

## CHARACTERIZATION OF FLUORIDATED HYDROXYAPATITE (FHA) SOL-GEL COATINGS ON TITANIUM SUBSTRATE

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### ABSTRACT

In this paper, FHA coatings [FHA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{F}_x$ ] (wherein  $0 \leq x \leq 2$ ) were deposited on titanium substrate by sol-gel method with heat treatment at 900 °C for 4 hours. Different concentrations of  $\text{F}^-$  were incorporated into the apatite structure during the sols preparation. The FHA sols were prepared using various amounts of ammonium fluoride [ $\text{NH}_4\text{F}$ ] with the [P]/[F] molar ratios of 12, 6, 4, 3 in order to have the corresponding compositions of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}_{0.5}\text{OH}_{1.5})$ ,  $\text{Ca}_{10}(\text{PO}_4)_6\text{FOH}$ ,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}_{1.5}\text{OH}_{0.5})$  and  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , respectively. The fabricated FHA coatings were assessed by various methods, namely: morphological structure and chemical composition of coatings were studied by scanning electron microscopy (SEM) and Energy dispersive spectrometry (EDS). The anti-corrosion properties of samples were evaluated by Potentiodynamic polarization curves and Nyquist impedance spectrum. The biocompatibility of FHA coatings on titanium substrates were evaluated by in-vitro tests in simulated body fluid (SBF) solution during 21 days, and ICPMS (Inductively Coupled Plasma Mass Spectrometry) analysis method has been used. The results showed that with dense structure, FHA coatings expressed higher anti-corrosion and biocompatibility performance as compared with that of HA coating.

*Keywords:* fluoridated hydroxyapatite, titanium, biocompatible, *in-vitro*, anti-corrosion.

### 1. INTRODUCTION

Hydroxyapatite [HA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] ceramics have been recognized as substitute materials for bones and teeth in orthopedics and dentistry due to their chemical and biological similarity to human hard tissues. Its good biocompatibility makes it to be extensively used in many prosthetic applications, especially as a porous material for optimal bone in growth [1-3]. However, the further investigation revealed that pure HA suffers relatively high dissolution rate in simulated body fluid which affects its long-term stability: high dissolution may lead to

disintegration of the coatings and hinder the fixation of implant to the host tissue [4-6]. Therefore, along with HA coatings, fluoridated hydroxyapatite [FHA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{F}_x$ ] coatings on metallic substrates have attracted a great deal of attention in areas which require the coating with long-term chemical and mechanical stability [7,8]. The incorporation of fluorine into HA crystal structure by substitution of F<sup>-</sup> ions for OH<sup>-</sup> groups to form fluoridated hydroxyapatite is named as the degree of fluoridation. Partial substitution of F<sup>-</sup> for OH<sup>-</sup> groups significantly reduces the solubility while maintaining a biocompatibility of HA coatings. In fact, fluorine itself is an essential element for the development of human hard tissues, such as bones and teeth. Moreover, the presence of fluorine in HA enhances the proliferation and differentiation of osteoplastic cells and thus promotes bone regeneration [7-10].

Some methods are used to deposit the HA and FHA coatings on the surface of metallic implants such as conventional press, ion beam sputtering, electrophoretic deposition, RF-magnetron sputtering, pulse laser melting, physical vapor deposition and electrochemical deposition etc. Among them, the sol-gel technique offers certain advantages such as the high chemical homogeneity, fine grain structure, easily adjustable thickness, and low crystallization temperature, as well as an economy and simplicity in fabrication technique. The sol-gel coating method includes two basic techniques: spin coating and dip coating [11].

In this study, the sol-gel fluoridated hydroxyapatite coatings (FHA) and HA coatings were deposited on Ti substrate by spin coating technique with heat treatment at 900 °C for 4 hours. The precursors ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  with stoichiometric amount Ca/P of approximately 1.67 and using various amounts of ammonium fluoride [ $\text{NH}_4\text{F}$ ] with the [P]/[F] molar ratios were 12, 6, 4, 3, respectively. The influence of various amounts of ammonium fluoride of FHA sols on the characterization of the FHA coatings were investigated and discussed.

