

Synthesis of Hydroxyapatite Coatings on Ti6Al4V Substrate by Biomimetic Method

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Abstract: In this study, synthesis of hydroxyapatite (HA) coatings on Ti6Al4V substrates by biomimetic technique was investigated. In this context, thin and continuous HA coatings were first deposited onto Ti6Al4V implant plates by immersion in 1, 1.5 and 3 times concentrated simulated body fluid (SBF) at 37 °C for different times at pH=7.4. The HA layers were formed in the range of 6 and 19 µm thick. The obtained coatings were characterized by XRD, optical microscope, SEM, surface roughness and microhardness machines. The experimental results clearly show that the biomimetic approach has coated them with HA globular crystals having various diameters. It was found that the coating structure was affected by solution concentration.

Introduction

Biomaterials have been used to replace or support the human organs or tissues in many years. These materials are classified into four groups as metals, ceramics, polymers and composites (Gumusderelioglu, 2002). Biocompatibility is considered as the most important feature in biomaterials, allowing the surrounding tissue to differentiate normally and preventing undesired reactions such as infection and blood clot (Wintermantel et al., 1996; Bajpai et al., in Yamamuro et al., 1980). Titanium (Ti) and its alloys are the materials of choice for most dental and orthopaedic applications. The many advantages of these materials include high compatibility with the surrounding tissue, good resistance to corrosion, and excellent mechanical properties. However, bone response and implant success depend on the chemical and physical properties of the surface. The integration with bone tissue can be improved and accelerated by the presence of a calcium phosphate (HA) coating onto the metal implant surface (Van Noort, 1987; Bigi et al., 2005).

Hydroxyapatite (HA: $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) is a calcium phosphate based bioceramic material and widely applied to the biomaterials for bone tissue implantation due to its good biocompatibility, osteoconductivity and bioactivity as well as the similarity to the inorganic component of the hard tissues in natural bones, and the HA coatings have been extensively applied with the aim of improving fixation between hard tissue and metal implants (Browne & Gregson, 1994; Bayraktar & Tas, 1999; Bigi et al., 2005). In addition, synthetic HA is a biocompatible prosthetic material, bonding strongly to the bone and promoting the formation of bone tissue on

its surface. The HA is mostly used in clinics for making artificial bone due to its biocompatibility (to be used in various prostheses), treating cracks and fractures in the bone and coating of metallic biomaterials (Abe et al., 1990; Tas, 2000; Miao et al., 2005).

For these applications, different methods such as plasma spray (Tong et al., 1995), high velocity oxy fuel spray (Li et al., 2002), sol-gel (Milella et al., 2001; Hsieh et al., 2002), electrochemical (Ban & Maruno, 1993), laser ablation (Katto et al., 2002), electrophoretic (Zhitomirsky, 1998), dip coating (Mavis & Tas, 2000) and biomimetic are used to coat implant materials with HA. Nonetheless, there have been some problems in the application. The major problem is the gradual weakening of the bond between coating and metal surface. This problem occurs due to the low bonding strength of the coating material (Ishikawa et al., 1997; Nishio et al., 2000; Yang & Chang, 2001). Of these methods, one of the most promising techniques for producing HA coatings is the biomimetic approach, which mimics the mineralisation process of bone. The biomimetic route utilises supersaturated aqueous solutions with ionic composition similar to that of human plasma, it allows to coat complex-shaped materials, and to co-precipitate biologically active molecules with apatite crystals onto metal implants (Abe et al., 1990; Browne & Gregson, 1994; Bayraktar & Tas, 1999; Bigi et al., 2005).

This situation sometimes necessitates a second operation on patients with implant, which is not desired because of health and financial concerns (Demircioglu et al., 2004). Strengthening and stabilizing the bond between metal surface and HA coating could prevent this from occurring. In addition to the one above, there are some inherent problems associated with these methods. These problems are (a) complex preparation procedures, (b) application of high temperatures which cause structural damages either on host (Ti6Al4V) or coating material, (c) getting unwanted phases in coatings, (d) employing complex equipment, (e) high cost, and (f) bonding strength that depends upon coating thickness (Weng & Baptista, 1999). Because of the difficulties listed above, biomimetic method is chosen. In this method, HA coating is realized in a simple biocompatible environment (under the conditions of human body temperature of 37 °C and pH=7.4) with chemical *in-situ* sedimentation method, where no high temperature is applied (Kokubo, 1998).

The aim of the present study was to deposit the HA coatings on Ti6Al4V implant substrates by biomimetic technique. The obtained coatings were characterized by X-ray diffraction (XRD), optical microscope, scanning electron microscope (SEM) and microhardness tester.

