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## **HYDROXYAPATITE COATINGS ON POROUS Ti AND Ti ALLOYS**

### ***Review Paper***

#### ABSTRACT

Deposition of hydroxyapatite coating on porous Ti and Ti alloys with electrochemical and biomimetic deposition approach is presented. The enhancement of phosphates deposition by well oriented and uniform titanium oxide nanotube array on the surface of titanium substrate is discussed.

**Key words:** *bioactivity, electrochemical deposition, hydroxyapatite, surface modifications, SBF, titanium*

#### INTRODUCTION

Due to the increased life expectancy of the population there has been an enormous increase in the incidence of bone fracture and the need for bone implant surgery. Titanium and titanium alloys are preferred materials for load bearing implants and exhibit high mechanical properties and biocompatibility but they are not bioactive and hence could not directly bond to living bone tissues. There have been many attempts to improve the surface properties of titanium-based implants which directly determine the implant-environment interactions after the implantation. The surface modification techniques include mechanical interlocking (e.g., sand blasting), chemical methods (e.g. acid etching), coating (e.g. plasma spraying), etc.

Hydroxyapatite (HA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) has been widely used as a coating material for dental and orthopedic implants for many years, due to its close similarity of chemical composition and structure, as well as high biocompatibility with natural bone tissue [1-3]. Various deposition techniques have been used to deposit HA coating on metal implant, like magnetron sputtering [4,5], plasma spray processing technique [6,7], pulsed laser deposition [8], ion beam deposition [9], hydrothermal reactions or electrophoretic deposition [10,11], sol-gel [12], and biomimetic techniques [13,14]. Among them, electrochemical methods get the most attention due to their numerous advantages, like operation at low temperature, possibility to coat complex shapes, easily controlled the coating thickness and the process relatively inexpensive. However, there is a problem of low interfacial bond strength of the HA coating on the untreated Ti substrate which is only 3.29 MPa as reported by Wang [15]. To overcome this problem, the electrochemical deposition of HA can be carried out onto the previously anodized Ti surface [16].

## TiO<sub>2</sub> NANOTUBE FORMATION

In order to improve bioactivity and enhance calcium phosphate formation the self-organized TiO<sub>2</sub> layers with controlled structure and morphology may be used [17-20].

Titanium oxide nanotubes can be prepared by various methods, like sol-gel [21], electrophoretic deposition (EPD) [22] and anodization [23]. The latest one is the best for nanotubular oxide layer creation for biological applications, as it enables to achieve the highest adhesion strength of the layer comparing to that of sol-gel and EPD.

There are different kinds of solutions used in EPD, among them several aqueous electrolytes used to create TiO<sub>2</sub> tubular structures [15,24]. Li [20] has noticed that when using aqueous electrolytes, nanotubes are short in length and contain ridges and circumferential serrations (*Table 1*). The smooth, long and ridges-free nanotubes can be achieved in highly viscous organic electrolytes like glycerol and ethylene glycerol electrolytes as well as fluorinated dimethyl sulfoxide and formamide [20,25-29].

**Table 1.** Electrolytes for anodic oxidation

Electrolyte	Reference
0,5 wt.% HF + H <sub>2</sub> O	[17,20,30-33]
1 m H <sub>2</sub> SO <sub>4</sub> + 0.3÷0.5 wt.% HF	[34-37]
1 m H <sub>2</sub> SO <sub>4</sub> + 0.1 m NaF	[38,39]
0.5÷1 m H <sub>3</sub> PO <sub>4</sub> + 0.3÷0.5 wt.% HF	[22,40-45]
0,5 m H <sub>3</sub> PO <sub>4</sub> + 0.138 m NaF	[15,22]
1 m NaH <sub>2</sub> PO <sub>4</sub> + 0.5 wt.% HF	[45,46]
1 m (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 0,5 wt.% HF	[47]
1÷2 m (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 0.1÷0.5 wt.% NH <sub>4</sub> F	[27,48-50]
0÷2 m (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 0.5 wt.% HF	[51]
1 m Na <sub>2</sub> SO <sub>4</sub> + 0.5 wt.% NaF	[39,57]
1.75 m H <sub>2</sub> SO <sub>4</sub> + 0.1÷0.5 m NH <sub>4</sub> F	[52,53]
0.3÷1 m H <sub>3</sub> PO <sub>4</sub> + 0.135 m NH <sub>4</sub> F	[54,55]

As-formed vertically aligned titania nanotube array is amorphous and can be transformed into anatase or a mixture of anatase and rutile phase by annealing process [32]. It is well established that anatase phase is more efficient in nucleation and growth of apatite than the rutile phase of TiO<sub>2</sub> because of the better crystal lattice match with HA phase [32]. As repeatedly reported the heat treatment at different temperatures (300-600°C) results in the phase change of tubular oxide [20]. After heat treatment at 300°C there is anatase tubular oxide phase while heat treatment in higher temperature of 500°C- 600°C gives some rutile TiO<sub>2</sub> phase (a mixture of anatase and rutile) [20]. Heating in a higher temperature, exceeding 600°C results in the undesirable rutile structure and even some collapse of TiO<sub>2</sub> nanotubes. It is well in line with the observation made by Macak *et al.* [56].

