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ELECTRODEPOSITION OF A HYDROXYAPATITE COATING ON A BIOCOMPATIBLE NiTi ALLOY

ELEKTRODEPOZICIJA HIDROKSIAPATITA NA POVRŠINO BIOKOMPATIBILNE ZLITINE NiTi

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The electrodeposition method was used to apply a hydroxyapatite coating (HAP) on the surface of a biocompatible NiTi alloy with the aim to enhance the corrosion resistance of the substrate and therefore decrease the release of nickel ions from the surface of the alloy. A uniform inner layer of HAP was formed and overlaid by clusters of spherical and flake-like morphological structures. The HAP coating exhibited super-hydrophilic wetting properties compared to the moderate hydrophilicity of the NiTi alloy. The barrier properties of the HAP coating were investigated by using potentiodynamic measurements. The HAP coating significantly enhanced the corrosion resistance of the NiTi alloy and confirmed the effective barrier properties of the coating, which can be used to minimise the nickel release in biomedical applications.

Keywords: electrodeposition, hydroxyapatite, NiTi alloy, SEM

Zaščitna plast hidroksiapatita je bila z elektrodepozicijo nanešena na površino biokompatibilne zlitine NiTi z namenom izboljšanja korozijskih lastnosti substrata in zmanjšanja izločanja nikljevih ionov. Tvorila se je zvezna notranja plast hidroksiapatita, ki je bila prekrita s skupki okroglih in podolgovatih morfoloških struktur. Z meritvami statičnih kontaktnih kotov smo potrdili superhidrofilne lastnosti hidroksiapatitne prevleke v primerjavi z zmerno hidrofilnostjo osnovnega materiala. S potenciodinamskimi meritvami smo potrdili, da se z nanosom zaščitne plasti izrazito izboljša korozijska obstojnost zlitine NiTi in s tem predstavlja ustrezno bariero za preprečevanje izločanja nikljevih ionov v biomedicinskih aplikacijah.

Ključne besede: elektrodepozicija, hidroksiapatit, NiTi zlitina, SEM

1 INTRODUCTION

NiTi alloys are extensively used in biomedical applications due to their unique combination of properties such as superelasticity, shape-memory effect, good corrosion resistance and biocompatibility.[1] In spite of its outstanding properties, nickel release is still an important issue of concern in using NiTi alloys for biomedical applications.[2] Research efforts have been directed to the elimination of Ni release from the surface and therefore improving the corrosion resistance and as well as the biocompatibility of the implants.[1–5] Nickel is known for its diverse effects on human body, including allergic reactions and toxicity.[6] Studies on commercially available orthodontic wires showed increased Ni release rate with time of exposure and type of solution, indicating the need for better understanding the processes at the interface between the implant and biological environment.[2,7] Various surface modification techniques have been used including mechanical, chemical and thermal treatments, as well as bioactive coatings such as calcium phosphate coatings.[4,5,8,9] Hydroxyapatite coatings (HAP) are appropriate candidates for biocompatibility improvement since they offer an excellent surface for cell growth.[8,10] However, they cannot be used in load-bearing applications due to their poor mechanical properties. Different methods for the deposition of hydroxyapatite coatings are known, such as plasma spraying, electrophoretic deposition, sol-gel deposition, ion beam deposition and electrochemical deposition.[4,10–13] Electrochemical deposition has the advantage of uniform coating formation, low cost, room temperature and simple setup.[14]

In this paper, the electrodeposition of hydroxyapatite coating on the surface of NiTi alloy was conducted. The prepared coating was additionally alkaline treated. The surface morphology, wetting and structural properties were evaluated by using scanning electron microscopy (SEM), contact-angle measurements and X-ray diffraction (XRD). The barrier properties of the prepared coating were studied by potentiodynamic measurements in simulated physiological solution.

2 EXPERIMENTAL PART

Materials

Discs of 20 mm diameter and with a thickness of 1 mm from 55 % Ni-45 % Ti alloy (NiTi) were employed as a substrate.

NiTi alloy substrate preparation

Prior to the application of the coating, the NiTi alloy discs were ground mechanically with SiC emery paper

(up to 4000 grit), diamond polished (up to 1 μm), ultrasonically cleaned with ethanol and dried in warm air.

Coating preparation

The NiTi alloy discs were immersed in 1 M NaOH solution at 80 °C for 1 h, rinsed in distilled H_2O and dried in warm air. The electrodeposition was performed in a solution containing 0.1 M $Ca(NO_3)_2$ and 0.06 M $NH_4H_2PO_4$ at –2 V and pH = 6 for 30 min in a cell using two electrode-system, where NiTi alloy was employed as a cathode and a graphite rod as an anode. After the electrodeposition the samples were treated with 1 M NaOH solution at 80 °C for 1 h, rinsed in distilled H_2O and dried in warm air.

Scanning electron microscopy (SEM)

SEM analysis using FE-SEM JEOL JSM-6500F was employed to investigate the surface morphology of the coating which were sputtered with gold prior to imaging.

