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Communications

Electrocrystallization of Brushite Coatings on Prosthetic Alloys[†]

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Although the mechanism by which fixation occurs has not yet been fully clarified, coating of metallic prostheses with phosphate ceramics has received much recent attention because of the apparent propensity of these coatings to accelerate bone fixation during the early stages after implantation.[1-8] There is also reason to believe that the rate of metal ion release from some alloys can be reduced by calcium phosphate coatings.[9] Reviews concerning applications of hydroxyapatite coatings on metallic implants have been published recently by Lemons[10] and by Lacefield.[11]

The most popular methods of preparing implants with phosphate coatings appear to be flame spraying and plasma spraying. These procedures are advantageous because it is not necessary to heat the metal substrate to the temperature at which the coating is sintered. Heating of the substrate surface can still be extensive, however, and thermal decomposition of the material being sprayed is often observed. Other high-temperature techniques such as dip coating and sputter coating can also suffer from thermal degradation.

Electrophoretic deposition of phosphate materials has recently been introduced by two groups.[12,13] In this procedure particles suspended in solution are driven onto an anode in the presence of a large electric field. Analysis of the coatings after sintering indicates the presence of hydroxyapatite and tricalcium phosphate. The technique is particularly attractive because irregularly shaped substrates can be coated.

An electrolytic method of preparing phosphate coatings on cathodes is described below. Like the electrophoretic technique, this technique is also attractive because highly irregular objects can be coated relatively quickly at low temperatures. Additionally, a high degree of control of deposit crystallinity can be obtained by using this procedure, and because the coating is formed on an alloy used as a cathode, corrosion of the metal surface should be minimized during deposition.

Given the number of arthroplasties performed yearly, the need for a physically stable, biocompatible material that can be easily deposited on implant surfaces is considerable. A report estimates that 120 000 total hip implants are required yearly in the United States.[14] In 1986 it was projected that 500 000 coated joint prostheses would be required annually in 1990.[15]

All deposits described here were formed at room temperature from aqueous solutions saturated with Ca(H_2P-

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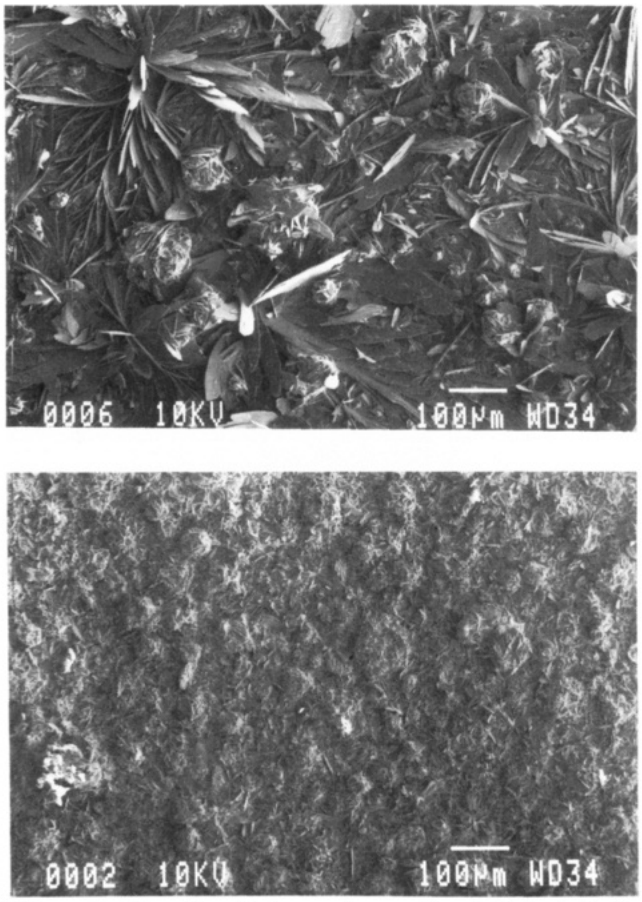

Figure 1. Scanning electron micrographs of electrolytically deposited calcium phosphate coatings on 316 L stainless steel. Top: deposit produced at 1 mA/cm^2. Bottom: deposit produced at 10 mA/cm^2.

$O_4)_2$. No other electrolytes were added. The pH of such a solution is 3.50. Additionally, the deposits were formed while controlling the current at constant value throughout the course of the deposition. Oxygen was not excluded.

Deposition is thought to occur as a result of an electrolytically induced pH gradient near the electrode surface. Upon reduction of the electrolyte solution a variety of half-reactions are possible. The dominant reaction is probably reduction of water to hydrogen gas and hydroxide ion. This reaction should result in a localized pH jump in the vicinity of the cathode. Because the electrolyte solution is already saturated with calcium dihydrogen phosphate, we reasoned that any pH increase near the surface of the electrode should convert $H_2PO_4^-$ to HPO_4^{2-} and result in the crystallization of less soluble calcium phosphates. With an increase in the current, both the pH and the pH gradient near the electrode should increase, thus producing more nucleation sites and faster crystal growth. The results shown in Figure 1 are consistent with this reasoning.