## 2. EXPERIMENTAL

### 2.1. Preparation of HA coating

Preparation process of HA and FHA sols were performed as follows:

- Dissolving precursors  $\text{H}_3\text{PO}_4$  and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in ethanol solvent with stoichiometric amount Ca/P of approximately 1.67. After then, the mixture was stirred for 24 hours to form HA sol. The pH value of the HA sols was adjusted to pH = 7 by  $\text{NH}_4\text{OH}$  solution 25 % wt.

- Afterward, various amounts of ammonium fluoride [ $\text{NH}_4\text{F}$ ] with the [P]/[F] molar ratios of 12, 6, 4, 3 were added slowly into these mixtures in order to receive FHA sols with the compositions of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}_{0.5}\text{OH}_{1.5})$ ,  $\text{Ca}_{10}(\text{PO}_4)_6\text{FOH}$ ,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}_{1.5}\text{OH}_{0.5})$  and  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , respectively. After adjusting pH, the HA and FHA sols were continuously stirred for aging time of 72 hours at 40 °C.

The Ti substrates were polished with SiC papers with grit in range of 240-800. After polishing, the Ti samples were ultra-sonicated in ethanol for 10 min and then were washed in distilled water for 5 times. Finally, the samples were dried at 100 °C for 24 hours.

The coatings were prepared by depositing HA and FHA sols on titanium substrates using spin coating technique. The coated samples were dried at 80 °C for a hour and this process was repeated 5 times. Finally, the samples were sintered at 900 °C for 4 hours. The samples were named to FHA0.5, FHA1, FHA1.5 and FHA2 corresponding to formulas of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}_{0.5}\text{OH}_{1.5})$ ,  $\text{Ca}_{10}(\text{PO}_4)_6\text{FOH}$ ,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}_{1.5}\text{OH}_{0.5})$  and  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , respectively

## 2.2. Characterizations

The morphological structure and chemical composition of coatings were observed and analyzed by emission scanning electron microscope (SEM, JSM-6710F/INCA Energy, /JEOL, 20 kV, 2007). The anti-corrosion behavior of samples were evaluated by potentiodynamic polarization curves and Nyquist impedance spectrum (PARSTAT 2273). The biocompatibility of HA and FHA coatings on titanium substrates was evaluated by *in-vitro* tests in simulated body fluid (SBF) solution with chemical composition: 8.8 g/L NaCl; 0.4 g/L KCl; 0.14 g/L CaCl<sub>2</sub>; 0.35 g/L NaHCO<sub>3</sub>; 0.2 g/L MgSO<sub>4</sub>.7H<sub>2</sub>O; 0,1 g/L KH<sub>2</sub>PO<sub>4</sub>.H<sub>2</sub>O; 0,06 g/L Na<sub>2</sub>HPO<sub>4</sub>.7H<sub>2</sub>O; 1.00 g/L Glucose; pH 7.3; at 37 °C. After 21 days of testing, chemical composition of SBF solution was analyzed by ICPMS method.

## 3. RESULTS AND DISCUSSION

### 3.1. Morphological structure of coatings

The surface morphologies of coatings are presented on Figure 1.