Experimental procedure

Commercial Ti6Al4V alloy substrates (sample size Ø 19.05×1 mm and 3×5×15 mm) were used in the study. The samples were abraded by SiC sandpaper numbers such as 400, 800 and 1200, then washed with acetone and distilled water in an ultrasonic cleaner.

The HA coatings were prepared by subjecting the metal to a chemical surface treatment to provide a surface layer conducive to apatite formation in a body environment. The HA layers were formed by soaking in a simulated body fluid (SBF) with pH and ion concentrations (pH 7.40, Na⁺ 142.0, K⁺ 5.0, Ca²⁺ 2.5, Mg²⁺ 1.5, Cl⁻ 125.0, HCO₃³⁻ 27.0, HPO₄²⁻ 1.0, SO₄²⁻ 0.5 mM) nearly equal to those of human blood plasma. Chemical compositions of SBF solutions were listed in Table 1. Commercially available Ti6Al4V alloy was subjected to 5.0 M NaOH treatment at 60°C for 24 h and subsequently to thermal treatment at 600°C for 1 h, and then soaked in SBF, see [Figure 1].

Chemical precursors	g / l	1 SBF mg / 250	1.5 SBF mg/ 250	3 SBF mg / 250
		ml	ml	ml
NaCl	6.547	1.6368	2.455	4.910
NaHCO ₃	2.268	0.5670	0.851	1.701
KCl	0.378	0.0933	0.140	0.280
Na ₂ HPO ₄ ·2H ₂ O	0.178	0.0445	0.067	0.134
MgCl ₂ ·6H ₂ O	0.305	0.0763	0.114	0.229
CaCl ₂ ·2H ₂ O	0.368	0.0920	0.138	0.276