Figure 1 shows calcium phosphates deposited at 1 (top) and 10 mA/cm^2 (bottom) on polished 316L stainless steel. A total of 8 C/cm^2 was passed (over 133 min.) to form the deposit in Figure 1, top. A total of 5 C/cm^2 was passed (over 500 s) to form the deposit in Figure 1, bottom. Much larger crystal growth occurs as expected at the lower current density. The crystals produced at 1 mA/cm^2 are probably too large and fragile to be useful as a practical coating for prosthetic alloys. In addition to nucleation arguments, we suspect that the vigorous rate of H_2 evolution observed at 10 mA/cm^2 is partially responsible for the decreased crystal size in this case.

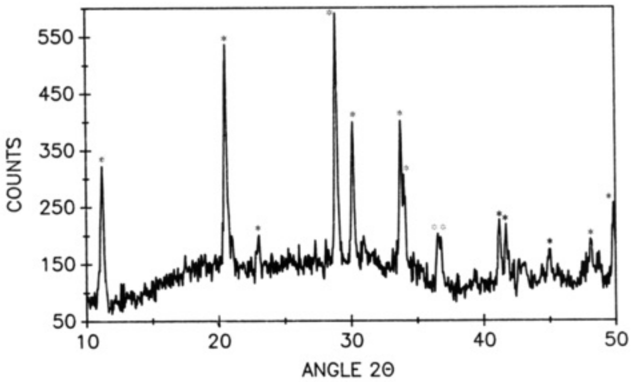

Figure 2. X-ray powder pattern of brushite scraped from surface of electrode coated at 10 mA/cm^2.

The deposits shown in Figure 1 are crystalline $CaHPO_4 \cdot 2H_2O$ (brushite). An X-ray powder pattern of material produced at 10 mA/cm^2 is shown in figure 2. Reflections marked by asterisks in Figure 2 denote those reflections expected on the basis of the *d* spacings known for brushite. No reflections for brushite expected to be greater than the background level are missing from this pattern. Additionally, there are no reflections present that might be associated with other materials. Determination of the amount of calcium in this material by atomic absorption spectroscopy gives 22% calcium by weight, which is in good agreement with the value of 23.3% expected for brushite.

Current efficiencies for production of the brushite coatings on 316L stainless steel are 50% at 10 mA/cm^2, 40% at 1 mA/cm^2, but only 10% at 0.1 mA/cm^2, presumably because the pH perturbation near the electrode surface is not large enough to produce extensive localized crystallization. The current efficiencies were determined gravimetrically by using the assumption that 100% current efficiency corresponds to 1 mol of $CaHPO_4 \cdot 2H_2O$ being deposited per faraday. All current efficiencies were calculated for electrodes on which 5 C/cm^2 coatings had been deposited. The possibility that current efficiency is not constant over time is presently being investigated.

The general applicability of electrolytically deposited phosphate coatings on metal substrates is exemplified in Figure 3. Scanning electron micrographs of the same coating at two different magnifications are shown. The substrate in this case is titanium mesh on the stem of a commercially available Ti-6Al-4V hip implant. This mesh provides an anchor for bony ingrowth into the implant. Strands of the mesh are the large cylindrical features in Figure 3 that are 250 μm in diameter. Crystallization was carried out at 1.0 mA/cm^2 until 8 C/cm^2 of charge had passed. The area used to determine the current density was based on the overall dimensions of the electrode and not the actual surface area of the mesh, which was not measured. All of the surfaces visible in Figure 3 are coated, and there are no discernible regions where preferential crystallization appears to have occurred. Although it is possible to grow thicker coatings, it is expected that the macroporosity necessary for bony ingrowth might be compromised if the coatings become too thick.

Our attempts to control the morphology and physical integrity of calcium phosphate coatings produced by electrolytic deposition are still in their infancy. Little work has been completed using controlled-potential electrolysis to produce the crystallization, and only a limited number of electrolyte conditions have been varied in solution. Although the results reported here are only preliminary, successful completion of these investigations may produce new and relatively uncomplicated procedures for tailoring

