

## ELECTRODEPOSITION OF NANO SIZE HYDROXYAPATITE COATING ON Ti ALLOY

M. Saremi and B. Mottaghi Golshan

saremi@ut.ac.ir

Department of Materials Science and Engineering, Faculty of Engineering, Tehran University, Tehran, Iran

**Abstract:** A film of osteoconductive and biocompatible material on biomedical metallic implants can create bioactivity of the implant and shorten healing time. Hydroxyapatite, that is the most important mineral part of human bone, was coated on Ti6Al4V using cathodic electrodeposition process. Pulse electrodeposition technique was used and the effects of different parameters such as potential, duty cycle (on time/ (on time+ off time)), temperature and current density on the morphology of the deposits were examined. Nano size deposits were formed under controlled temperature and optimization of voltage and current density.

**Keywords:** Hydroxyapatite, Electrodeposition, pulse electrodeposition, morphology.

### 1. INTRODUCTION

Calcium phosphates are the most important inorganic constituents of biological hard tissues [1] that in the form of hydroxyapatite (HA), with the formula of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , are present in bone and teeth [2]. Biologically formed calcium phosphates are often nanocrystals that are precipitated under mild conditions (ambient pressure, near room temperature) [1], but their poor mechanical properties are not favorable for bone-repair purposes [3]. A solution to this problem has been its use as coating for metallic implants, in which the good mechanical properties of metal is combined with the biocompatibility of HA [4].

The morphology and crystal structure of HA is important for its biocompatibility and osteoconductivity; moreover in recent years, there are growing approaches toward nano particles and nano coatings which can provide improved properties on their applications. Nano hydroxyapatite coating can have structure that is more matched to the bone structure in which the implants should function and have lower sintering temperature [5].

There are several techniques to produce HA coating on metallic implants including sol-gel [6], pulse laser deposition [7], plasma spraying [7], electrophoretic and electrolytic deposition [8], among them electrodeposition is more attractive due to its low cost, ease of operation

and the possibility to cover complex shape surfaces.

Electrodeposition of HA is based on cathodic reactions composed of two steps of oxygen reduction to produce hydroxyl ions followed by precipitation of calcium phosphates under alkaline condition on the surface. While crystallization by itself composed of nucleation and growth, controlling electrodeposition parameters can control the microstructure and composition of HA deposits. Pulse electrodeposition in which the amount and duration of applied current and potential are controlled is a good means to obtain nano deposits [9].

The aim of this work is to apply HA on Ti alloy by pulse electrodeposition and to study the effect of electrodeposition parameters on the morphology of the crystals.

### 2. EXPERIMENTALS

Commercial Ti6Al4V alloy were cut into samples of of 20×30 mm having 3mm thickness and with abrasive papers No.180, (some were mirror polished) degreased with acetone and washed in distilled water.

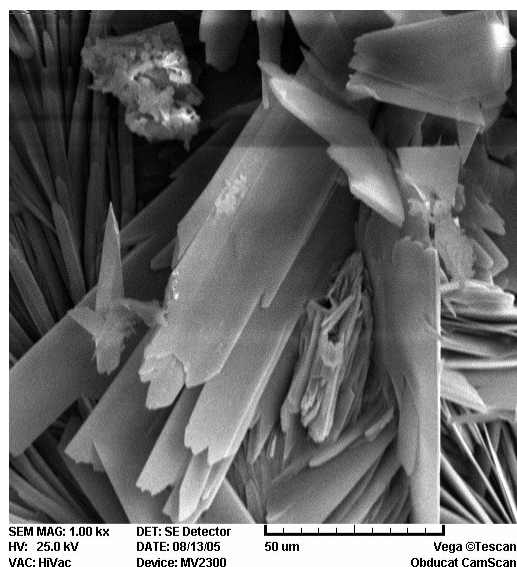
Conventional and pulse electrodeposition were carried out in 0.042M  $\text{Ca}(\text{NO}_3)_2$  and 0.025M  $\text{NH}_4\text{H}_2\text{PO}_4$  solution at pH4.1. Electrodeposition was also conducted at different potentials of 3, 4.5 and 6 volts, duty cycles; 0.4, 0.5, 0.05, at

room temperature and at 12°C. The duty cycle is described as  $t_{on}/(t_{on} + t_{off})$  in which  $t_{on}$  is time of applied pulse potential and  $t_{off}$  is time of no current/potential. AMEL model 568 potentiostat/golvanostat was used for constant current as electrodeposition. Morphology of the HP deposits were examined using Scanning Electron Microscope (SEM) Model CamScan Mv 2300. The crystal structures were characterized using X-ray diffractometer Model Philips Xtert.

