Corrosion behaviour of hydroxyapatite (HAP) coated AISI 316Ti austenitic biomaterial

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Abstract. HAP bioactive coatings are widely applied to improve the bone response in orthopedic and dental stainless steels implants. Mechanical properties of the metallic implant are preserved and moreover, HAP improves the corrosion resistance of the biomaterial. This article deals with the corrosion resistance of AISI 316Ti austenitic biomaterial with electrochemically deposited HAP coating. Corrosion behaviour is evaluated on the bases of two independent methods - the electrochemical potentiodynamic polarization test and exposure immersion tests, both carried out in physiological solution (0.9 % NaCl) at the temperature 37 ± 0.5 °C. The microstructure and chemical composition of HAP coating is evaluated by SEM and EDX analysis. According to the results of the potentiodynamic test, the HAP coated biomaterial shows considerably higher corrosion resistance compared to that without the HAP coating. However, the corrosion losses and SEM analysis after the exposure test revealed severe disruption of the HAP coating and the stainless steel substrate started to corrode.

1 Introduction
Austenitic stainless steel implants are characterized by acceptable corrosion resistance, high strength and fracture toughness [1, 2], but their bonding ability to bone tissue is very low. In order to obtain bioactive and strong material, the formation of hydroxyapatite (HAP) ceramic coating on an austenitic implant with appropriate mechanical properties is considered a good approach [3]. Hydroxyapatite is a naturally occurring mineral form of calcium apatite with the formula Ca₅(PO₄)₃(OH) (usually written as Ca₁₀(PO₄)₆(OH)₂ to express that the crystal unit cell comprises two entities). HAP is chemically, structurally and biologically similar to the calcium phosphate minerals in biological hard tissue and it has ability to form a strong chemical bond with bone [4]. However, the mechanical weakness of the HAP limits its practical applications to those requiring little or no load-bearing locations. If used in the form of surface coating, mechanical properties of the metallic implant are preserved and moreover HAP improves the corrosion resistance of the biomaterial by forming a barrier against the dissolution of metal ions from the substrate at the same time as promoting its bone bonding ability [3, 5, 6]. Therefore, HAP coating is widely applied to improve the bone response in orthopedic and dental stainless steels implants.

There are several techniques to obtain HAP surface coating including plasma spraying [7], sol-gel method [8], pulse laser deposition [9], biomimetic methods [10], and electrochemical deposition [11, 12]. Currently, plasma spraying is the most widely used commercially available method for preparation of the HAP coatings [7, 9]. However, the plasma-sprayed HAP coatings indicate some deficiencies in the
clinical applications related to the low adherence on the metal surface and to the absence of consistency in morphology and crystallinity [13]. The electrochemical deposition (based on the reaction: \(10\text{Ca}^{2+} + 6\text{PO}_4^{3-} + 2\text{OH}^- \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\)) is one of the simplest and most widely used methods of HAP coating. Recently, this HAP coating method became technologically important for various biomedical applications [12]. Presented article is focused on an assessment of the corrosion resistance of AISI 316Ti austenitic biomaterial with electrochemically deposited HAP coating. Corrosion behavior is evaluated on the bases of two independent methods - the electrochemical potentiodynamic polarization test and exposure immersion tests, both carried out in physiological solution (0.9 % NaCl) at the temperature 37 ± 0.5 °C. The microstructure and chemical composition of HAP coating is evaluated by SEM and EDX analysis.

2 Material and methods

The experimental material AISI 316Ti is Cr-Ni-Mo austenitic stainless steel stabilised by titanium, with the chemical composition shown in table 1.

|      |    |    |    |    |
|------|----|----|----|----|
| Cr   | 16.50 |    |    |    |
| Ni   | 10.50 |    |    |    |
| Mo   | 2.12  |    |    |    |
| Mn   | 1.69  |    |    |    |
| Ti   | 0.41  |    |    |    |
| N    | 0.12  |    |    |    |
| C    | 0.04  |    |    |    |
| Si   | 0.043 |    |    |    |
| P    | 0.026 |    |    |    |
| S    | 0.002 |    |    |    |
| Fe   | balance |    |    |    |

Table 1. Chemical composition of AISI 316Ti stainless steel (wt. %)

HAP surface coating was obtained by electrochemical deposition (on the mechanically polished steel surface) in the electrolyte containing 0.042 M Ca(NO\(_3\)) and 0.025 M NH\(_4\)H\(_2\)PO\(_4\), pH=4.2. The deposition process proceeded at a stable cathode potential ranging from 2.25 to 3 V for 30 minutes at the room temperature. Microstructure of the obtained HAP coating was observed by SEM and its chemical composition was evaluated by EDX analysis. 0.9 % sodium chloride solution at the temperature of 37 ± 0.5 °C for simulation the internal environment of the human body was used as the corrosion environment for electrochemical potentiodynamic test and exposure immersion test.