Contact-angle measurements

The static contact-angle measurements of water (W) on the nanoparticle coatings were performed using a Surface energy evaluation system (Advex Instruments s.r.o.) and repeated at least five times for each sample. The contact angles were determined by using Young-Laplace fitting. All the contact-angle measurements were carried out at 20 °C and ambient humidity.

X-ray diffraction

The composition and structural properties of the hydroxyapatite coating were investigated using a PANalyitical 3040 X-ray diffractometer fitted with a Cu-$K\alpha$ (λ = 0.154 nm) monochromated radiation source.

Electrochemical measurements

Electrochemical measurements were performed on HAP-coated NiTi alloy and bare NiTi alloy samples in a simulated physiological Hank's solution, containing 8 g/L NaCl, 0.40 g/L KCl, 0.35 g/L $NaHCO_3$, 0.25 g/L $NaH_2PO_4{\times}2H_2O$, 0.06 g/L $Na_2HPO_4{\times}2H_2O$, 0.19 g/L $CaCl_2{\times}2H_2O$, 0.41 g/L $MgCl_2{\times}6H_2O$, 0.06 g/L $MgSO_4{\times}7H_2O$ and 1 g/L glucose, at pH = 7.8 and 37 °C. All chemicals were from Merck, Darmstadt, Germany. The measurements were performed by using BioLogic Modular Research Grade Potentiostat/Galvanostat/FRA Model SP-300 with an EC-Lab Software and three-electrode flat corrosion cell, where working electrode (WE) was the investigated specimen, reference electrode (RE) was a saturated calomel electrode (SCE, 0.242 V vs. SHE) and the counter electrode (CE) was a platinum net. The potentiodynamic curves were recorded starting the measurement at 250 mV vs. SCE more negative than the OCP using a scan rate of 2 mV s^{-1}.

3 RESULTS AND DISCUSSION

The SEM microscopy was used to investigate the surface morphology and structure of electrodeposited HAP coatings on the surface of NiTi alloy. A typical micrograph of the HAP coating is presented in **Figure 1**. The coating surface exhibited different morphological characteristics from flake-like structure (**Figure 1b**) to sphere-like particles (**Figure 1c**) on the top of the compact HAP layer (**Figure 1d**). The mean size of spherical particles was under 1 μm compared to larger flake like particles. Both types of particles were randomly distri-

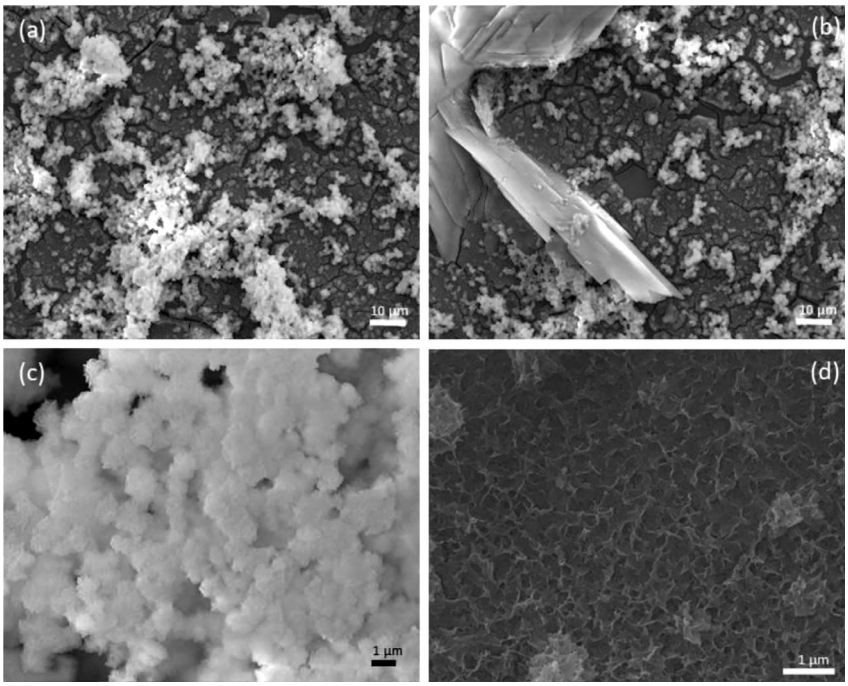

Figure 1: SEM images of surface morphology of HAP coating applied on the surface of NiTi alloy

buted and formed agglomerates over the bottom compact HAP layer.

