

Dip Coating of Calcium Hydroxyapatite on Ti-6Al-4V Substrates

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Ti-6Al-4V alloy is the most commonly used metallic material in the manufacture of orthopedic implants. The main inorganic phase of human bone is calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA). To achieve better biocompatibility with bone, metal implants made of Ti-6Al-4V are often coated with bioceramics. Dip-coating techniques scarcely are used to apply HA onto metallic implants. New dipping-solution recipes to be used for HA coatings are described in this work. Scanning electron microscopy and X-ray diffractometry have been used for sample characterization.

I. Background

CHEMICALLY precipitated calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA) powders first were prepared by Hayek and Newesely in 1963.¹ In this route of HA synthesis, a solution of calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), of proper concentrations, were reacted with each other at high pH values in the presence of ammonium hydroxide (NH_4OH).^{2–7} HA powders prepared and used in this study were synthesized using the previously published method of Taş and co-workers,^{8,9} which was basically a modification of the route used earlier by Hayek and Newesely.¹ The best use of HA in load-bearing orthopedic applications has been as a coating layer on one of the stronger implant metals. Uncoated metal surfaces generally are responsive to the tissues that surround them; however, coating these surfaces before implantation, by some means, will be beneficial in accelerating the formation of new bone.^{10,11}

Current techniques that are used in the coating of HA bioceramics onto metallic substrates include plasma spraying,^{10–14} electrophoretic deposition,¹⁵ and sputtering.¹⁶ However, all these techniques may yield either noncrystalline coatings or coated layers that are contaminated with crystalline calcium phosphate phases other than HA. Sol–gel-based dip coating of HA also has been studied recently by several researchers.^{17–23}

The study presented here is focused on the development of recipes of appropriate solutions for the dip coating of HA on Ti-6Al-4V substrates, using chemically precipitated hydroxyapatite precursor powders.

II. Experimental Procedure

HA precursor powders used in the preparation of dip-coating solutions were synthesized as follows.^{24,25} A 3 mL aliquot of 0.1

g/L methyl cellulose solution (99% pure, Sigma, St. Louis, MO) was mixed (to act as a dispersant) with 1440 mL of deionized water. Then, 0.152 mol of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99% pure, Merck, Darmstadt, Germany) was dissolved in the above-described solution. Then, 0.090 mol of $(\text{NH}_4)_2\text{HPO}_4$ (99% pure, Merck) was dissolved in that solution. Following that step, 115 mL of 24 vol% NH_4OH (99% pure, Birpa, Ankara, Turkey) was added, in its entirety, into the above-described opaque solution. The solution was heated and vigorously stirred at a temperature of 60–70°C for 90 min on a hot plate. The precipitates that formed (which had an average particle size of 200 nm; X-ray diffractometry (XRD) and scanning electron microscopy (SEM) characterizations were reported elsewhere previously^{8,9,24}) were recovered from the supernatant in the form of a cream via vacuum filtration, using a Büchner funnel. Poly(ethylene glycol) (PEG) (99.5% pure, molecular weight of 15 000, Merck), gelatin (hereafter called GEL) (99.9% pure, Riedel-de Haen, Seelze, Germany), and glycerol (hereafter called GLY) (99.5% pure, Birpa) were blended with mixtures of ethanol (hereafter called EtOH) (99.9% pure) and water (H_2O) that contained the HA suspensions. The ingredients of the dip-coating suspensions (hereafter called SOLs) were mixed in appropriate amounts in water-cooled glass containers, using a sonicator (UD) probe with a tip surface area of $\sim 1.3 \text{ cm}^2$ (Model XLS-2015, Misonix, Inc., New York).

Ti-6Al-4V strips with dimensions of 20 mm \times 7 mm \times 1 mm were used. These strips first were abraded with silicon carbide (SiC) papers (grit range of 400–1200), followed by washing in distilled water. A belt-and-pulley-type apparatus was built and used in this study to dip the strips into the HA suspensions; the apparatus had a two-way electronic switch, to descend (and ascend) the substrates into (and out of) the dipping suspensions, at constant speeds in the range of 15–300 mm/min.

