



The potential-assisted deposition as valuable tool for producing functional apatite coatings on metallic materials



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ABSTRACT

Nitinol was coated with hydroxyapatite (HA) by the two-step method that includes electrodeposition of the calcium phosphate (brushite) film, as a precursor for the HA deposition, which is the second reaction step.

This work concerns direct comparison of structural and barrier properties of the HA coatings produced by the phase transformation of brushite to HA in (i) an alkaline solution (NaOH) and (ii) a simulated body fluid solution (SBF).

Chemical composition and morphology of the surface films were characterized using field emission scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS).

The corrosion resistance was determined using *in situ* method of electrochemical impedance spectroscopy (EIS), under *in vitro* conditions, in order to optimize the production of bioactive HA coatings on metallic (Nitinol) implants for medical applications.

The combination of advantages of the electrodeposition of the HA precursor film on the Nitinol surface and the treatment in an SBF solution, under *in vitro* conditions, has the potential to provide the HA coatings with the structural and microstructural homogeneity, excellent barrier properties (corrosion resistance) as well as bioactivity.

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1. Introduction

Nitinol, the titanium-nickel alloy, has been widely used in the field of dentistry and orthopedic surgery owing to its unique properties, such as shape memory effect, superelasticity, and high damping capacity [1–3]. Nitinol possesses high corrosion resistance in physiological solutions caused by the spontaneously formed film of TiO₂ [3,4]. However, in a long-term contact with aggressive body fluids Nitinol corrodes by releasing Ni²⁺ ions that act as an allergen for many people [5]. Thus, to prevent the unwanted nickel dissolution, the surface properties of Nitinol have been modified using different coatings or other surface treatments [1,6–8]. Additionally, the bone formation is not induced on the unmodified surface of Nitinol and the integration of its bare surface with bone tissues takes generally several months [9–11]. On the other hand, HA is recognized as biocompatible and bioactive material due to its similar

chemical and crystallographic structure to living bone and ability to accelerate bone ingrowth [11,12].

Hence, the formation of the HA coatings on Nitinol implant material combines benefits of the favorable properties of Nitinol and HA [13,14]. The HA coatings enhance implant surface bioactivity, accelerate attachment to the surface of implant during the early stage after implantation [13,15]. Various methods have been used for the formation of the HA coatings on titanium/titanium alloys [16–18]: plasma spraying, thermal spraying, vapor deposition, polymeric route, electrocrystallization, biomimetic processes, electrophoretic deposition, sol-gel method, and sputtering deposition. Plasma-spraying, as a state-of-art and an extensively used commercial method, results in formation of unwanted phases (Ca₃(PO₄)₂, CaO, etc.) due to HA decomposition during the high-temperature plasma spraying process [19]. Presence of these phases induces a higher dissolution rate than crystalline HA in aqueous solutions [19].

The electrochemically assisted deposition method has gained much attention due to its versatility (ability to coat porous, geometrically complex-shaped objects) at low temperatures and using cost effectiveness [20–25]. Additionally, the thickness, chemical

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composition and morphology of the coatings can be well controlled through adequate conditions of the process [1,17]. The potential-assisted deposition of the calcium phosphate (CaP) coatings includes an electrochemical reaction (hydrogen evolution from phosphate ions present in the deposition solution), an acid-base reaction (consecutive pH-dependent transitions among phosphates) and a precipitation reaction (deposition of apatite coatings) [25,26]. Recently, the influence of the deposition parameters (current densities, pH, potential) on the phase composition, crystallite domain size and the morphology of the CaP precursor film [27] as well as the CaP (brushite) film nucleation-electrocrystallization on various metallic implant materials has been investigated [28–30]. It was found that the nucleation of brushite on Nitinol from the deposition solution under potentiostatic conditions occurs via 3D progressive nucleation under diffusion control [30].

In this work, the conversion mechanism of the precursor film to the HA coating upon treatment in an alkaline solution and in an SBF solution on Nitinol was investigated using *in situ* (potentiodynamic polarization, EIS) and *ex situ* (SEM/EDS, XRD, XPS) techniques. The aim was to understand deeper the deposition process in producing bioactive HA coatings on metallic implant materials. The two-step procedure of the brushite film fabrication on metallic implant substrates followed by the conversion to the HA coating in NaOH and SBF solutions is well documented in the existing literature [23–27]. In addition, XRD characterization has shown the formation of extraneous phases, like CaO/Ca(OH)₂, besides HA under NaOH treatment [31,32]. The presence of those compounds in the coated implant materials can yield unwanted side effects in terms of implant integration in the human body. Thus, the novelty of this work was to explore the barrier properties and the corrosion resistance of the HA coated Nitinol electrodes prepared by the two treatments (NaOH and SBF). Electrochemical/corrosion measurements were performed *in situ*, under *in vitro* conditions of real implant applications using EIS.

