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CHARACTERIZATION OF HYDROXYAPATITE LAYER ON AISI 316L STAINLESS STEEL

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Abstract

Bioactive coatings can be divided into two main groups - organic and inorganic coatings. Hydroxyapatite (HA) is well known as one of inorganic part of mammal's bone structure and is highly recommended for use in implantology. This paper is mainly focused on characterization of hydroxyapatite particles electrochemically deposited from water solution of $Ca(NO_3)_2$ and $NH_4H_2PO_4$ on surface of AISI 316L (1.4404) stainless steel with different roughness profiles and surface treatment. The effect of surface roughness itself is discussed as well as heat treatment (400 °C) of samples after coating deposition. Electrodeposition of HA was carried out at cycling of potential values of −2.0 V for 2 s and 0 V (NHE) for 1 s; 200 cycles was used for this study. Electrochemical properties of such treated samples were characterized using voltammetry and EIS methods. It was found, that time of deposition significantly changes electrochemical parameters of equivalent el. circuit used for closer characterization of coating properties but only marginally affects corrosion properties like open circuit potential (OCP), corrosion potential (E_{corr}) or potential of passive layer breakdown (E_{break}). Pull-off test also proved significant correlation between surface roughness, heat treatment and adhesion of deposited coatings.

Keywords: corrosion resistance, biomaterials, hydroxyapatite, implants, electrochemical treatment

1. INTRODUCTION

Metallic materials are still most common materials used in medicine and its related branches. Proper grade of stainless steel may be selected if fulfils all requirements (time of implantation, type of surrounding tissue, etc.). Biological or corrosion properties of each application can be improved by surface coatings, which make the final product more biocompatible or even bioactive to achieve proper tissue reaction. Surface of parts made from stainless steels can be electrochemically roughen to obtain higher level of free surface to contact with surrounding tissues [1]. If bioactive particles are applied on surface, proper body reaction have been observed. Hydroxyapatite (HA) is studied for many decades for its favourable mechanical properties close to spongia type of bone and good biocompatibility to mammal's organism. Surface of the implant can be covered with these particles directly using PVD methods, or HA particles can be synthetized from precursors using electrochemical deposition methods. Main problem of direct synthesis is that new created particles shows only weak bonding to the substrate so there is risk of coating damage when friction stress is applied. For better substrate-particles bond previous electrochemical substrate roughening or postdeposition heat treatment may follow [2]. Each change of surface parameters leads to change of its electrochemical properties. Even very small changes of surface parameters can be revealed by electrochemical impedance spectroscopy method (EIS). Basic corrosion properties of studied materials can be studied by standardized polarization methods (e.g. ISO EN 10993, ASTM G5-94, ASTM F746, etc.) Results of these measurements are used for comparison of each material with respect to its electrochemical behaviour under simulated body conditions. For determination of coating adhesion a pull out test or scratch test can be used [3]. In this research paper influence of hydroxyapatite coating on 1.4404 steel substrate is studied in terms of corrosion and electrochemical properties, adhesion and wettability.

2. MATERIAL AND METHODS

2.1. Material and its characteristics

Stabilized stainless steel of medical grade 1.4404 (X2CrNiMo17-12-2, AISI 316L) supplied by EKOMOR Inc. was chosen for this particular study. The 3.0 mm thick sheet was cut into 150 x 50 mm samples, which were ultrasonically degreased. Chemical composition according to ASTM A240 [4] is shown in **Table 1**. For this experiment three samples have been prepared and forth sample has been used without any treatment as reference for contact angle comparison. These samples have been processed according to **Table 2.**

Table 1 Chemical composition according ASTM A240

Chemical composition (max. % wt. or range)									
C	P	S	Si	Mn	Cr	Ni	Mo	N	Fe
0.03	0.045	0.03	0.75	2	16-18	10-14	2-3	0.1	Balance

Table 2 Processing of samples

	Type of processing			
Sample	**Degreasing**	**Roughening**	**HA synthesis**	**Heat treatment**
1	Yes	No	Yes	No
2	Yes	Yes	Yes	No
3	Yes	Yes	Yes	Yes
Ref.	Yes	No	No	No