### 3. RESULTS AND DISCUSSION

Fig.1 shows the SEM micrograph of the HA deposit obtained using conventional electrodeposition at 3V applied potential. A micro size flake type structure having hexagonal crystals structure (PDF No.771243) which is shown in its X-ray diffraction pattern in Fig.2. Other forms of calcium phosphates may be obtained during electrodeposition, that Dicalcium Phosphate Dehydrate ( $CaHPO_4 \cdot 2H_2O$ , pdf No.040740) is the most important deposit that was found with HA in the coating.

Successful application of cathodic electrodeposition requires understanding of deposition mechanism, though there is limited published literature in this regard. In cathodic electrolytic deposition, metal ions or complexes are hydrolyzed by an electrogenerated base to form deposits on cathodic substrates.



**Fig. 1.** SEM micrograph of the micro size coating obtained at 3V.



**Fig. 2.** X-ray diffraction pattern of HA coating.

Recent advances in this regard come from the theory of DLVO (Derjaguin-Landau-Verway-Overbeek); theory of colloidal stability which considers two main forces of double layer repulsion and Van der Wals attraction [10]. However recent research activities revealed that force of other sources can also act between particles. The thickness of double layer is very sensitive to electrolyte concentration and there is a critical electrolyte concentration for coagulation, therefore interactions could also be influenced by ions presence or produced in electrode reactions. Electrodeposition is composed of two steps of nucleation and crystal growth which develop after electronation step [11]. Parameters such as applied current/potential, pH, temperature and time of deposition have considerable effect on these steps and consequently on deposit morphology and crystal structure which are investigated in the following parts.

#### 3.1. The Effect of Potential

Fig. 3a-c shows SEM image of the HA coating deposited at 3, 4.5 and 6V at room temperature. It is shown that the flake-like morphology is obtained at different potentials, though the size of the flakes has been changed and smaller particles are obtained at higher potentials. There is a heterogeneous nucleation but the potential effect is the same for all of them and flake type crystals are resulted at all potentials.

Coagulation is enhanced by electric field and electrodynamic flow, therefore potential is the main electrodeposition parameter that can affect the coating properties. An increase in the applied potential results in increase in nucleation process with the consequent increase in the number of particles and since the growth process is diffusion controlled finer particles are obtained.



Fig. 3. SEM micrographs in 3.5(a), 4(b) and 6 volt(c) at room temperature.

### 3.2. The effect of duty cycle

Fig 4 shows the effect of duty cycle in which smaller particles are obtained at higher duty cycles. The duty cycle is the time that potential is applied on the electrode and electronation takes place. During  $t_{on}$  base generation occurs and in high pH values deposition starts and as a result the concentration of active species around the electrode is reduced.



Fig. 4. SEM images in duty cycles 0.4(a) 0.5(b).

At  $t_{off}$  deposition is almost stopped and the electrolyte has time to diffuse toward the surface and recover electrolyte concentration. Cathodic reactions result in a significant increase in pH value near the cathode. The rate of  $OH^-$  formation is crucially important for the deposition process. When there is an unbalance between  $OH^-$  generation and consumption, the high pH boundary moves away from the electrode resulting in lower coagulation of deposits. This is due to pulsating diffusion layer and pulse limiting current density, at which concentration at the electrode surface of reacting species reaches to zero, therefore, it can be said that by increasing the duty cycle mass transformation is limited and there is less opportunity for concentration recovery and as a result new nuclei don't find enough particles to grow.

Moreover, an increase in the number of cycles resulted in grain growth which is seen at different potentials. The reason is that after several cycles more base is generated and proper condition of pH and critical concentration of acting species are provided for agglomeration and grain growth. This is shown in fig.5a-d in which the deposits formed at 500 cycles are smaller than those obtained at 2000 cycles.

### 3.3. The effect of temperature

At low temperatures diffusion will be limited and grain growth that is a result of diffusion process will be stopped. The change in temperature on HA deposit, not only will decrease the grain growth but also the morphology of the coating will be changed from flake structure to spongy grains (Fig. 6).



Fig. 5. SEM micrographs at duty cycle 0.04 at: 4.5V 500 (a-1) 2000(a-2) cycles and 6V 500(b-1)2000(b-2) cycles.