Then, the coated strips were heat-treated in a PID-controlled horizontal tube (mullite) furnace (Model Protherm-1250, Alser, Ankara, Turkey) with a flowing (4 L/min) nitrogen-gas atmosphere at a temperature of $840^\circ \pm 3^\circ\text{C}$ (2 h of peak soaking time), using heating and cooling rates of $2^\circ\text{C}/\text{min}$. The heat-treated substrates were characterized using SEM (Model 6400, JEOL, Tokyo, Japan) and XRD (Model D/MaxB, Rigaku, Tokyo, Japan). To test the bonding strength of the HA coatings, two steel cylinders 5 mm in diameter were attached to both sides (coated and uncoated after the coating layer was ground off) of the dipped strips by a thin layer of glue, as described by Weng *et al.*²³ Then, the adhesive strengths were determined in a universal tester by measuring the tensile stress needed to separate the cylinders from the strips.

III. Results and Discussion

The HA precursor powders that have been synthesized (as reported elsewhere⁸) and used in this study yielded stable (against sedimentation) dip-coating solutions. The as-precipitated powders (after drying at 90°C) were not totally X-ray amorphous; however, additional heating at higher temperatures in an air atmosphere for 6 h improved the crystallinity of the HA powders (see Fig. 1). The powders were single-phase HA, even at 1200°C.

P. Li—contributing editor

Manuscript No. 189527. Received February 25, 1999; approved January 11, 2000.
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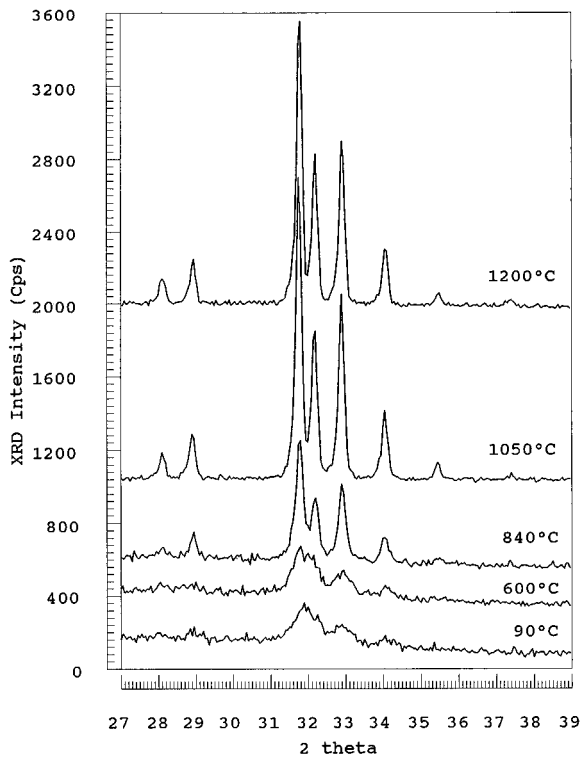


Fig. 1. XRD spectra of the chemically precipitated HA powders, as a function of temperature (in an air atmosphere for 6 h).

The method of preparation of the HA dip-coating solutions has been described in greater detail elsewhere.^{24,25} Table I and Fig. 2 together show the crucial details of the optimized solution-preparation recipes. In the processing flowchart in Fig. 2, the ellipsoids represent the ultrasonication steps (via UD), whereas the numbers in the ellipsoids refer to the mixing time in minutes and the ultrasonication intensity (in units of watts/cm²), respectively.