Na ₂ SO ₄	0.071	0.0178	0.027	0.053
(CH ₂ OH) ₃ CNH ₂	6.057	1.5143	2.271	4.543

Table 1: Chemical compositions of SBF

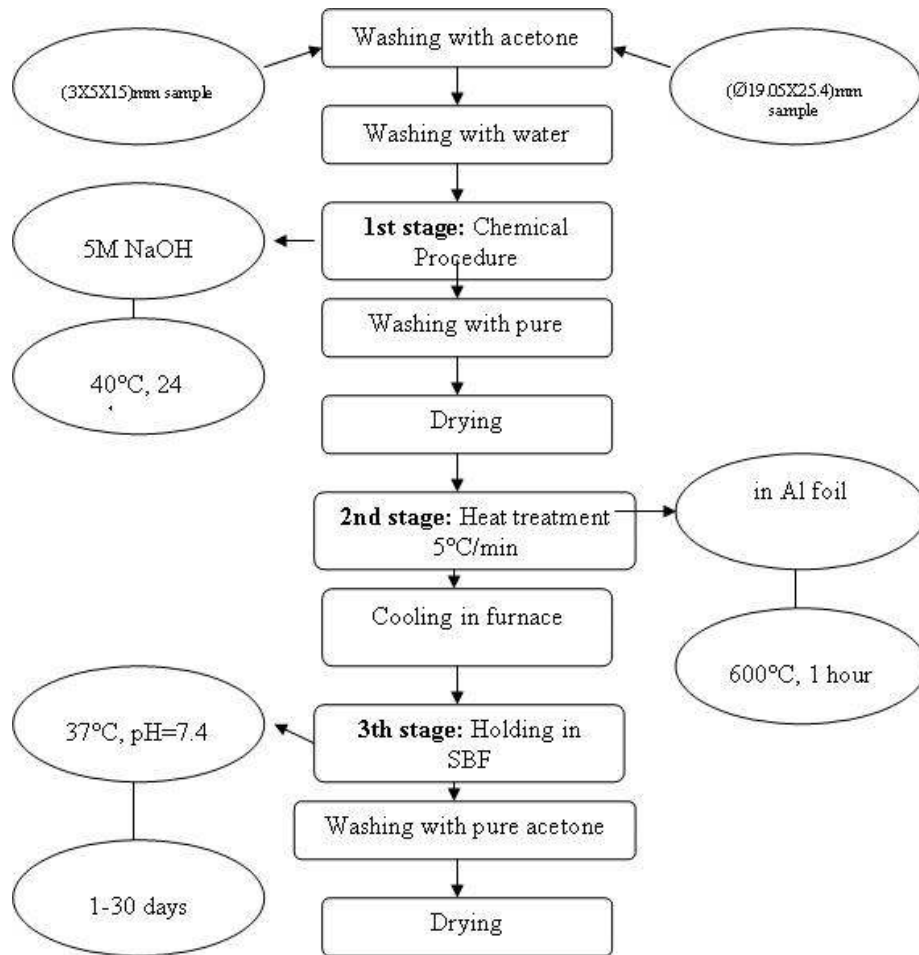


Figure 1: Coating stages for the HA formation

The film structures were analyzed by X-ray diffraction (XRD; Philips X'pert pro) with CuK_α radiation 40 kV 200 mA at a scanning speed of 4.00°/min with a scanning range (2θ) from 25° to 45°. The microstructure of sample surface was observed under scanning electron microscopes (SEM-Philips XL 30S FEG), Cross-sections of the films were observed and thickness was measured by optical microscopy (Nikon Eclipse ME600) with image analyzer Lucia 4.1 programme. The surface roughness of the coating was measured using a standard surface roughness machine. The microhardness of the coatings was measured by using a standard microhardness tester with Vickers indenter. The load applied on the samples was 0.98 N and the indentation was applied for 15 s. Five readings were taken for each sample.

Results and Discussion

Figure 2 shows XRD patterns of HA coatings on Ti6Al4V alloy substrate by using biomimetic method. Small and broad HA peaks were obtained at 2θ of 25.70, 29.32, 32.14 and 40.34 corresponding to (002), (210), (211),

(310) and (113) orientations for the samples that were immersed for 30 days in the 1.5 and 3 SBF solutions. These peak locations were validated and appeared much sharper when the SBF solution was changed from 1.5 SBF to 3 SBF. Similar results can be found in Reference (Baker et al., 2006). It is also clear from Fig. 2 that Ti peaks were obtained at 2θ of 40.26, 35.25, 38.47 and 53.20 corresponding to (001), (010), (002) and (012) orientations respectively. After chemical and heat treatment processes, Na-titanate and TiO_2 peaks having rutile and anatase phases were determined from XRD patterns. Rutile TiO_2 peaks were determined at 2θ of 27.40, 35.98 and 48.10. It is believed that the TiO_2 phases were formed between HA coating and the substrate after heat treatment process as reported (Kukobo, 1998; Li et al., 2002; Baker et al., 2006). In as much as NaOH was chemically treated with HA coatings on Ti6Al4V substrate and the SBF solutions had Na^+ ions, NaTiO_2 , $\text{Na}_2\text{Ti}_5\text{O}_{11}$ and Na_2TiO_3 phases were formed in the coatings. We have a good agreement with research of Takadama's team. Takadama et al. (2001) commented that the peak values of $2\theta=23.31^\circ$ and 48° in addition to Ti peaks occurred as a result of sodium titanate ($\text{Na}_2\text{Ti}_5\text{O}_{11}$) and rutile (TiO_2) crystals during their XRD investigation of biomimetic study. In addition to these, Kim et al. (1997) investigated the effects of heat treatment performed at different temperatures (400-800°C) on the apatite formation on chemically treated metal surfaces. Because peak point around 23° , 29° and 48° after the heat treatment at 600°C were found to be related to sodium titanate hydrogel layer, gel layer was started to turn into $\text{Na}_2\text{Ti}_5\text{O}_{11}$ and rutile TiO_2 at 600°C . After 7 days of soaking, the apatite phase was formed at all temperatures. As a result, the apatite coating of titanium implants after chemical and heat treatments increased the bone-implant interface bonding strength, and thus this method was found to be advantageous for load bearing implants.

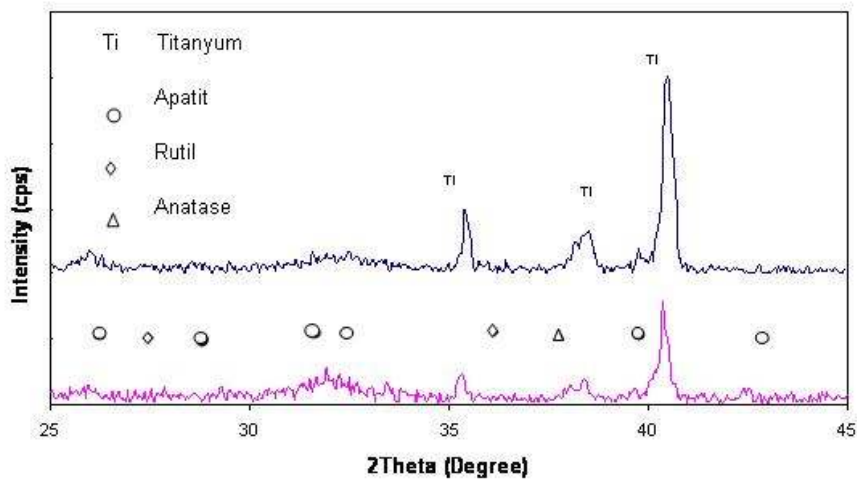


Figure 2: XRD pattern of the HA coatings prepared on Ti6Al4V alloy substrate from (a) 1.5 (top pattern) and (b) 3 SBF (bottom pattern) solutions by using biomimetic method. Characteristic peaks are found at approximately 25.70, 29.32, 32.14, and 40.34 2θ . The most intense peaks correspond to titanium