To analyze the surface wettability, five static contact-angle measurements were performed with water (W) on different spots all over the samples and used to determine the average contact-angle values with an estimated error in the reading of $\theta° \pm 1.0°$. The corresponding static water contact angles are reported in **Table 1**. It was shown that both types of investigated surfaces exhibited hydrophilic characteristics. However, the electrodeposition with further NaOH treatment significantly reduced the water contact angle towards the complete wettability limit. In the electrodeposition process $CaHPO_4{\times}2H_4O$ (calcium hydrogenphosphate dihydrate) and $Ca_3(PO_4)_2$ (calcium phosphate) are formed and further transformed to more stable HAP after the NaOH treatment.[15]

Table 1: Static water contact angles (θ^W) of HAP coating on the surface of NiTi alloy and polished NiTi alloy

Substrate	Contact angle θ^w (°)
NiTi alloy	71
HAP coating on NiTi alloy	< 5

A typical XRD pattern of a HAP coating is presented in **Figure 2**. XRD results revealed the presence of crystalline HAP phases, which were consistent with the phases listed in the COD database (00-009-0432 and 01-072-1243). The main (h k l) indices for HAP: (002), (102), (210), (211), (112), (202), (220), (221) and (222) are indicated in **Figure 2**.

Figure 3 shows the potentiodynamic behaviour of HAP coated NiTi alloy and bare NiTi alloy in a simulated physiological Hank's solution. The polarization and the passivation behaviour of tested material after surface modification was studied. The corrosion potential (E_{corr}) for the NiTi alloy in Hank's solution was approximately –173 mV vs. SCE and for the HAP coated NiTi alloy was –270 mV vs. SCE. Following the Tafel region, the both studied materials exhibited a broad passive region.

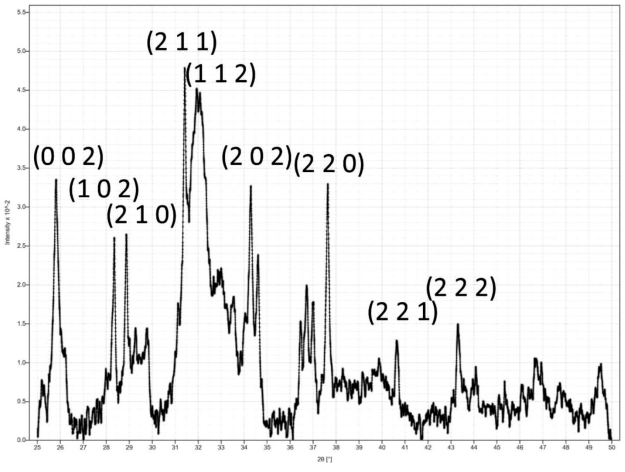

Figure 2: XRD diffractogram showing the HAP phases present in the coating

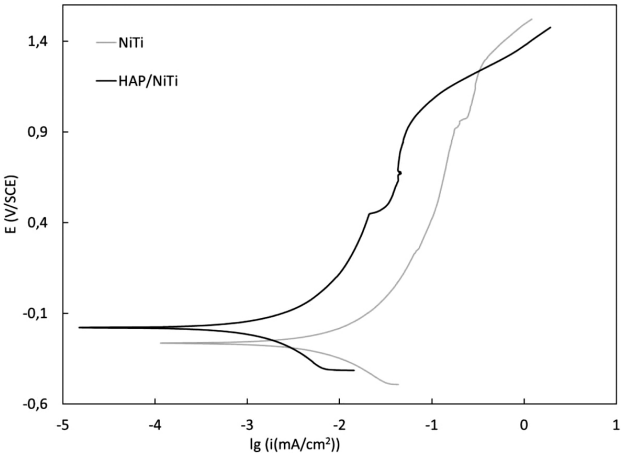

Figure 3: Potentiodynamic curves for HAP-coated NiTi alloy and bare NiTi substrate in a simulated physiological Hank's solution

The passivation region for the HAP coated NiTi specimen was significantly moved to the lower corrosion-current densities compared to bare NiTi alloy, indicating the efficient barrier properties of the coating. The application of HAP coating significantly enhanced corrosion resistance of NiTi alloy which was confirmed by the corrosion parameters calculated from the potentiodynamic measurements. The results showed significantly decreased corrosion-current densities and corrosion rate as well as increased polarisation resistances of the specimens coated with HAP coating compared to bare NiTi alloy (**Table 2**).

Table 2: Corrosion parameters calculated from potentiodynamic measurements

Material	$E(I{=}0)$ (mV)	I_{corr} (μA)	R_p (kΩ)	v_{corr} (μm/year)
NiTi alloy	–270	5.34	8.4	48
HAP-coated NiTi alloy	–173	0.62	35.8	6

4 CONCLUSIONS

The hydroxyapatite coating was successfully applied on the surface of NiTi alloy by the electrodeposition method. SEM evaluation revealed uniform inner layer of HAP which was overlaid by smaller spherical and larger flake-like morphological structures. XRD evaluation revealed the presence of crystalline HAP phases. Wetting properties evaluation showed that the electrodeposition and further treatment with NaOH significantly reduced the water contact angles of HAP coating towards the complete wettability limit compared to moderate hydrophilicity of NiTi alloy. Corrosion study showed that HAP coating significantly enhanced corrosion resistance of NiTi alloy and confirmed the effective barrier properties of the applied coating, which is critical for biomedical applications.

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