2.2. Surface structure, roughness analysis and contact angle tests

Surface profile measurement was performed by Taylor Hobson Talysurf 50 device equipped by standard stylus arm with 2 µm radius diamond tip. Speed rate of the tip was 1 $mm \cdot s^{-1}$ for this particular measurements and length of measured line was set to 40 mm. Two measurements were done in cross shape with 90° angles between lines. Scanning electron microscope JEOL JSM-6490 with accelerating voltage 15 keV was used for observation of surface structure and parameters. Wettability (contact angle) of samples was inspected by optical contact angle measuring system, snapshots of drops on surface were taken and pictures were evaluated by ImageJ software using DropSnake and LB-ADSA methods. For this procedure 2 µl droplets of artificial Tyrode's physiological solution prepared according to ISO 10993 were used [5]. Chemical composition of Tyrode's physiological solution is: NaCl (8.00 g / l), $CaCl_2$ (0.20 g / l), KCl (0.22 g / l), $NaHCO_3$ (1.00 g / l), Na_2HPO_4 (0.05 g / l), $MgCl_2$ (0.20 g / l), Glucose (1.00 g / l). All chemicals (g.r.) were supplied by VWR International.

2.3. Process of roughening, hydroxyapatite synthesis and heat treatment

The main aim of roughening process was to nanostructure substrate surface. To obtain this kind of surface profile anodization process was chosen. During the anodization, specific phases and particles has been dissolved leaving surface pitting-like look. There was 2 electrode cell used for anodization, where platinated titanium plate was used as negative electrode and sample was fixed to positive electrode. Anodization solution of distilled water, ammonium fluoride (0.1 M, purity > 99.5 %) mixed with glycerine in weight ration 10 : 90 (90 % glycerine). DC laboratory power source Matrix MPS-3005D generated stable voltage of 10 V for 10 minutes during the procedure. Ratio of solution volume vs. anodized surface was approx. 3 $ml \cdot mm^{-2}$. The procedure was carried out at room temperature 20 ± 2 °C [6].The electrolyte for direct HA synthesis contained 0.042 M

$Ca(NO_3)_2$ and 0.025 M $NH_4H_2PO_4$ in water. The initial pH of the bath was 7.4 and this was achieved by suitable addition of dilute HCl. Synthesis was performed using Voltalab PGZ 100 potentiostat and samples were connected as a working electrode. Synthesis itself consisted from 200 cycles, each cycle lasted for 3 s and consisted from polarization -2.0 V for 2 s and 0.0 V for 1 s, these potential values are expressed relative the NHE. The 1 s time gap in each cycle was chosen to improve adhesion of particles to the substrate [7]. Heat treatment at temperature 400 °C was applied to increase adhesion of HA particles to the substrate. Low vacuum chamber (~10 Pa) with heating rate 10 $°C \cdot min^{-1}$ was used and time lag was 20 min. Sample was cooled in the chamber under vacuum till the temperature decreased to room temperature.

2.5. Corrosion tests and electrochemical impedance spectroscopy

Potentiodynamic polarization tests were performed according to ASTM 2129 standard [8] in corrosion cell of 1000 ml volume tempered to temperature 37 °C. Tyrode's solution was used as corrosion environment for these experiments. Potentiostat Voltalab PGZ 100 with software Voltamaster 10 was used for this particular experiment and polarization rate 1 mV / s was set. Sample was fixed to working electrode, saturated calomel electrode was used as reference one and platinated titanium grid was fixed as auxiliary electrode to create homogenous electric filed. Exposed surface was 0.50 cm^2. Samples were immersed in electrolyte for 1 hour to stabilize corrosion potential. After that interval OCP was measured. During next step pitting or crevice corrosion was initiated and tested by potentiodynamic polarizing of sample to potential more noble values than corrosion potential. During this polarization pitting or crevice corrosion is detected by general increase of current density. When current density increased to value 2.0 $mA \cdot cm^{-2}$, polarization was stopped. Electrochemical impedance spectroscopy (EIS) was used for closer observation of electrochemical properties of each specimen. Wave amplitude of 10 mV was set and measurements were carried out at OCP. Subsequently, the frequency of AC was changed from 10^5 Hz to 0.5 Hz. Experimental data were exported to EIS Analyser software where equivalent electric circle and its parameters were found out [6].

2.6. Pull-off test

The purpose of this test is to measure the bond tensile strength of a coating - adhesiveness. The sample will be subjected to increasing tensile stresses until the weakest path through the material fractures. The weakest path could be along an interface between two coatings, a cohesive fracture within one coating and a adhesive fracture between the substrate and coating or a combination of these cases [9].

3. RESULTS AND DISCUSSION

3.1. Influence of roughening to surface structure, roughness and wettability

Surface of tested samples has been studied by electron microscopy using secondary electron detector to observe surface relief. **Figure 1 A** shows surface structure with small pits after anodization roughening and **Figure 1 B** illustrates surface of sample after direct HA electro-synthesis from precursors. Roughness tests have been done to find relation between surface roughness and other properties. Average roughness parameters for as receives sample surface were values: R_a = 0.42 µm, R_z = 1.84 µm. Average roughness parameters of roughened surface were: R_a = 0.87 µm and R_z = 3.61 µm. Contact angle has been evaluated using two methods: DropSnake method, where interface droplet-air-surface is marked with points and LB-ADSA method where the shape of droplet is measured. All measurements may be affected by user's interpretation, total deviation for each sample has not been higher than 2°. **Table 3** illustrates average values of contact angles for each sample.