Figure 3 demonstrates cross-sectional optical micrograph of the HA coating on the Ti6Al4V substrate. Thickness of the coatings was measured by using optical microscope for different SBF concentrations. As listed in Table 2, the thicknesses of coatings were in the range of 6.50 μm and 18 μm . It is obvious from Fig. 3 that the structure with sodium titanate was formed on the substrate and the HA started to nucleate and grow in SBF solutions after periods of 4, 12 and 19 days. After obtaining homogeneous HA coatings, the thicknesses of coatings prepared from 1, 1.5 and 3 SBF solutions were found to be as 6.78, 8.93 and 18.25 μm respectively. From these results, it can be concluded that coating thickness increased with increasing the solution concentration. When Ti alloy substrate which had been polished to remove its surface oxide layer was soaked in 3 SBF solutions with ion concentrations 3 times those of SBF, a dense layer of apatite was formed on its surface. The apatite nuclei grew spontaneously by consuming the calcium and phosphate ions from SBF solution.

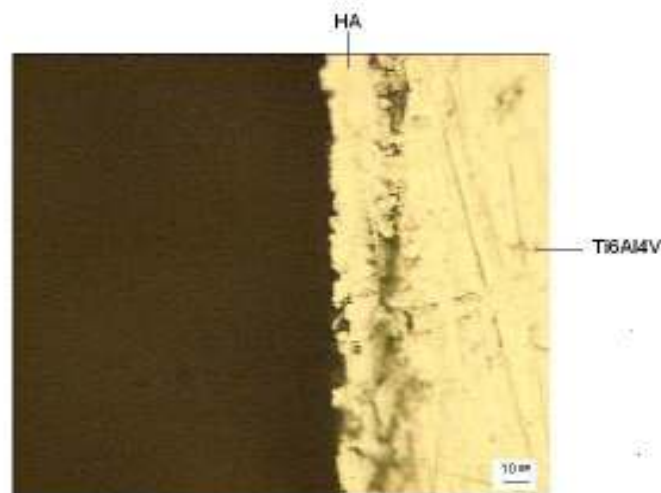


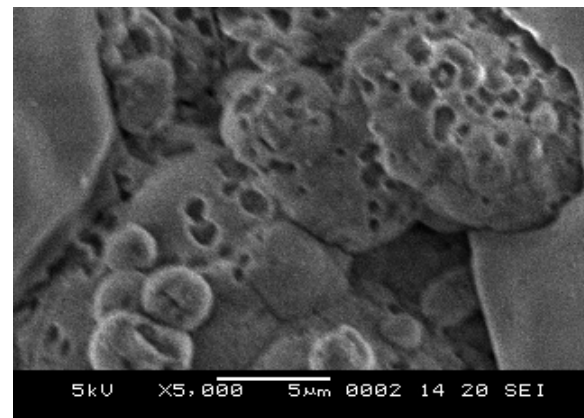
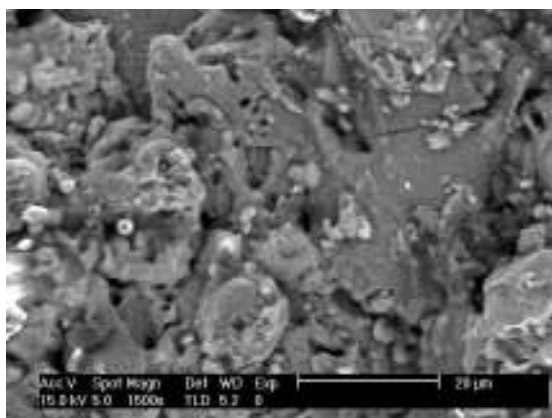
Figure 3: The cross-sectional optical micrograph of HA coating on the Ti6Al4V substrate

The resultant apatite layer was tightly bonded to Ti-based substrate, since it is integrated to the Ti alloy substrate through the hydrated titania and titanium oxide which are gradually changed in their concentration (Kokubo, 1998). Furthermore, surface roughness values of the coatings prepared from 1, 1.5 and 3 SBF solutions were found to be 1.9, 2.2 and 2.6 respectively. In this context, it is said that surface roughness of the HA coatings increased as solution concentration and coating thickness increased as shown in Table 2.

