

SURFACE MODIFICATION OF ANODIZED TITANIUM FOR CALCIUM PHOSPHATE COATINGS

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ABSTRACT

The anodization of titanium involves the formation of a thin, dense and compact, oxide layer. In this process the rutile structure of the original titanium oxide is converted into an anatase structure. It is this anatase structure and how it influences the bonding properties of the sol gel coating of hydroxyapatite (HAp) was the main aim of this research project.

The titanium samples were anodized in phosphoric acid (H_3PO_4) at varying concentrations with one solution utilizing sulphuric acid (H_2SO_4) in addition to the phosphoric acid. The samples were also anodized at 3 different voltages, 12V, 15V and 20Volts for 30 minutes. Both anodized and unanodized samples were spin coated with alkoxide-derived hydroxyapatite and examined with x-ray diffraction and scanning electron microscopy.

The samples anodized utilizing a mixture of phosphoric acid (H_3PO_4)/ sulphuric acid (H_2SO_4) solution were found to produce a more adherent and homogenous HAp coated surface. It is envisaged that this improved anodizing technique could aid the generation of more effective HAp coatings on titanium and titanium alloy orthopaedic and dental implants.

1. INTRODUCTION

The anodization of titanium allows for the formation of an oxide layer whose thickness can be accurately controlled by a combination of electric current and time to achieve film thicknesses of the order of Angstroms (10^{-10} m). The thin film of titanium oxide created by anodizing is almost entirely an anatase type structure. By controlling the initial oxide layer on the titanium before HAp coating it is hoped to produce a thin coherent HAp coating on this surface with minimal surface preparation.

Hydroxyapatite is an established material for applications such as maxillofacial reconstructive surgery and for non-load bearing orthopaedic applications [1]. One method of overcoming the low mechanical properties of bulk hydroxyapatite (HAp) is by the coating of HAp onto a suitable substrate such as titanium and its alloys [2].

There are several different techniques for production of HAp coatings, from dip coating in a powder suspension [3], pulsed laser deposition, electron beam evaporation combined with ion beam mixing, electrophoretic deposition [4], sputter coating [5], and plasma coating [6]. For the spin coating technique to achieve a thin homogenous coating, the sol-gel route is preferable where lower sintering temperatures; high purity and homogeneity are of primary importance [7].

2. MATERIALS AND METHOD

The anodizing of the titanium alloy was conducted in three different solutions, all based on phosphoric acid. The samples were then anodized at voltages of 12V, 15V and 20Volts for a period of 30 minutes.

The Steps used in anodizing process were; cleaning, immersion, anodizing and rinsing.

1/ *Cleaning* – this step involved removing oil, grease, and other soil by appropriate conventional processes such as vapour degreasing and alkaline cleansing [8]. For this project all samples cleaned with methyl ethyl ketone (MEK) and rinsed.

2/ *Immersion* – this step involves placing samples into anodizing solution and leaving for a period of 2-3 minutes before anodizing was commenced. This was mainly used as an additional cleaning process.

3/ *Anodizing* – samples were placed on an aluminium jig with stainless steel (martensitic) cathodes; the current was slowly increased over a one-minute period to desired anodizing current and then anodized at that current for 30 minutes.

4/ *Rinsing* – the samples were rinsed thoroughly in water before drying and then placed in sample containers.

2.1 Hydroxyapatite Preparation

This work employs a conventional alkoxide route, which has been modified from Chai *et al.* [9], calcium alkoxide precursor solution was prepared by dissolving calcium diethoxide $\text{Ca}(\text{OEt})_2$ in ethanol and ethylene glycol and stirred for 10 minutes, then adding diethyl phosphite $\text{HOP}(\text{OEt})_2$. [10-11] The solution was then stirred for another 10 minutes at which time the solution is complete. Vials were capped to avoid volatisation. All preparation was carried in a dry nitrogen atmosphere.

2.2 Hydroxyapatite Coating Procedure

All titanium samples were ultrasonically cleaned for a period of 5 minutes. The sample was then placed on a spin coater (Headway Research USA) and the solution was then placed via a dropper on the surface and spun for a short time-10 seconds at 2500 RPM. After coating the sample was placed in a furnace at 500°C for 20 minutes pre-firing.

The sample was then removed and cooled for a 5-minute period and then a further coating layer was added, going through the cycles until 4 layers were placed on the sample surface. After the final coating was placed on the sample, the sample was placed in the furnace for 180 minutes at 700°C.