### 3.4. The effect of surface roughness

The flake deposits were obtained from a rough surface which provided preferred sites for deposition. We decided to polish the surface to eliminate or reduce such preferred sites to reduce the deposit size. Fig.7 shows this effect on the deposit which is composed of two layers. The underneath layer is a homogeneous fully covered deposits having some cracks which are due to high electric field passing through the nonconductive HA film. On the top there are agglomerated particles which are formed from the hydroxyl ions generated through the surface crack. Fine particles are obtained on polished surface because when the surface is polished, the nucleation may change from heterogeneous to homogeneous mode therefore finer particles will be produced. Non-uniform deposits may form easily when the applied current density is over  $4.5\text{mA}/\text{cm}^2$ , which results in formation of defects (Fine particles aggregation) on the deposit layer. Maximum thickness of the coating is restricted by deposit spilling or cracking (it is difficult to obtain crack-free coating with the thickness of over  $\sim 50\text{ }\mu\text{m}$  by single deposition). Repeated deposition was employed in this work, which successfully gave a valid way for solving the deposit spilling problem for the formation of thick layer.



Fig. 6. The morphology of the coating deposited at  $12^\circ\text{C}$ .



Fig. 7. the effect of surface roughness on the morphology of the coating.

### 3.5. The effect of current density

By increasing current density from  $1\text{ mA/cm}^2$  to  $4\text{ mA/cm}^2$ , on a polished surface the electronation is increased and more base was formed on the surface. At high pH values (and because the preferred sites on the polished surface were also reduced and the temperature was adjusted to  $12^\circ\text{C}$ ) the conditions was fully provided for a homogeneous nucleation of small size deposits to form on the surface. Fig 8 shows the deposition of nano size particles on the surface as a result of the provision of all of the above mentioned effective electrochemical parameters. The thickness of the coating is bellow 50 microns depending on the time of deposition, but repeated deposition can be used where thicker deposits is needed.



Fig. 8. The effect of current density.

### 4. CONCLUSIONS

Based on the above mentioned points it can be concluded that:

- Electrodeposition is a favorable process to produce HA coating.
- Electrodeposition parameters have a marked effect on the morphology and crystal size of the coating particles.
- The most uniform coatings were obtained at applied potential of 4.5V and at  $12^\circ\text{C}$ .
- Nano structured hydroxyapatite coating can be obtained under controlled current and potential during pulse electrodeposition.

### REFERENCES

1. Sergey Dorozhkin and, Matthis Epple Angew in " Biological and Medical Significance of Calcium Phosphates". Chem. Int. Ed. 41, 2002, 3130-3146.
2. Gultekil Goller, Faik Nuzhet Oktar in " Sintering Effects on Mechanical Properties of Biologically Derived Dentine Hydroxyapatite". Material Letters 56, (2002), 142-147.
3. Wen Shi, Akira Kamyu, Jun Zhu, Akira Watazu in " Properties of Titanium Biomaterial Fabricated By Sinter Bonding of Titanium/Hydroxyapatite Composite Surface Coated Layer to Pure Bulk Titanium". Materials science and engineering A337, (2002), 104-109.
4. P. Monderagon-Cortez, G. Vargas-Gutierrez in " Electrophoretic Deposition of Hydroxyapatite Sub micron Particles at High Voltages". Materials Letters 58, (2004), 1336-1339.
5. Wengian Weng, Sam Zhang, Kui Cheng, Haibo Qu in "Sol-Gel Preparation of Bioactive Apatite Films". Surf. Coat. Technol, 167(2003) 292-296.
6. C. K. Wang, J. H. Chern Lin in "Pulse Laser Deposition of Hydroxyapatite". Biomaterials 18, (1997), 1331-1338.
7. Cong Wang, J. Mo, Wen Cheng, Ruifang Zhang in " Thick Hydroxyapatite Coatings By Electrophoretic Deposition". Materials Letters 57(2002) 99-105.
8. M. C. Kue, S. K. Yen in " The Process Of Electrochemical Deposition Hydroxyapatite on Biomedical Titanium at Room Temperature". Materials Science and engineering C, 20(2002) 153-160.
9. I. Zhitomirsky in "Cathodic Electrodeposition of Ceramic and Organoceramic Materials. Fundamental Aspects". Advanced in Colloid and Interface Science. 97(2002) 279-317.
10. Subir Bhattacharjee, Menachem Elimelech, Michal Borkovec. "DLVO Interaction between Colloidal Particles: Beyond Derjaguin's Approximation". Croatia Chemica Acta 71 (1998) 883-903.
11. Derek Pletcher and Frank C. Walsh. "Industrial electrochemistry" 2nd edition. London, New York Academic Press, 1993, p.167.