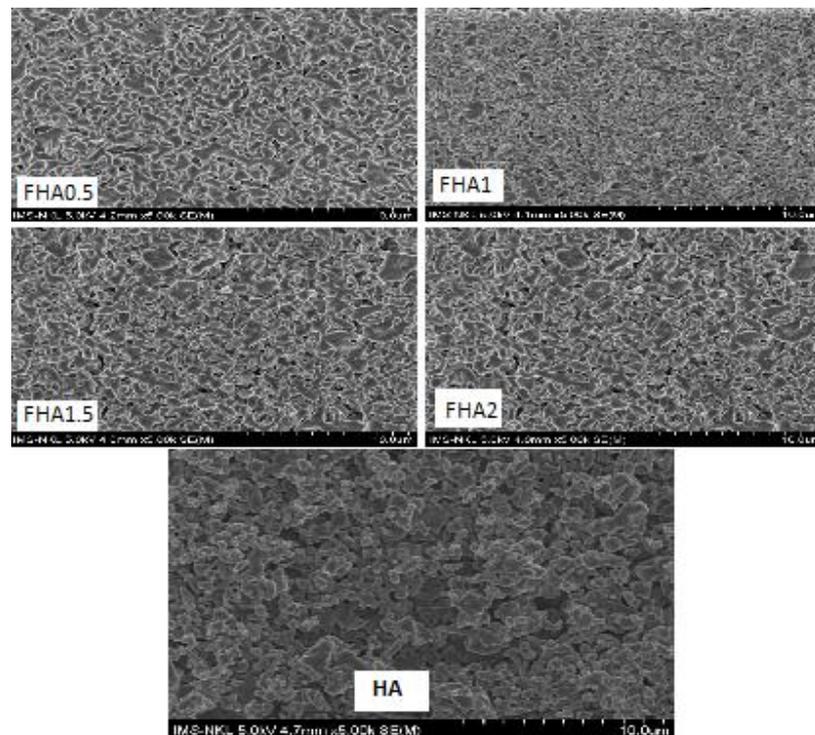


Figure 1. SEM paragraphs of the coatings.

Figure 1 shows that the surface morphologies of HA coating ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  wherein F content = 0) was un-homogeneous with large size agglomerated grains and high roughness. While, the surface morphologies of FHA0.5, FHA1, FHA1.5 and FHA2 coatings were relatively homogeneous with higher compact structure. This may be caused by partial substitution of F for

OH<sup>-</sup> groups and incorporation of fluorine ion into HA structure which make the change in structures of FHA coatings.

### 3.2. Corrosion protection behavior of Ti substrate with coatings

Corrosion protection behaviors of HA coatings and FHA coatings on titanium in SBF solution were investigated by potentiodynamic polarization curves and impedance spectrum. Figure 2a expresses the potentiodynamic polarization curves of FHA coatings with various F<sup>-</sup> concentration of sols. From the plot of potential versus log *i*, using software to fit Tafel mode, an extrapolation of linear line to corrosion potential gave the slopes of both *ba* and *bc* and the corrosion current density. The corrosion potential ( $E_{\text{corr}}$ ) and the corrosion current density ( $i_{\text{corr}}$ ) for coatings are presented in Table 1. The results show that the  $i_{\text{cor}}$  values of FHA coatings decrease significantly in comparison with the value of HA coating. This means that the corrosion protection of FHA coatings was better than that of HA coating. It may be caused by the density of structure of coatings.