3. RESULTS AND DISCUSSION

3.1 Anodizing

The three solutions utilized, resulted in varied colouring depending on the current used. The differing colours resulting from the refraction of light and this is attributable to the resulting film thickness obtained during anodization.

The samples anodized at 12 volts yielded a gold colour with no variation across the solutions. The samples anodized at 15 volts yielded a bluish purple colour and the samples anodized at 20 volts resulted in a cobalt blue colour.

3.2 SEM Analysis of Calcium Phosphate Coatings

The calcium phosphate (CaP) coating was carried out on the 20-volt samples of the three solutions and the original titanium sample. SEM analysis of the CaP coated samples anodized in the H_3PO_4 solutions and the unanodized sample showed a similar type coating with areas of coral-like structure and regions where large particulate grains were observed.

SEM elemental analysis of these samples showed the presence of a calcium and phosphorus containing film, and incomplete CaP film formation. This is further reinforced with analysis of the 10,000 X and 20,000 X magnification micrographs. These samples showed distinct regions of coral like film formation with large particulate grains embedded throughout the structure.

The anodized samples in the H_3PO_4 / H_2SO_4 solution when coated and scanned with the SEM at 5,000 X magnification showed a distinct coral like structure over the entire coated surface of the sample, there was no evidence of large particulate grains and it appeared to be a homogenous coral like structure. When scanned at 10,000 X and 20,000 X magnifications the CaP film continued to show the homogenous coral like structure throughout the coated sample surface.

3.3 SEM Elemental Analysis

The elemental analysis using the EDAX system yielded the elements of oxygen, calcium, phosphorous in addition to the base titanium alloy elements of titanium, vanadium and aluminium. The anodized samples in the H_3PO_4/H_2SO_4 solution when coated yielded comparatively larger calcium and phosphorous peaks in comparison to the titanium alloy peaks of the H_3PO_4 solutions in the anodized and unanodized samples.

The SEM elemental analysis shows a CaP film present on the surface of the anodized sample, further XRD analysis is needed to definitively state that the CaP containing film is hydroxyapatite or biphasic phosphate. Given previous sol gel coatings of hydroxyapatite on polished titanium by this method. We can argue that the CaP film formed on the surface is hydroxyapatite, as previously published work showed that monophasic hydroxyapatite would be formed using this sol-gel route. [10-12] The SEM micrographs show a homogenous CaP film with a coral like porous structure on the surface of the anodized titanium sample utilizing phosphoric/sulphuric acid solution.

This study dealt with the anodizing of titanium alloy and how this affected the coating of hydroxyapatite on the titanium oxide layer created by the anodizing. The scanning electron microscopy showed a distinct coral like structure on the surface of all samples. Comparison with the titanium calcium phosphate coated sample under the scanning electron microscope clearly shows a more coherent coral like structure on the sample anodized in phosphoric/sulphuric acid solution. The other anodized samples demonstrated a similar structured coating to the titanium HAp coated sample.

The elemental analysis of the HAp coated anodized samples showed presence of calcium, phosphorus, oxygen and the titanium alloy substrate consisting of titanium, vanadium and aluminium.



Fig. 1 SEM of anodized titanium.