As suggested by Kunze *et al.* [57] the nucleation rate of apatite is high also for non-annealed TiO<sub>2</sub> nanotubes, but no homogeneous growth of apatite occurs due to the

amorphous structure of the oxide. However, at later growth stages, the crystallographic structure of the titania nanotubes is substantial for homogeneous apatite formation as only on crystalline substrate the stable growth of apatite is possible [57].

## HYDROXYAPATITE DEPOSITION ONTO NANOTUBULAR OXIDE LAYER

The vertically aligned titanium oxide nanotube arrays can act as an intermediate layer for improving the bonding strength between HA and Ti substrate.

The nanotubular surfaces may be about 46 times as large as the respective compact TiO<sub>2</sub> surfaces [57], so the nucleation of apatite is accelerated because a larger specific surface area is available for nucleation. As a result, nanotubular surface can carry more OH<sup>-</sup> groups and leads to a very dense formation of apatite nuclei. It is well known, that hydroxyl groups adsorbed on the oxide layer, play an important role in nucleation process attracting Ca ions and the adsorption of Ca is supposed to initiated the nucleation of apatite.

### Electrochemical deposition of HA onto nanotubular TiO<sub>2</sub>

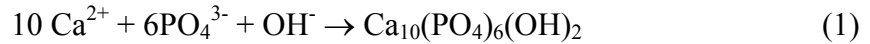
The investigations on the preparation of HA coating on the TiO<sub>2</sub> nanotubes array were seldom reported [15,32]. Calcium phosphate can be deposited onto nanotubular TiO<sub>2</sub> layer by electrodeposition in an electrolyte containing salts (*table 2*) [15,22]. The coating thickness, chemical composition, and morphology can be controlled in the process of electrochemical deposition by varying the electrochemical potential, current density, electrolyte concentration and temperature [58].

**Table 2.** *Electrolytes for calcium phosphate electrodeposition*

Electrolyte	Temp. [°C]	pH electrolyte	Reference
0,04 m Ca(NO <sub>3</sub> ) <sub>2</sub> +0,027 m NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> + 0,1m NaNO <sub>3</sub>	25	4,5	[15]
Ca(OH) <sub>2</sub> + 0,02 m (NH <sub>4</sub> ) <sub>2</sub> HP <sub>4</sub>	25		[62]
0,04 m Ca(NO <sub>3</sub> ) <sub>2</sub> + 0,027 m NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> + 0,5M NaCl	65	4 and 6	[22]

Kar *at al.* [16] have noticed that electrodeposition of HA carried out immediately after anodization of Ti without any post-anodization surface treatment results in non-uniform coating with low bond strength about 16 MPa. They have proposed the alkali treatment in 0.5 M NaOH before electrolytic deposition of HA coating. The authors have used as an electrolyte a modified simulated body fluid reported by Ban and Marino [59] prepared by dissolving 1.67 mM K<sub>2</sub>HPO<sub>4</sub> with 2.5 mM CaCl<sub>2</sub> and 0.15 M NaCl in water. The deposition was carried out at 80°C in a two step process. First, pulsing the current density of 10 μA/cm<sup>2</sup> at every 10 s and after 100 pulsing cycles the deposition was carried out at a constant current density. As a result of alkali pretreatment, the ring-like sodium titanate appeared at the neck of the nanotubes which enhanced the formation of HA coating and improved the bond strength of the coating with the oxide layer. The pulsed cathodic current caused the nucleation of hexagonal nano-rods of

calcium phosphate crystals starting at the bottom of nanotubes with the electrostatically attracted  $\text{Ca}^{2+}$  ions, because of more negative potential at these sites. Also, after alkali pretreatment of nanotubular oxide layer there were sufficient concentration of hydroxyl ions for deposition of HA according to the following reaction (1):



A similar results have been achieved by Raja *et al.* [22] who have applied also two step process composed of first pulsing the potential between -1200 mV and 200 mV for 60 cycles and then applying a constant potential of -1200 mV. Before the cathodic deposition of nanocrystalline calcium phosphate coating onto the nanotubes, similarly to Kar [16], Raja have proposed alkali pretreatment in order to enhance the HA deposition. The pulsing potential resulted in flacky in shape, nanoscale calcium phosphate crystal deposition starting from the bottom of the nanotubes.

In contrast, Wang *et al.* [15] used cathodic deposition of calcium phosphate onto nanotubular oxide by applying a constant potential of 3V, where the HA nanocrystals were anchored inside and between the nanotubes. It is noteworthy, that after anodization process of Ti surface, the directly deposited coating is mostly consisted of calcium hydrogen phosphate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , DCPD), known as a precursor of HA. The transformation of DCPD into HA is achieved by post-deposition alkaline solution treatment in  $0.1 \text{ mol/dm}^3 \text{ NaOH}$  for 2 h.