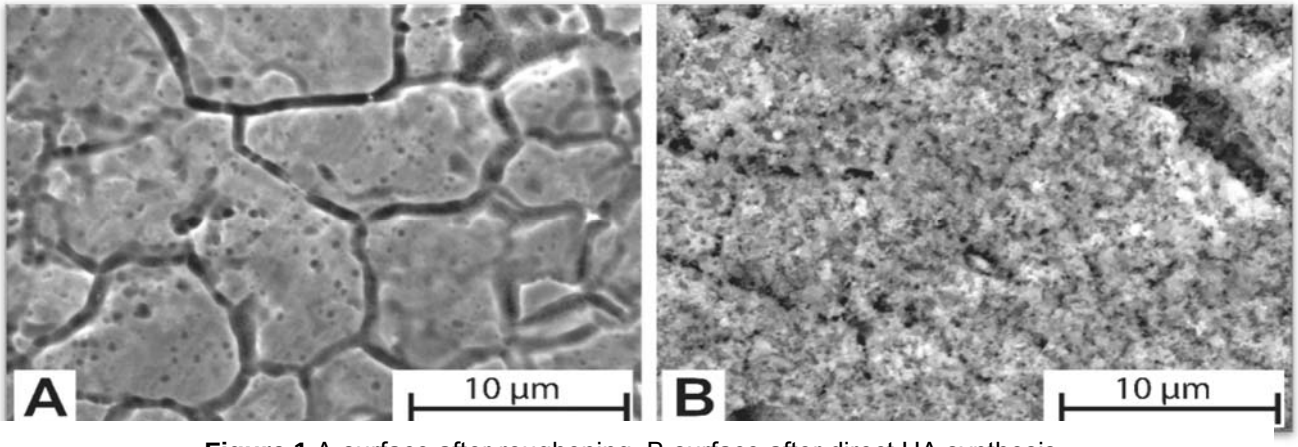

Figure 1 A-surface after roughening, B-surface after direct HA synthesis

Table 3 Average values of contact angles

	Contact angle-methods	
Sample	**Drop-snake (°)**	**LB-ADSA (°)**
1	39	41
2	30	29
3	24	26
Ref.	89	94

3.2. Corrosion tests, EIS method and pull-of test

During polarization testing, relation between potential and current was studied. All corrosion curves were registered, recorded and evaluated by Voltalab software. Basic parameters as corrosion potential, polarization resistance (R_p) or corrosion rate were found using Tafell and Stern methods. Since E_{corr} can be considered as indicator of surface oxide layer stability, R_p mostly indicates dielectric character of material and can be significantly affected by even tiny imperfections or defects (like tiny pits on surface of sample 2) [10]. Breakdown (depassivation) potential was found out by intersection method (extrapolation of polarization curve and its intersection with X axis). Also conventional method was used: the values of breakdown potential were found by polarization curve where the current density reaches the value of 10^{-4} A·cm^{-2} [8]. Polarization curves can be seen at the **Figure 2** and corrosion parameters are illustrated in **Table 4**.

Table 4 Corrosion parameters

	Corrosion potential E_{corr} (mV vs. SCE)		i_{corr} (nA·cm^{-2})	Polar. resistance R_p (kΩ.cm^2)		Breakdown potential (mV vs. SCE)	
Sample	Taffel	Stern	Taffel	Taffel	Stern	convent.	from curve
1	-155	-154	825	12	12	630	641
2	-489	-491	198	35	32	413	447
3	-191	-190	341	30	29	670	1220