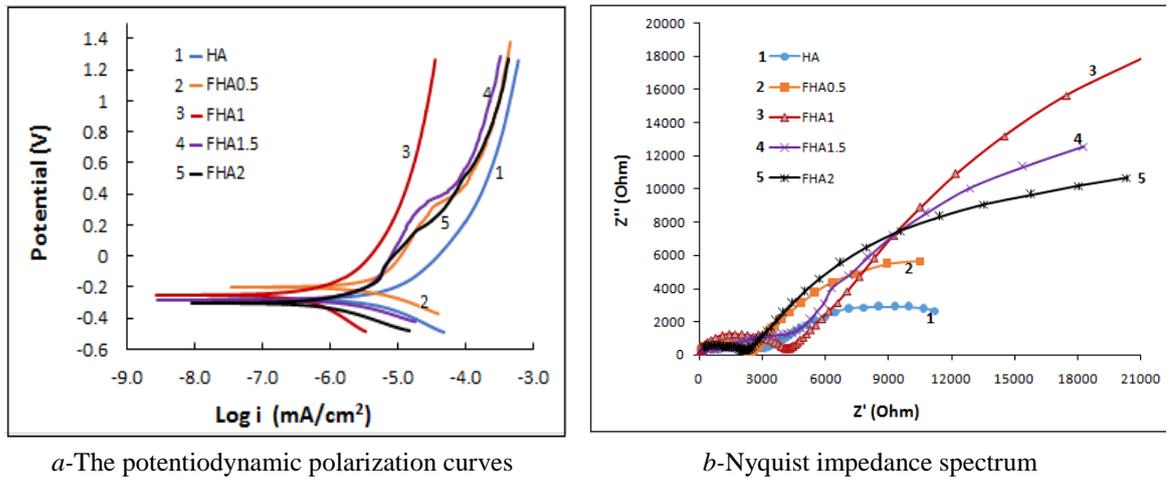


Figure 2a. The potentiodynamic polarization curves and Nyquist impedance spectrums of samples in SBF.

Table 1. Electrochemical parameters.

Sample	$E_{\text{corr}}$ (mV)	$b_a$ (V/dec)	$b_c$ (V/dec)	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$R_{\text{ct}}$ (k $\Omega$ )
HA	-329	0.28	0.33	6.30	14.87
FHA0.5	-194	0.098	0.115	1.64	17.20
FHA1	-251	0.166	0.137	0.28	95.13
FHA1.5	-281	0.111	0.179	1.22	39.20
FHA2	-302	0.126	0.139	1.02	36.60

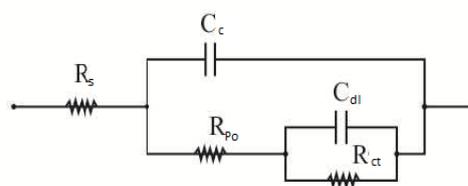


Figure 3. The equivalent circuit model of Nyquist impedance spectrum in SBF solution.

Figure 2b presents Nyquist impedance spectrum of HA and FHA coatings. Nyquist plots show two semicircles indicating that: a high frequency response due to the parallel arrangement of coating capacitance ( $C_c$ ) and pore resistance ( $R_{po}$ ), and a lower frequency response due to the corrosion cell formed at the substrate surface, which can be expressed by parallel arrangement of double layers capacitance ( $C_{dl}$ ) and charge transfer resistance ( $R_{ct}$ ). Therefore the equivalent circuit model of Nyquist plots is shown as in Figure 3. Using this mode to simulate and fit,  $R_{ct}$  values were given and summarized in Table 1. The  $R_{ct}$  values of FHA coatings are higher than that of HA coating. The results of impedance measurement are suitable with the received potentiodynamic polarization results. This suggests that significant improvement in anti-corrosion capacity of FHA coatings with the present of  $F^-$  ion in coating. The received results also show that the FHA1 coating gave the best corrosion protection behavior and was used for the next research.

### 3.3. Biocompatibility of coatings on titanium substrate

In the *in-vitro* tests, the biocompatibility was characterized by the formation of apatite layer on the samples which could be explained by appearance of a lot of small white particles on the surface of samples as observed in SEM images. Figure 4 presents surface morphologies of samples before and after *in-vitro* test. After 21 days test, small white and agglomerated particles have been observed on the surface of both HA and FHA1 samples. The chemical composition analysis of these samples by EDS gave the data in Table 2. It shows that P and Ca contents increased after *in-vitro* test for both HA and FHA coatings. The formation of hydroxyapatite-rich layer on the samples in SBF happened follows reaction (1) due to the absorption process of ions such as  $Ca^{2+}$ ,  $OH^-$ ,  $PO_4^{3-}$ ... in the SBF solution on the samples surface. That may be caused by increasing of P and Ca content.



Table 2. The chemical composition of sample analyzed by EDS method.