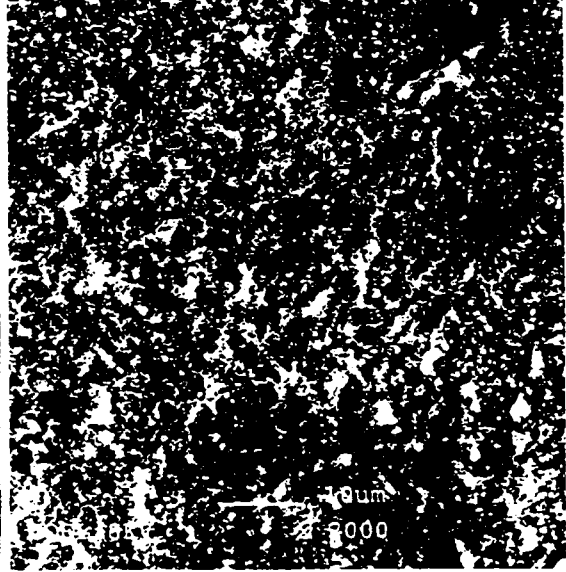
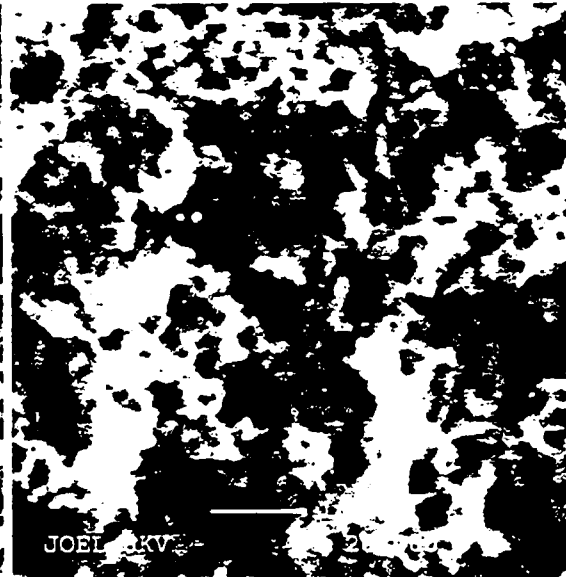
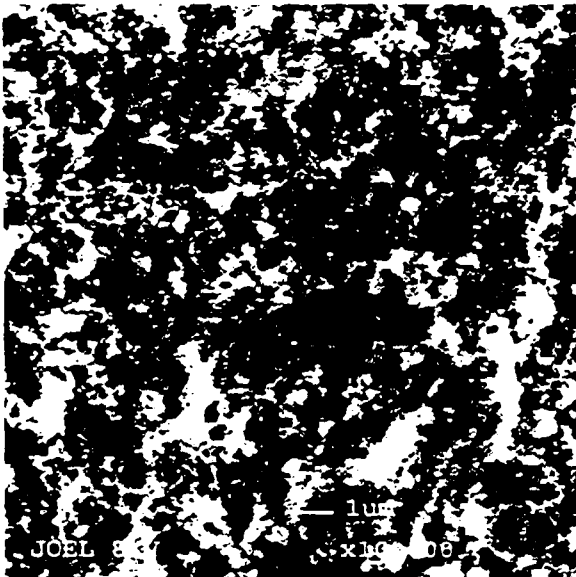


Fig. 2 SEM of Ca-P coated anodised Ti



Figs. 3 and 4 SEM of calcium phosphate coated titanium.

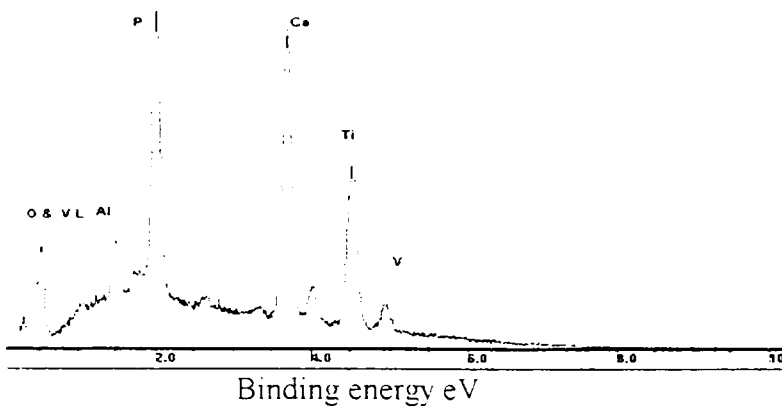


Fig. 5 SEM elemental analysis of surface of HAp coated anodized (H_3PO_4/H_2SO_4) titanium sample showing the elements of calcium, phosphorus and underlying titanium alloy.

Analysis of the coated samples using x-ray diffraction with a glancing angle of 0.5 degrees was insufficient to determine the coating of hydroxyapatite. Due to the thickness of the coating all that could be determined was the nature of the titanium alloy substrate. As only four coats of hydroxyapatite was applied and spin coated, future experiments will be directed at ensuring the coating is of sufficient thickness to be analysed by X-ray Diffraction.

As this is an ongoing project and further research is needed to investigate the mechanical properties of different coating and substrate combinations. Other properties to be investigated are the effect of differing HAp coatings and coating thicknesses, and the effect of various anodizing currents on the thickness and structure of the oxide layer. Surface roughness is an important property of the sample preparation and the effect of this on the titanium samples before anodizing needs to be investigated. In addition, further work is required into other ceramic coatings to see if there is any benefit to be gained by using this technique.

4. CONCLUSION

From the results currently obtained the anodized titanium alloy samples did produce thin coherent calcium phosphate coatings, in particular the samples anodized in the Phosphoric/Sulphuric acid solution.

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