### Apatite formation in SBF

The apatite layer on  $\text{TiO}_2$  nanotubes can be obtained by biomineralization in the solution with high calcium and phosphate concentration [32,60]. The apatite deposition can be evaluated by immersion test in a simulated body fluid (SBF) with the ionic concentration of human blood plasma [60,61] at  $37^\circ\text{C}$  for 1-14 days with or without the changing the solution during immersion time. In order to accelerate the apatite deposition, the SBF solution with 1.5 (1.5SBF) [30] and 3.0 (3SBF) [60] and 10.0 (10SBF) [62] times ion concentrations of Kokubo's SBF were used (table 3).

In SBF solution, calcium and phosphate ions can rapidly deposit onto the surface of the nanotube layer. After prolonged time of immersion, Ca and P ions transformed to the column-like HA crystals of nanometric size aggregated into clusters with island-shapes [60]. The increase in the immersion time makes the size of HA larger. At the same time, there is an evident advantage of nanotube layer which offers the large specific surface area. Moreover, SBF and supersaturated SBF get into nanotubes due to capillary action and as result, a number of nucleation sites would easily form [60].

**Table 3.** The ionic concentration in blood plasma and in SBF solution (mM/l)

	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{HCO}_3^-$	$\text{HPO}_4^{2-}$	$\text{SO}_4^{2-}$	Ref.
blood plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	1.0	[60]
SBF	142.0	5.0	1.0	2.5	126.0	10.0	1.0	1.0	[57,60]
3SBF	142.0	5.0	1.5	2.5	117.62	35.23	1.0	0.5	[63]
5SBF	710.0	25.0	7.7	12.7	739.7	21.0	5.0	2.5	[64]

In addition, although Kunze *et al.* [57] and Feng *et al.* [60] reported that the titania nanotubes could induce HA growth on the surface without any pretreatment, it is evident that the alkali treatment enhances bioactivation of the titania nanotubes, resulting in formation of sodium titanate layer on the top of the nanotube walls which accelerates the apatite formation in SBF [30,32]. When biomimetic technique is applied, the crystal shape of HA coating is different than in electrochemical method, having spherical shape.

For the comparison, Kodama *et al.* [62] proposed quite simple alternative immersion method (AIM) treatment which preloads nanotubes with synthetic HA by a simple procedure of repeated cycles of immersion in saturated  $0.02 \text{ mol/dm}^3 \text{ Ca(OH)}_2$  and  $0.02 \text{ mol/dm}^3 \text{ (NH}_4)_2\text{HPO}_4$  at room temperature, achieving flake-like deposits on the nanotube layer as well as inside each single tube. The experiments also revealed that the key factors that influence the deposition are the pore size of the oxide nanotube and the ion contents in the oxide layer, giving the best results for the 100 nm in diameter tubes.

### BOND STRENGTH OF APATITE LAYER

The failure of the implant usually takes place when decohesion of the coating occurs, so bond strength of the HA coating on the tissue implant material is very important and it has to withstand bone growth stress assuring the stability of the implant. The ISO Standard 13779-4:2002 [65] for surgery apatite coating implants 'established' the bond strength between the coating and substrate to be higher than 15 MPa. Apatite deposition by biomimetic method described by Feng *et al.* [60] measured by pull-off test was about  $15.3 \pm 2.5$  MPa. The carbonated apatite coating on the titania nanotube layer was obtained only by biomineralization without any pretreatment techniques which could increase this value. Similar results have been achieved by Raja *et al.* [22] who have used the cathodic deposition of calcium phosphate ceramic nanocrystalline coating using pulsed potential. Their experiments revealed the bond strength of 16-19 MPa between the apatite coating and the nanotube oxide layer. Kar *et al.* [16] who deposited the apatite coating over the nanotubular oxide layer using two step electrodeposition in modified SBF achieved similar results. The bond strength between HA coating and the oxide layer without alkali and heat treatment reached 16-21 MPa.

A remarkable lower values of bond strength HA coating/oxide layer have been measured by Wang *et al.* [15] who used cathodic electrochemical deposition of HA coating by applying a constant potential of 3V. The bonding strength between HA coating and the substrate was only 7.41 MPa.

As the stability and adhesion strength properties are among the most important features of implant tissue materials, it is significant to improve adhesion between the bioactive layer and implant materials as well as between bioactive layer and bone. Kar *et al.* [16] have proved that when using alkali pretreatment and the following annealing at  $600^\circ\text{C}$  for 30 min, the bond strength increases up to 38 MPa, which is due to the better crystallization of HA and relaxation of electrodeposited stresses.

## CONCLUSIONS

Hydroxyapatite deposition onto the nanotubular oxide layer has many advantages. One of them is the possibility of the irregular object to be coated in a relatively short time in low temperature. The thickness of the coating deposition can be easily controlled by adequate conditions of the electrodeposition process. The nanotubular oxide layer itself contributes to the increasing of the surface roughness and surface area provided for the subsequent coating deposition thus acting as an anchor of HA top coating, improving mechanical interlocking between the coating and the substrate [20,38]. The morphology and the size of calcium phosphate crystals in the coating is a strong function of the coating method used. The nano-scale HA on TiO<sub>2</sub> nanotubes form 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 [17].

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