Element	HA coated sample		FHA coated sample	
	Before in-vitro test	After in-vitro test	Before in-vitro test	After in-vitro test
O	66.78	57.5	67.61	57.11
P	13.98	15.86	14.19	16.37
Ca	19.24	26.39	17.63	26.52
Ti	-	0.25	-	-
F	-	-	0.57	-

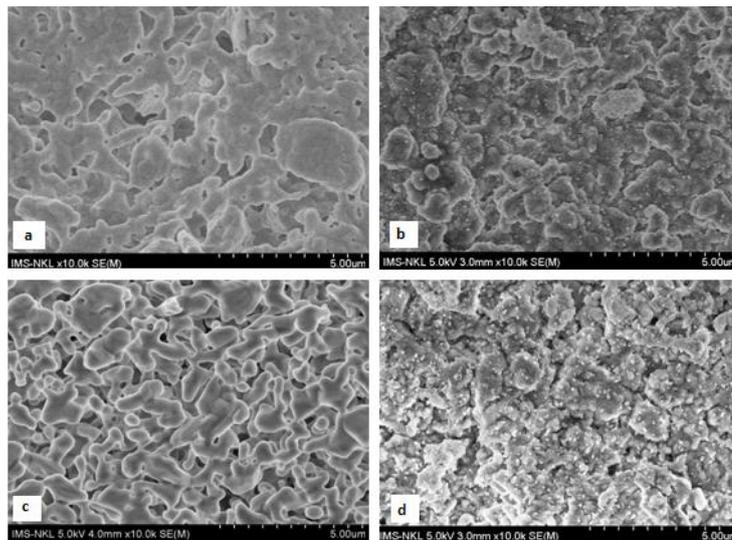


Figure 4. SEM paragraphs of the samples: a- HA before testing, b-HA after testing, c-FHA1 before and d-FHA1 after testing.

On the other hand, the ICPMS analysis results of SBF solution after 21 days in-vitro test are presented in Table 3.

Table 3. The composition of the ions dissolved in the SBF after 21 days of test.

No	Species in SBF solution	Concentration before in-vitro test (mg/L)	Concentration after in-vitro test with HA coated sample(mg/L)	Concentration after in-vitro test with FHA1 coated sample(mg/L)
1	Cd	<0.0002	<0.0002	<0.0002
2	Pb	0.011	0.002	0.005
3	As	0.003	<0.001	<0.001
4	Hg	0.0004	0.0002	<0.0002
5	Fe	0.220	0.165	0.170
6	Ti	0.013	0.010	0.010
7	Ca <sup>2+</sup>	49.50	32.90	32.60
8	PO <sub>4</sub> <sup>3-</sup>	25.09	23.5	20.25

In general, concentration of Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> ions of solution decreased. Concentration of Ca<sup>2+</sup> ion decreased from 49.50 mg/L (before in-vitro test) to 32.90 mg/L in SBF solution in case of HA coated sample while this value was 32.60 mg/L in SBF solution for FHA1 coated sample. For PO<sub>4</sub><sup>3-</sup> ion, the concentration decreased from 25.09 mg/L to 23.50 mg/L and 20.25 mg/L in SBF solution for HA and FHA coated samples, respectively. Thus, the decline of Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> ions concentration of SBF solution in case of FHA1 testing was higher than in comparison with HA testing. This decline may be caused by the formation of apatite layer on samples surface and this means that FHA1 coating promoted for growth of apatite layer better than that in comparison with HA coating. In addition, the ICPMS analysis also showed that there was no increasing of toxic heavy metal concentration (Cd, Pb, As, Hg...) and their amounts were still under ASTM F1185-03 standard limitation for living human body after in-vitro test.

#### 4. CONCLUSION

The sol-gel hydroxyapatite HA and fluoridate hydroxyapatite (FHA) coatings were deposited on Ti substrate by spin coating technique with heat treatment at 900 °C for 4 hours. The incorporation of fluorine ion into HA crystal structure by substitution of F<sup>-</sup> ions for OH groups lead to improve properties of biocompatible coatings. Anti-corrosion behavior and biocompatibility of FHA coating was better than that of HA coating. Therefore, along with HA coatings, FHA coatings on metallic substrates promise to become potential biomaterials in the future and need to further investigate.

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