APS) employed under atmospheric conditions, low-pressure plasma spraying (LPPS), also known as vacuum plasma spraying (VPS), operates at 3-7 kPa, and very low-pressure plasma spraying (VLPPS) operates at 50-200 Pa ^{[36][37][38][39][40][41]}.

Although PS is the preferred method in most cases, its excessively high temperature and the subsequent rapid cooling procedure generate a large amount of amorphous HA, and variations in the structure of HA occurs^{[1][2][38]}. In addition, the interior coating of the 3D porous implants is not accessible due to the line-of-sight nature of the spraying process^{[36][38]}.

Thus, this coating method has significant drawbacks/limitations like coating porosity, residual stress at the coating

interface, and drastic changes in the composition and crystallinity of the calcium phosphate (CaP) powder^[36]. Thus, there is poor uniformity in coating thickness and its adherence to substrate, phase impurity, low crystallinity, the degradation of bending strength and fatigue life caused by the dissolution of hydroxyapatite phase in long-term contact with body fluids, poor mechanical properties like tensile strength, wear resistance, hardness, toughness and fatigue, and not being able to produce a uniform hydroxyapatite coating with complex geometry^{[1][2][3][4][5][37]}. As this technique often does not ensure adequate adhesion of the coating to the substrate, a large coating thickness is required to ensure uniform coatings, and delamination of the coatings may often occur. Due to the very high process temperatures, it is less suitable for temperature-sensitive materials (e.g. organic coatings, heat-labile biological molecules) and also limits (but does not rule out) the possibility of drug release applications ^{[38][39][40][41][42]}.

High-Velocity Suspension Flame Spraying Technique (HVSFS)

It is a new method of acquiring the nanostructured dense surface coatings on the titanium implant surface by spraying the nanoparticles with hypersonic speed for which the powder is dispersed in aqueous or organic solvent and fed axially into the combustion chamber of a modified High-Velocity Oxyfuel spray-torch^{[41][42][43][44][45]}. This has been developed because the conventional High Velocity Oxygen Fuel (HVOF) spraying processes are not suitable to achieve nanoparticles coatings. The powder is processed in the form of a suspension (in aqueous or organic solvent) to solve the problems related to handling of powders composed of nanosized particles, and by doing this its feeding is also facilitated with quite simple thermal spray techniques^{[42][43]}.

Examples are the suspension plasma spraying (SPS) or the solution precursor plasma spraying (SPPS) methods. The liquid solvent used in this technique permits to inject particles in the thermal flow which is then heated, accelerated and sprayed onto the substrate. Thus, as compared to conventional plasma spraying, SPS and SPPS are more complex methods because fragmentation and vaporization of the liquid solvent control the coating buildup mechanisms ^{[43][44][45][46][47]}.

Physical vapour deposition (PVD)

It refers to the vacuum deposition methods where materials are evaporated or sputtered, transferred in the form of atoms, molecules, or ions and deposited onto the substrate surface in the form of thin films. Vapour generation can occur by two physical processes ^{[48][49][50]}:

- i. Thermal evaporation (heating of the material until its vapour pressure exceeds the ambient pressure) and
- ii. Sputtering (bombardment of the solid surface by energetic ions and ejection of neutral atoms for example ion beam deposition and magnetron sputtering). The latter is more useful for hydroxyapatite deposition.

Thermal evaporation involves the phase change from solid to vapor under vacuum conditions (to minimize contamination), in which evaporated atoms of a solid precursor (here hydroxyapatite) placed in an open crucible can travel directly and

condense onto the surface of a substrate (implant).

Sputtering involves a process of ejecting neutral atoms from a target surface using energetic particles (argon ions) which can be easily accelerated towards the cathode by means of an applied electric potential, hence bombarding the target. These ejected atoms are then transferred and condensed on the surface of the substrate to form a coating. There are several variants of sputtering method the simplest model being the diode plasma, which consists of an anode and a cathode, inside a vacuum system ^{[49][50][51][52]}. The sputtering target is mounted on the cathode. Appropriate potential difference is applied between the cathode and anode which ionizes argon gas and creates a plasma discharge. The argon ions then get attracted and accelerated toward the sputtering target and displace some of the target atoms. This results in electron emission that subsequently collide with gas atoms to form more ions that sustain the discharge ^{[48][51]}.

PVD technology includes a wide range of techniques, like cathodic arc deposition, electron beam deposition, evaporative deposition, pulsed laser deposition, ion plating, ion beam deposition, magnetron sputtering, etc ^{[53][54][55][56][57]}. For the deposition of bioactive hydroxyapatite based coatings on titanium implants, sputtering techniques are the ones found to be more convenient than others.

However, Ion beam sputtering has disadvantages, such as a high cost, Iow deposition rates and a relatively small capacity per chamber batch. Another type of sputtering employs radio fre- quency diodes that operate at high frequency. Magnetron sputtering is one option to overcome the problems such as delamination and Iow bond strength that may arise with plasma spray methods^[46]. Magnetron sputtering allows operation at lower voltages and pressures, because it uses magnets to form a magnetic field parallel to the target which allows trapping of the secondary electrons near the target^[54]. This induces more collisions with neutral gases and increases plasma ionisation. Overall, the method provides a high deposition rate, high purity, outstanding adhesion of the coating to the substrate.

It has been noted that sputtered films possess higher adhesion to the substrate compared to the evaporation method. Sputtering is a promising method due to its ability to produce dense and thin coatings, as well as provide good bond strength^{[48][49]}.

Thus, the beneficial features of PVD are high coating density, high bio-adhesion strength, formation of multi-component layers, and low substrate temperature.

Pulsed laser deposition (PLD)

It is a <u>physical vapor deposition</u> (PVD) technique where a high-power pulsed <u>laser</u> beam is focused inside a <u>vacuum</u> chamber to strike a target of the material that is to be deposited^[55].

In this a laser having a high-power density and narrow frequency bandwidth is used as a source for vaporizing the desired material and there is almost no restriction on the target material to be used. This technique can be considered when other techniques have failed to make the deposition and has been used to synthesize the <u>nanotubes</u>, <u>nanopowders</u>^{[56][57][58]}.

This technique has shown to produce various bioceramic coatings including stoichiometric HA onto metallic substrates under controlled experimental conditions. These HA coated metal implants are expected to be superior in function ^{[59][60]}

Chemical vapour deposition (CVD)

CVD is similar to PVD in the basic process of utilizing vapour and generating a thin film on a substrate. It differs from PVD in that it does not generate vapour from a solid or liquid source in a vacuum chamber. Instead, vapours or gasses are introduced into the chamber from an external source which then gets deposited on the substrate surface in multiple directions in the form of non-volatile solids through a chemical reaction^{[2][3][61]}. Thus, unlike PVD, it involves a chemical reaction of vapour-phase precursors and the chemical reactions of precursors occur both in the gas phase and on the substrate which results in better adhesion to the surface. Another significant difference from that of PVD is that it is not limited to line-of-site application and thus, can be theoretically applied to any area the coating gas can get into, coating gas will coat all areas of a part including threads, blind holes, and interior surface. Activation energy is often required to initiate the reaction and the gaseous by-products produced during the reaction are periodically pumped out^{[61][62]}.

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