

## MORPHOLOGICAL INVESTIGATION OF CALCIUM PHOSPHATES ELECTRODEPOSITED ON Ti IN THE PRESENCE OF TARTARIC ACID

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### **Abstract**

The electrochemical deposition method was employed to deposit calcium phosphates on Ti substrates in the presence of different concentrations of tartaric acid. Scanning electron microscopy was used to investigate the morphology of the obtained specimens. The micrographs indicate that as the tartaric acid concentration increases, the size and number of calcium phosphate irregular structures increases as well. At the highest concentration a new morphology is evidenced, represented by flat ordered structures with high aspect ratio.

### **Introduction**

Calcium phosphates constitute a class of ceramic materials with applications in domains such as orthopedics, dentistry, catalysis, in the manufacturing of fuel cells and gas sensors, in corrosion protection and the development of drug delivery systems [1-4]. The most studied and application wise useful member of this class is hydroxyapatite (HA) -  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  - a biocompatible material with composition similar to that found in human bones and teeth [5].

The present work is a continuation of a previous study by Bucur *et al.* [6] in which HA was synthesized in the presence of tartaric acid *via* the hydrothermal method. The use of organic acids in the synthesis of calcium phosphates affects the morphology and properties of the resulted structures. Specifically, depending on concentration, they impoverish or prevent crystal growth on at least one crystallographic direction, by forming a complex with the Ca ion [7,8]. In this study, we replaced the hydrothermal method with electrochemical deposition. The latter is known to be an alternative way for obtaining calcium phosphates in general and HA in particular [9].

### **Experimental**

Analytical grade  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Sigma Aldrich) and  $(\text{NH}_4)_2\text{HPO}_4$  (Merck) were used as Ca and P precursors, in the presence of tartaric acid (racemic, Merck). The Ca:P molar ratio between the solutions was 1.67, corresponding to stoichiometric HA. Double distilled water was used throughout the study. Polished and cleaned Ti discs, cut from pure Ti plate, were employed as substrate for calcium phosphates electrodeposition. The electrochemical setup for obtaining the specimens consisted in a VoltaLab PGZ 402 potentiostat, three electrodes and a glass cell with heating mantle connected to a thermostat set at 80 °C. Each Ti disk was inserted into a support and used as working electrode ( $S_{\text{geom}} = 0.28 \text{ cm}^2$ ). Every electrodeposition experiment lasted for 1h and was performed at a constant potential of -1.5 V. The electrolyte solutions used to obtain the specimens consisted in a mixture of the two precursors and tartaric acid, having the concentrations and volumes presented in Table 1.

Scanning electron microscopy (SEM) micrographs of the specimens were acquired with a Phillips Inspect S scanning electron microscope.

Table 1. Specimen codes and the electrolyte solutions used to obtain them

Specimen code	Electrolyte solution					
	Ca precursor		P precursor		Tartaric acid	
	Volume [mL]	Conc. [mM]	Volume [mL]	Conc. [mM]	Volume [mL]	Conc. [mM]
S1	50	0.875	50	0.525	2.5	0.875
S2	50	0.875	50	0.525	5	0.875
S3	50	0.875	50	0.525	10	0.875
S4	50	0.875	50	0.525	15	0.875
S5	50	1.75	50	1.05	2.5	1.75
S6	50	1.75	50	1.05	5	1.75
S7	50	1.75	50	1.05	10	1.75
S8	50	1.75	50	1.05	15	1.75

### Results and discussion

The morphological investigation *via* SEM imagery of specimens S1 to S4 indicates the following: In the case of S1, the Ti surface is covered with disconnected and sparse irregular structures having micrometric dimensions. By doubling the tartaric acid quantity in the electrolyte solution, the main observed change is an increase in the size of the micrometric irregular structures. As the acid solution amount is further increased, the surface of the Ti substrate becomes covered to a higher degree with calcium phosphate irregular structures that are bigger in size. In the case of S4 these structures are revealed to be porous and complex, but they do not organize into higher order symmetrical formations.

The SEM micrographs recorded for specimens S5 – S8, obtained from electrolyte solutions containing concentrations of precursors and tartaric acid twice as high as those used for the S1 – S4 specimens, increase the understanding of how the organic acid affects the calcium phosphate structures morphology. As the tartaric acid concentration increases, so does the size of the electrodeposited irregular structures evidenced for the S5 – S7 specimens. The main difference is outlined in the case of the S8 specimen, where many flat and elongated ordered structures are observed (Figure 1a). It can also be seen that the surface of the Ti substrate is covered with a discontinuous layer of small irregular particles (Figure 1b).

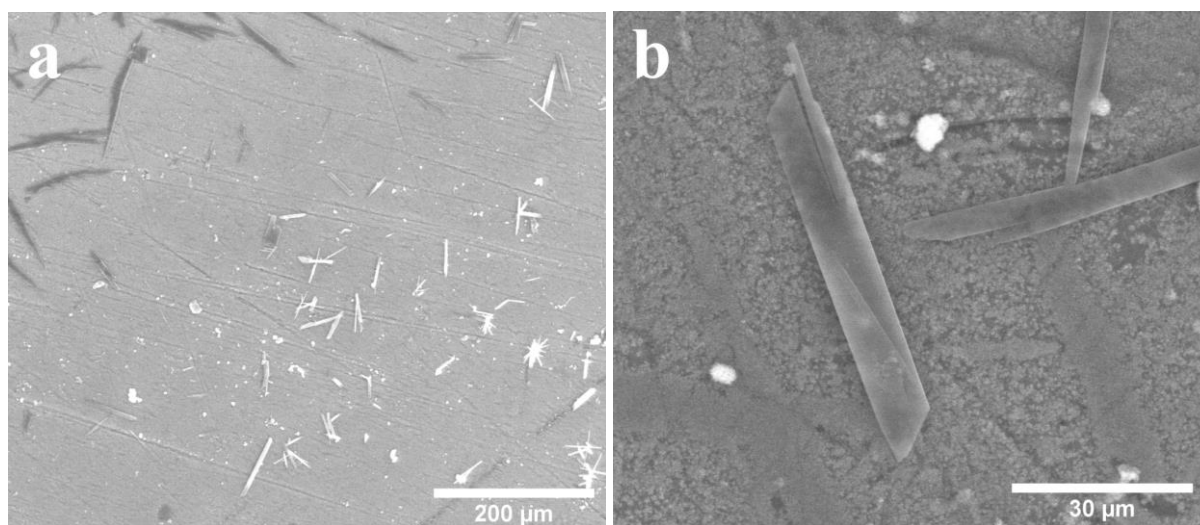


Figure 1. SEM micrographs recorded on the S8 specimen (a and b)

The results acquired for the S8 specimen are in agreement with the previously mentioned literature data regarding crystal growth prevention by organic acids along at least one crystallographic direction. In the case of the observed ordered calcium phosphate structures, their growth occurred almost entirely in length and was significantly slowed down when it comes to their width and height.

### **Conclusion**

Out of the eight electrolyte solutions used in the present study, only the one with the highest concentrations of precursors and tartaric acid leads to the formation of ordered structures. These structures bear the shape of elongated plates and their morphology is probably due to the influence of tartaric acid affecting crystal growth by complexing the calcium ion. Future studies will be aimed at identifying the calcium phosphates formed during the electrodeposition of the S8 specimen.

### **References**

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