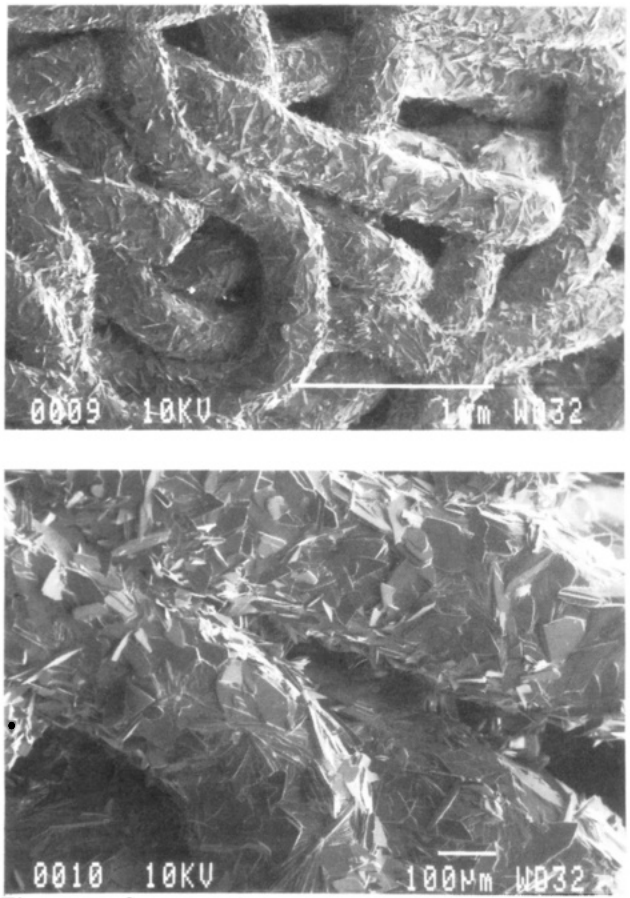

Figure 3. Scanning electron micrographs of electrolytically deposited brushite coatings on titanium mesh.

metal surfaces that will promote bone fixation to metallic prostheses.

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Registry No. Brushite, 14567-92-1; 316L stainless steel, 11134-23-9.

Highly Organized Molecular Assemblies of Porphyrin Guest Molecules in Mica-Type Silicates: Influence of Guest–Host Interactions on Molecular Organization

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The need for materials with well-defined molecular architectures that can be manipulated into technologically useful forms such as thin films is well recognized.[1] Toward this goal we have been using intercalation of layered solids as an alternative to the Langmuir–Blodgett technique for manipulating molecular and polymeric guest species into well-defined multilayered thin-film structures.[2] The technique provides an opportunity to control the thickness and molecular organization of guest species by fine-tuning the guest–host molecular interactions.[3]

Table I. UV–Visible Absorptions in the Soret Region of CuTMPyP in Solution and Intercalated Form[a]

solvt or host	band posn, nm	solvt or host	band posn, nm
H_2O	422	hectorite	446
1 N HCl	422	fluorohectorite	413

[a] The spectra of intercalated samples were recorded in suspension at maximum loading (i.e., 0.175 and 0.475 mmol of porphyrin/g of hectorite and fluorohectorite, respectively).

In the present work we report the synthesis of well-organized assemblies of the Cu-metalated form of tetrakis(1-methyl-4-pyridyl)porphyrin (CuTMPyP) in the galleries of Na hectorite and Li fluorohectorite. The molecular orientation of the gallery molecules is dictated by the surface area available per exchange site, which in turn depends on the layer charge density (isomorphous substitution) of the host lattice.

Although intercalation of naturally occurring macrocycles and synthetic porphyrins in the galleries of layered silicates has been studied before, none of the studies focused on the effect of the inorganic host on the organization of the guest molecules.[4-6] In addition, the use of the Cu-metalated form in this study provides an excellent probe for distinguishing possible molecular orientations by ESR spectroscopy.

Natural hectorite and synthetic fluorohectorite belong to the general family of mica-type layered silicates. Their lattice structure consists of two tetrahedral sheets fused to an edge-shared octahedral sheet.[7] The stacking of these layers leads to the formation of interlayers or "galleries" normally occupied by hydrated cations that balance the charge deficiency generated by the isomorphous substitution in the tetrahedral or octahedral sheets. The strong intraplanar and weak interplanar binding forces that arise from the two-dimensional structure allow the introduction (intercalation) of guest species into the galleries of the host lattice by simple ion exchange. CuTMPyP was chosen as a model compound because of the presence of permanent charge on the pyridyl substituents and its resistance to demetalation in acidic media.

Addition of stoichiometric amounts of CuTMPyP from an aqueous solution to a suspension of either hectorite or fluorohectorite (0.175 and 0.475 mmol of porphyrin/g of silicate, respectively) results in almost complete adsorption of the porphyrin molecules within a few minutes. X-ray diffraction patterns of fluorohectorite and hectorite intercalated products show that crystallographically well-ordered structures are obtained with (001) harmonics corresponding to a primary repeat unit (*d* spacing) of 20.1 and 14.0 Å for fluorohectorite and hectorite, respectively. The difference of 4.4 Å from the corresponding 9.6 Å for the silicate framework for hectorite is in accord with the expected size of the porphyrin ring lying parallel to the silicate layers. In contrast, the observed 10.5-Å difference for fluorohectorite is consistent with either a bilayer of porphyrin molecules or an inclined arrangement of the porphyrin plane with respect to the silicate layers. The latter arrangement has been observed for alkylammonium

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