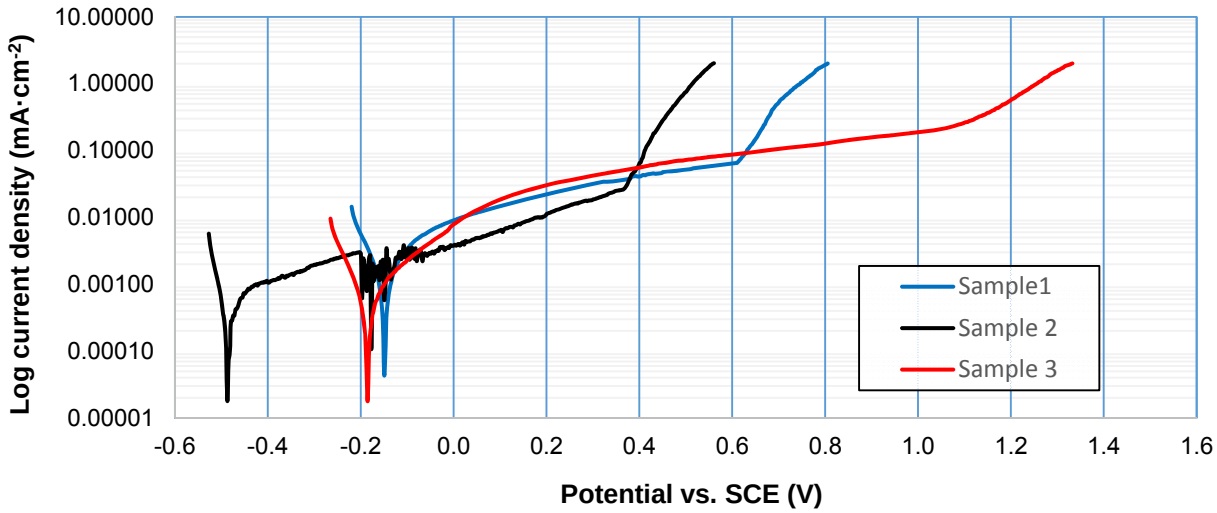

Figure 2 Potentiodynamic polarization curves

By EIS measurements the equivalent electric circle was set up and its parameters were found out. From these parameters equivalent capacitance of anodized surface was calculated using derivate equation of ZARC element (1), where *C* is capacitance, R_1 is resistance of contact and electrolyte, R_2 is resistance of surface layer and *P* and *n* are parameters of constant phase element (CPE) [11]. Values of capacitance are illustrated specified in **Table 5**. The Equivalent circuit is visible at **Figure 3** [6].

$$C = \frac{(Q \cdot R_2)^{\frac{1}{n}}}{R_2} \quad (1)$$

Table 5 Values of equivalent circuit parameters

Sample	R_1 (Ω)	R_2 (Ω)	$P \cdot 10^{-6}$	n	C (μF*cm^{-2})
1	62	13516	129	0.70	61275
2	60	32675	39	0.87	339
3	72	26550	59	0.75	7010

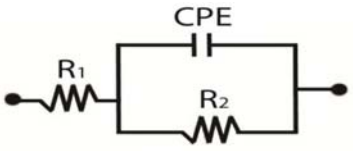

Figure 3 Equivalent electric circuit

3.3. Pull-off test

Before pull-off test the aluminium dolly was glued on tested surface using epoxy resin. After 24 h aging time, the pull-off test itself was carried out. Pull-off stress was applied continuously until de-adhesion of dolly from substrate supervened. Maximal pull-off stress was measured and recorded. Test setup can be seen in **Figure 4** [12]. The average values of test are illustrated at **Table 6**. There was significant difference in location and mechanism of final de-adhesion, which was further confirmed by light microscopy.

Table 6 Average values of pull-off test

Sample	Adhesion (MPa)	Location of de-adhesion
1	2.8	80 % substrate / coating, 20 % coating / glue
2	6.2	50 % epoxy / dolly, 50 % coating layer
3	8.4	80 % epoxy / dolly, 20 % coating / glue

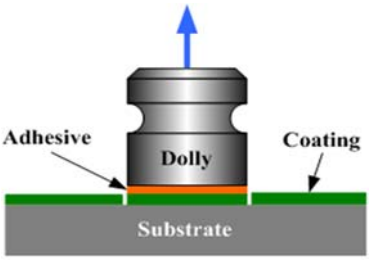

Figure 4 Pull-off test setup

4. CONCCLUSION

Three samples form 1.4404 (X2CrNiMo17-12-2, AISI 316L) steel were coated with hydroxyapatite particles using direct electrochemical synthesis method. It was found that electrochemical anodization process which was used for roughening of surface before synthesis effects final electrochemical properties highly. It was found out that anodization decreases the corrosion potential of studied samples and breakdown potentials, on the other hand, polarization resistance was increased nearly three times in comparison to sample with HA synthetized on as received state surface. EIS method confirmed assumption that passive layer has been removed during anodization which results in very low capacity of CPE which represents oxide layer on surface of the sample. HA particles on the surface effects the capacity only fractionally as they are more separate and don't create homogenous layer. Heat treatment of samples with synthetized HA can reinforce the particles adhesion to the substrate, which was proofed by pull off test, so heat treatment can be recommended to improve final properties of HA coatings.

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