

A Review on Different Coating Methods of Hydroxyapatite on Titanium Implants

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ABSTRACT: The unique properties of commercially pure titanium (cpTi) and its alloys makes it best suited for medical applications. This silver-gray metal has impressed everyone with its features like light weight, strength and above all its ability to bind with the human bone in a process known as *osseointegration* or *biointegration*. The metal is coated with a ceramic called hydroxyapatite (HA) for developing a better bone bonding. This paper gives an overview on the different methods used for coating HA onto cpTi.

KEYWORDS: cpTi, Osseointegration, Hydroxyapatite

I. INTRODUCTION

Metals are part of many medical applications. Their attributes like strength, toughness, stiffness and impact resistance, form the basic reason for their accountability in the medical field. The use of medical implants has expanded dramatically during the past decades owing to increased life-expectancy, changing lifestyles and improved implant technology. Health problems related with damaged or diseased bone tissues represent an annual cost of more than 40 billion Euro worldwide [1].

The most commonly used metal implants in medical applications are stainless steel (20% chromium and 17% nickel), cobalt-chrome (70% cobalt and 30 % chromium), cpTi and Ti alloy. Ti has far superior properties like high elasticity, high corrosive resistance which makes it the best choice. The need for more superior property led to the development of Ti alloy (Ti-6Al-4V). [2]

Artificial materials implanted into bone defects are generally encapsulated by a tissue of collagen fibers and are isolated from the surrounding bone. This is a normal reaction against a foreign presence by the protection mechanisms in our bodies. Owing to this encapsulation, artificial material cannot be fixed rigidly to the surrounding bone [3]. Bio-ceramic coatings on the metal implants are used as a substitute for bone tissues and are extensively used in medical application to enhance the bonding with the living bone.

The first implantation probably dates back to the pre historic periods. Both natural and synthetic bioceramics/ bioactive ceramics are available in the present market. Inaccessibility and large expense led to the rampant use of synthetic bioceramics for medical applications. Bioglass (Na₂O-CaO-SiO₂-P₂O₅) developed by L. Hench *et al* in the beginning of 1970's showed a certain capability of adhering to the bone, but it cannot be employed in an area of high mechanical stresses on account of their brittleness [4].

Calcium phosphate- based ceramics constitute the preferred bone substitute used in orthopedic surgery. They are very similar to the mineral phase of the bone, by their structure and their chemical composition. Calcium phosphates usually found in ceramics are: hydroxyapatite (HA)- Ca₁₀(PO₄)₆(OH)₂; tricalcium phosphate β (β TCP)- Ca₃(PO₄)₂; mixtures of HA and β TCP (accidentally prepared and then made deliberately) [2,4]. At high temperatures HA maintains its thermal stability and that makes it most suitable one for coating metal implants for higher applications [4].

The term "apatite" is derived from a Greek word meaning "to deceive". HA ceramic is usually available in two forms: as a bulk material and as granules [5]. Several methods have been utilized for the synthesis of HA, which include

precipitation technique, Sol-gel approach, hydrothermal technique, multiple emulsion technique etc [6]. The stability of HA in biological environment is still a controversy. When a large number of studies show that HA is biodegradable [7] [8] [9], few studies contradict this findings [10].

II. COATING TECHNIQUES

Hydroxyapatite coating on titanium implants can be carried out by several methods. These coating methods can broadly be classified into pyroprocessing and hydroprocessing techniques. Pyroprocessing methods include plasma spraying, sol-gel method, sputtering method, pulsed laser deposition, ion beam assisted deposition etc, and hydroprocessing methods include electrophoretic method, dip coating etc.

Plasma spraying

Plasma spraying is the most widely applied method to deposit HA coating onto Ti implants. This method consists of injection of HA particles into a high temperature (>10000 K) plasma jet generated by a plasma torch, at atmospheric pressure (Atmospheric plasma spraying, APS), under vacuum (Vacuum plasma spraying, VPS) or under reduced pressure (Low pressure plasma spraying, LPS) [11, 12]. Intensive heating of HA particles may lead to dehydration and decomposition of HA and fast cooling of crystal phases in a solid core at impact results in conservation of high temperature phases.



Fig. 1 plasma spraying of HA

Though plasma spraying has attained a commercial success over other alternatives, due to the high temperature range used in the process, it can easily destabilize the HA crystal structure.

Sol-gel method

The sol-gel approach received more attention during the past few years because of its low temperature nature and ease of processing. Laurent *et al* [13] adopted the following way- A sol of TiO_2 , Obtained by hydrolyzing a 1 M solution of tetrabutyl ortho-titanate ($Ti(O(CH_2)_3CH_3)_4$) in absolute ethanol denatured with 5% of methanol with acidified water and a solution of calcium nitrate ($Ca(NO_3)_2$)/phosphoric acid esters were mixed together and deposited at room temperature by either dip-coating or spin coating on the samples [12]. The coating thickness can be changed by using varied coating speeds. After the deposition of three layers, the coatings were crystallized for 10 min at $850^\circ C$ in air. The major drawback in this approach is that no much research has been carried out to find out its adhesive strength [14].