The solutions labeled A–D (Table I) could not provide crack-free deposits upon drying and calcination. However, the dip-coating solutions reported in Table I (SOL 1 and SOL 2) both were able to yield homogeneous and crack-free, green, coated layers on

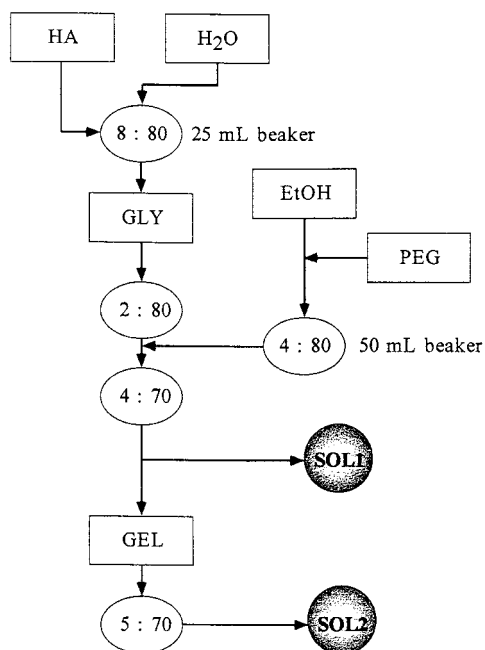


Fig. 2. Process flowchart of the preparation of the HA dip-coating solution.

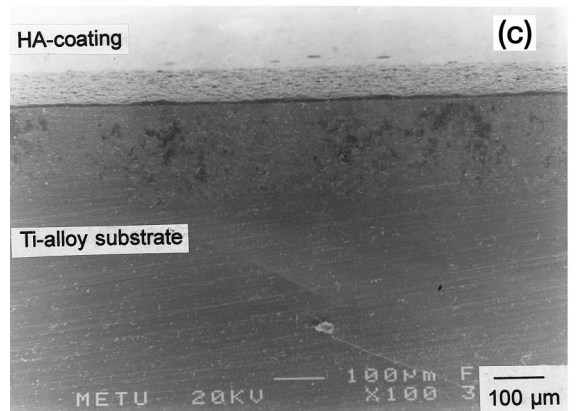
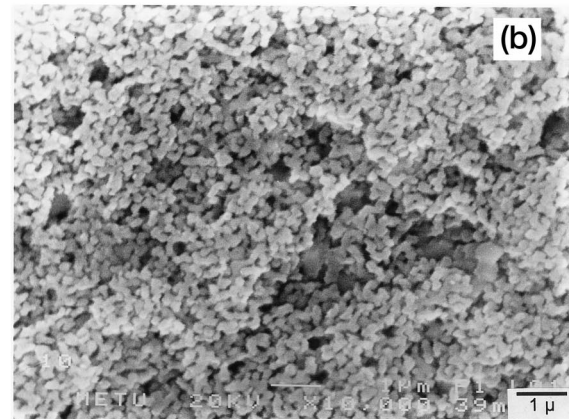
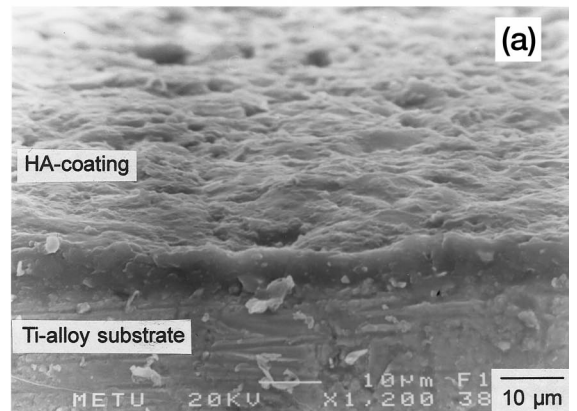
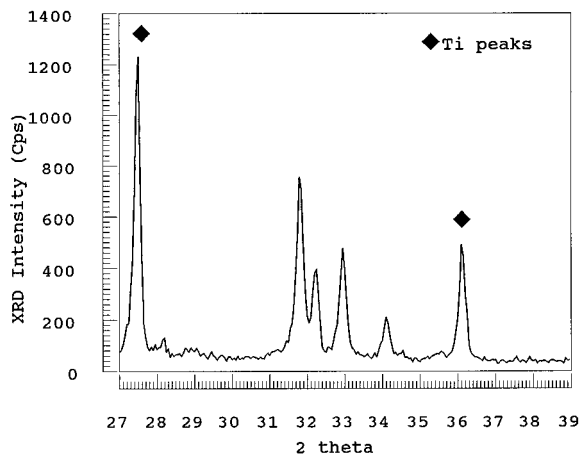