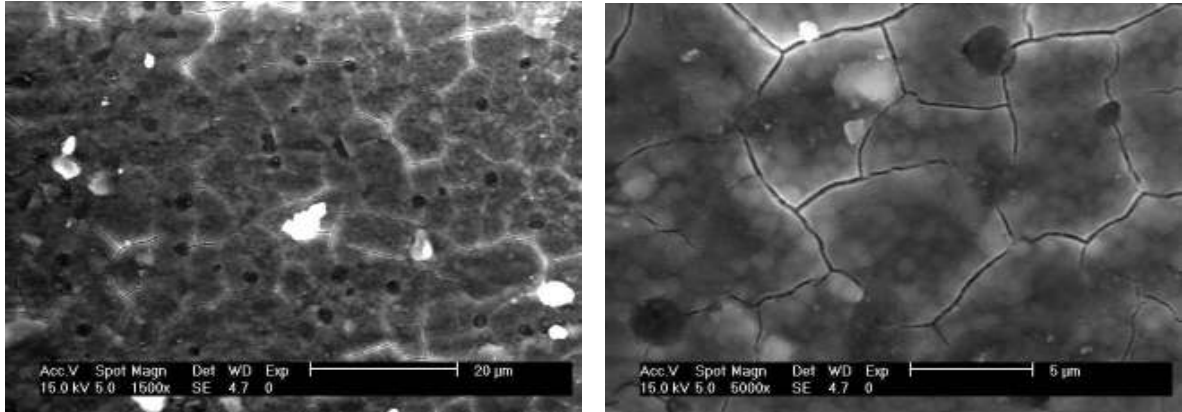
Solution concentration	Coating thickness (μm)	Surface roughness (μm)
1 SBF	6.50	1.8-2.0
1.5 SBF	10.50	2.0-2.4
3 SBF	18.25	2.0-2.8

Table 2: Thicknesses and surface roughness of the HA coatings

Figure 4 depicts surface morphologies of the HA coatings with different concentrations such as 1, 1.5 and 3 SBF concentrations. When the coating thickness increased, cracks were observed from SEM studies. The layers were dense and uniform in thickness, showing some cracks of several tens of microns in length as shown in Fig. 3. The homogeneous HA coatings were formed from diluted SBF solutions. Spherical particles having diameters between 1-5 μm and porous structure of HA crystals are shown in coating with 1.5 SBF at different magnifications in Figure 4.a. However, the structures having cracks were coated from viscous SBF solutions, see [Figure 4.b]. The cracks were formed as a function of solution concentration and coating thickness as explained elsewhere (Barrere et al., 2002; Tas & Bhaduri, 2004).



(a)



(b)

Figure 4: Surface morphologies of the HA coatings with different concentrations such as (a) 1.5 and (b) 3.0 SBF concentrations.

The cracks in SEM micrographs were formed during heat-treatment owing to thermal expansion and thick coating. It is also obvious from SEM observations that the HA coatings have some spherical grain and porosity. Since the coating on the surface is thin, the metal surface is visible through the coating and the apatite nuclei were started to deposit at the peak points of the rough surface. The coating was uniform and contained small particles having diameters about 1-2 µm. It is concluded that the small particles on the surface were found to be important for adhesion and bigger particles affected coating homogeneity.

Microhardness values of surface of coating, HA coating and substrate amounted about 343, 445 and 230 HV, respectively (Table 3). The surface microhardness of HA coating is lower than that of coating layer because some inhomogeneities such as open porosity, cracks and so on.

In the future, in *in-vivo* studies, minimum coating thickness can be determined for metal implant surface thus the SBF concentration and soaking time can be optimized. Also, coating adhesion strength can be modeled numerically; effects of coating thickness, coating surface area on the adhesion can be investigated.

Conclusion

The HA coatings were deposited on Ti6Al4V implant substrates from SBF solutions by biomimetic technique. HA, Ti, TiO₂, NaTiO₂, Na₂Ti₅O₁₁ and Na₂TiO₃ phases were found from XRD study. The thickness of coatings was ranged from 6.50 µm to 18 µm. As the solution concentration is increased the coating thickness increased. The homogeneous HA coating was formed in diluted SBF solutions. The cracks were formed as a function of solution concentration and coating thickness. The HA coatings have some spherical grain and porosity. Microhardness values of surface of coating, HA coating and substrate were measured about 343, 445 and 230 HV, respectively.

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