Sputtering method

Sputtering method is known since 1852 when Sir W.R Grove observed this effect during his investigations on plasma discharges, and soon it evolved as a technique for deposition of thin films. Sputter deposition process are classified according to the source used-DC plasma conductors, RF-plasma insulators, ion beam, the simplest sputtering system, though is DC sputtering [15].

In a vacuum chamber the target material, which is eroded, is at cathode side and the substrate for the film is opposed at the anode side. A potential of several hundred volts are applied between these plates and this leads to the ignition of a plasma discharge for some typical pressures and the positively charged ions are accelerated to the target. These accelerated particles sputter off the deposits, which arrive at the substrate mostly as neutral atoms [15, 12]. The disadvantages with this technique are low sputter yield and poor conformality of the deposition [15].

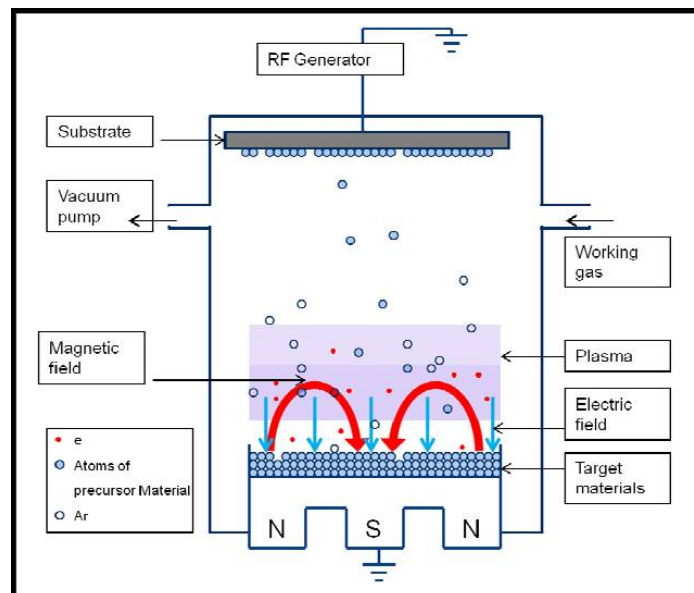


Fig. 2 RF magnetron sputtering

Pulsed laser deposition

The concept of a pulsed laser experiment is basically simple. A short and energetic pulsed laser beam from an excimer laser is focused to a target. The pulse energy of 1J per pulse leads to the immediate formation of a plasma due to the high energy density of 3-5J/cm² at the target surface. The plasma contains energetic neutral atoms, ions and molecules and reaches the substrate forming a thin film coating. [15, 16, 17]

The most important advantage of pulsed laser deposition is the transfer from a complex multi elemental ceramic target material to the substrate without significant separation between the constituents and the rather fast deposition rates [15]. Small substrate sizes can only be used for this type of coating.

Ion beam assisted deposition

Ion beam assisted deposition (IBAD) is a vacuum technique that has also been used to deposit very thin ceramic coating layers on metals, polymers or ceramics. A typical IBAD system consists of two main elements: electron or ion bombarded precursor materials that vaporize forming an elemental cloud that covers the surface of a substrate as well as an ion gun that irradiates the substrate with highly energetic gas ions that can be inert like Ar⁺ or reactive like O²⁺ to induce adhesion of the precursors from the above-mentioned elemental cloud. [15, 18]

Electrophoretic coating

Electrophoretic deposition of hydroxyapatite is a low cost flexible technique, and, being a non-line-of sight coating process, it can be used to deposit formation on conductive substrates even for complex shapes. Electrophoresis involves the migration of charged electrode, from which deposition occurs. Deposition relies on the coagulation of particles to a dense mass. Broad thickness to less than 1µm of coating thickness can be achieved with this process [19].

Dip Coating

Dip coating is one of the wet coating techniques used for coating HA onto the titanium substrate. Tuantuan et al [20] proposed a dip coating procedure as follows- HA crystals used were less than 100nm in length and had a plate-like morphology. The crystals were dispersed into distilled water in order to prepare HA sols. CpTi rods were dipped once and seven times into HA sols of concentrations between 1.5% and 10 wt %. It was noted that coating thickness ranged from 10 µm to 200 µm and depended on the dipping time and concentration of HA sol. The coating thickness increased notably with the number of dips and in sols of concentration of 7wt% or more [20, 21]. Ti pretreated by sandblasting provided a much better coating substrate.

III. CONCLUSION

This paper presents an overview on different coating methods of HA on CpTi substrates. It is seen that pyroprocessing techniques affects the stability of HA crystals and therefore adhesion decreases after few weeks, whereas the hydroprocessing techniques are lacks the control over the coating thickness. A better detailed study is suggested to arrive at the optimized and appropriate technique for coating HA on Ti implants.

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