Fig. 3. SEM micrographs of HA coatings (via SOL 2) on Ti-6Al-4V substrates after heating at 840°C ((a) macroscopic appearance, (b) porous microstructure of the HA coat layer, and (c) cross-sectional view of the HA coating layer).

Ti-6Al-4V strips. These strips were dipped (and withdrawn) into these solutions at a constant speed of 100 mm/min, using the electronically controlled dipping apparatus. The most significant characteristic of the solution recipes of SOL 1 and SOL 2 was that the green, coated strips could be immediately and rapidly dried in air at a temperature of 90°C, without the need for controlling the humidity and the maintenance of slow drying conditions. The SEM micrographs given in Figs. 3(a) and (b) display the macroscopic appearance and the microstructure of the HA coatings (which were produced using the SOL 2 recipe), after calcination at 840°C in a nitrogen atmosphere for 4 h. The HA particles that are shown in Fig. 3(b) had an average particle size of ~0.25 μm. The XRD spectrum of the HA layer (on the Ti-6Al-4V strip) after calcination at 840°C is given in Fig. 4.

Table I. Development of HA Dip-Coating-Solution Recipes

SOL	Composition (wt%)						Microcracks
	HA	H ₂ O	EtOH	PEG	GEL	GLY	
A	7.3	84.9			0.8	7.0	Present
B	7.3	16.7	64.4		1.6	10.0	Present
C	7.3	16.7	73.0	2.0	1.0		Present
D	7.3	14.0	65.2	2.5	1.0	10.0	Present
1	7.3	16.7	66.5	2.8		6.7	Crack free
2	7.3	13.8	66.2	2.2	0.3	10.2	Crack free

**Fig. 4.** XRD spectrum of HA coating (via SOL 2) layer (after calcination in air at 840°C) on a Ti-6Al-4V strip.

The dip-coating-solution prescriptions that have been presented here could produce a 25- μ m-thick, uniform HA layer (Fig. 3(c), SOL 2) on metal substrates at the stated dipping and withdrawal rate. The coating thickness can be varied by varying the solution (by keeping the weight ratios of PEG, GEL, and GLY constant in the SOL 2 recipe), HA concentration (5–20 wt%), and dipping/withdrawal rates (50–250 mm/min).

The glue used for adhesive-strength tests had a tensile strength of 31 ± 2 MPa, and the breaks always occurred at a tensile-strength value in this vicinity. Thus, it was concluded that the adhesive strength of HA coatings was 30 MPa. The HA coatings, with the SOL 1 and SOL 2 recipes (after calcination), also were completely resistant to the fingernail-scratch tests.²⁶

IV. Conclusions

Calcium hydroxyapatite (HA) dip-coating-solution recipes were developed to coat Ti-6Al-4V substrates. The organic additives that were used in these solutions consisted of poly(ethylene glycol), glycerol, and/or gelatin. The dip-coating process was performed using a special apparatus that could provide constant dipping and withdrawal speeds (e.g., 100 mm/min). The HA dip-coating solution recipes developed in this study did not require the drying of the green, coated strips under controlled humidity conditions. Calcination of the HA dip-coated Ti-6Al-4V strips was performed in a nitrogen-gas atmosphere at a temperature of 840°C. The HA coatings obtained were highly porous, with bonding strengths of >30 MPa.

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