The potentiodynamic polarization test was carried out in a three electrode cell of the measuring system (VoltaLab 10 with VSP unit). Polarization curves were obtained by the EC-LAB SOFT software. Potential between the sample and the electrolyte has been settled for 5 minutes before the polarization. Scan range was -0.3V – 0.9 V vs the open circuit potential and the scan rate was 1 mV/s. The measured surface of 1 cm\(^2\) area was rinsed with ethanol before measurement. The saturated calomel electrode (SCE) was applied as the reference electrode and platinum foil as a counter electrode. At least five experiment repeats were carried out for both HAP coated surface and the for the steel surface without HAP coating (HAP coating was removed by grinding). For each of both types of surface, the most appropriate curve was chosen and according it, the electrochemical parameters were determined. The exposure immersion test was carried out for three HAP coated rectangular-shaped specimens (it means steel substrate + Ca/P coating) with dimensions 75 mm x 30 mm x 4 mm. The specimens were degreased by ethanol and weighted out with accuracy ± 0.000 01 g. After 50-days exposure the specimens were washed by de-mineralized water and by ethanol, freely dried up and weighted out again [14]. The specimen surfaces were SEM observed after immersion test. Average corrosion rate (g.m\(^{-2}\).day\(^{-1}\)) was calculated from corrosion losses (g.m\(^{-2}\)) of the three tested specimens.

3 Experiment results and discussion

The SEM analysis revealed a non-uniform HAP-like coating with microstructure created by flake-like rounds shapes (figure 1).
EDX point analysis (figure 2) confirmed the high content of Ca and P, Ca/P ratio 1.35. This ratio differs from the ideal Ca/P one (1.67) considered by the authors [15] and it points to the defected HAP coating obtained by used experimental method.

Potentiodynamic polarization curves of the HAP coated surface and of the steel ground surface without HAP coating are shown and can be compared in figure 3. The electrochemical characteristics determined from the curves are listed in table 2. The pitting potentials ($E_p$) of both tested curves were determined as the potentials of a sudden, strong increase of current density, which denotes the breakdown of the passive film and the beginning of stable pit growth. The shift of the HAP coated steel $E_p$ to the more noble value ($E_p$ position shown by the blue arrow) and the lower passive current...
density compared to the steel without HAP coating point to the rise of the resistance to the pitting [16-18]. The corrosion potential ($E_{corr}$) and the corrosion current density ($i_{corr}$) as the additional electrochemical characteristics were determined according to the Tafel analysis of the curves [19, 20]. The $E_{corr}$ values of the both curves are similar, but the thermodynamic stability of HAP coated material is slightly higher (higher $E_{corr}$ value). The $i_{corr}$ values, which have the relationship to the kinetics of the corrosion process, also point to the higher corrosion resistance of the HAP coated steel (lower $i_{corr}$ value).

![Figure 3. Potentiodynamic polarization curves of the AISI 316Ti working electrode with/without HAP coating. The arrows point to the $E_p$ positions.](image)

**Table 2.** The electrochemical characteristics of the AISI 316Ti working electrode with/without HAP coating.

|                   | With HAP coating | Without HAP coating |
|-------------------|------------------|---------------------|
| $E_p$ (V)         | 0.385            | 0.191               |
| $E_{corr}$ (V)    | -0.277           | -0.288              |
| $i_{corr}$ (µA.cm$^{-2}$) | 0.776           | 1.402               |

As shown by SEM (figure 4), the HAP coating was markedly reduced during the long-term (50-days) exposure immersion test in 0.9 % NaCl solution at the temperature of 37 ± 0.5 °C. Moreover, the uncovered steel surface was locally attacked by the pitting. The observed phenomena were reflected in corrosion losses of the three tested samples and the average corrosion rate 0.128851 g.m$^{-2}$.day$^{-1}$ was calculated (standard deviation 0.0133). The authors [14] recorded the significantly lower average corrosion rate of the similar Cr-Ni-Mo stainless steel (without HAP) exposed to 0.9 % NaCl solution at the same temperature for the comparable time. Therefore, can be assumed that the reduction of HAP-like coating by the mechanical exfoliation during the immersion test (clearly visible in figure 4) contributed most to the higher corrosion loss of the tested AISI 316Ti biomaterial. It can be stated that the electrochemically deposited HAP-like coating did not show sufficient stability in the given long-term test conditions.
Figure 4. Reduced HAP coating after 50-days exposure immersion test. Stainless steel substrate is attacked by the pitting corrosion.

4 Conclusion
Based on the results of performed experiments can be concluded:

- The SEM and EDX analysis before the corrosion tests confirmed the non-uniform HAP-like coating with flake-like microstructure and with the Ca/P ratio 1.35.
- The corrosion losses and the SEM analysis after the exposure test showed that the HAP coating was severely disrupted upon exposure and the stainless steel substrate started to corrode locally by the pitting.
- According to the results of the electrochemical potentiodynamic test the HAP coated biomaterial had the considerably higher pitting potential, lower passive current density and also lower corrosion current density (i_corr) compared to that without the HAP coating. Thus, the stainless steel substrate (without the HAP coating) showed the lower corrosion resistance in this test.

It can be concluded that the experiments confirmed the HAP-like material properties close to commercially produced "young" hydroxyapatite-based materials. If this type of biomaterial comes into long-term contact with saline, it could lead to corrosion damage and thus to a reduction in the biocompatibility and the lifetime of the implant.

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