2. Experimental

2.1. Materials and electrochemical reactor

The Nitinol foil (Alfa Aesar, with the wt% content of: 55.82 Ni, ≤ 0.05 C, ≤ 0.05 O, ≤ 0.20 other metal impurities, and balance Ti) was cut into 0.38 mm-thick disks with 13 mm diameter. Circular shaped Nitinol samples were abraded with SiC papers of 240–1200 grit, ultrasonically cleaned with acetone and redistilled water and were used as working electrodes. A standard three electrode cell (PAR, Corrosion cell system, model K47) was used for electrochemical measurements. The counter electrode consisted of two graphite rods and the reference electrode, to which all potentials in the paper are referred, was an Ag | AgCl, 3.0 mol dm⁻³ KCl ($E = 0.208$ V vs. standard hydrogen electrode, Metrohm Autolab).

2.2. Electrodeposition of the calcium phosphate film on Nitinol

The electrodeposition of the calcium phosphate film was carried out potentiostatically at -1.15 V for 2 hours. The deposition conditions were determined from the potentiodynamic polarization curve recorded at scan rate of 10 mV s⁻¹. The electrodeposition solution was 0.1 mol dm⁻³ with aspect to Ca(NO₃)₂ (p.a., ≥ 99.2%, Lach-Ner) and 0.06 mol dm⁻³ with aspect to NH₄H₂PO₄ (p.a., ≥ 99.7%, Lach-Ner). The pH value of solution was 5 (adjusted with 0.5 M HNO₃). During the electrodeposition, the solution was stirred to avoid concentration gradients of Ca²⁺ and H₂PO₄²⁻ ions in the deposition process. Potentiostatic deposition governs the formation of a single morphology across the whole substrate. The formation of a uniform morphology requires a critical energy for

nucleation [33] in potentiostatic deposition. Hence, by controlling the applied potential deposits with uniform and desired morphologies can be obtained using potentiostatic deposition. Additionally, the usage of two-step method strongly benefits in production of coatings with desired controllable structure and composition [21,23,24].

The conversion of the calcium phosphate films to the hydroxy-apatite coatings was performed in two ways; one group of samples was treated in the 1 M NaOH solution (p.a., ≥ 98%, T.T.T. d.o.o.) for 1 h at 80 °C and subsequently rinsed in redistilled water and dried in air. The other group was immersed for 7 days in an SBF—the Hanks' solution, which pH value was adjusted to pH = 7.4. Its content was: 8 g dm⁻³ NaCl (p.a., ≥ 99.5%, Alkaloid) 0.4 g dm⁻³ KCl (p.a., ≥ 99.5%, Kemika), 0.35 g dm⁻³ NaHCO₃ (p.a., ≥ 99.5%, Kemika), 0.06 g dm⁻³ MgSO₄·7H₂O (p.a., ≥ 99%, Fluka), 0.19 g dm⁻³ CaCl₂·2H₂O (p.a., ≥ 99%, Fluka), 0.06 g dm⁻³ Na₂HPO₄·2H₂O (p.a., ≥ 98%, Kemika), 0.25 g dm⁻³ NaH₂PO₄ (p.a., ≥ 99%, Fluka), 1 g dm⁻³ C₆H₁₂O₆ (p.a., ≥ 99%, Kemika) and 0.19 g dm⁻³ MgCl₂ (p.a., ≥ 98%, Fluka). The whole amount of a solution was replaced every 48 hours.

2.3. Characterization of calcium phosphate coatings formed on Nitinol by the electrochemically assisted deposition method

The coatings formed on Nitinol were characterized using: X-ray photoelectron spectroscopy (XPS), X-ray diffraction analysis (XRD) field emission scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

The XPS spectra were recorded under UHV conditions (typical pressure in the 10⁻⁷ Pa range) in a SPECS XPS system with the Phoibos MCD 100 electron analyzer and monochromatized Al K_α X-rays of 1486.74 eV. For the pass energy of 10 eV used in the present study, the total energy resolution was around 0.8 eV. All spectra were simulated with several sets of mixed Gaussian-Lorentzian functions with Shirley background subtraction. The relative fraction of several chemical components was determined from the deconvoluted spectra of the main peaks. Phase identification was based on XRD using a D4 Endeavor, Bruker AXS diffractometer with a Sol-X energy-dispersive detector within the angular range 2θ from 3 to 70°, a step size of 0.02° and a collection time of 3 s. The microstructure and morphology of the coatings on Nitinol substrates were determined by field emission SEM using Jeol Ltd. FE SEM, model JSM-7000F. An elemental analysis was performed by EDS using Oxford Instruments Ltd. EDS/INCA 350 in addition to SEM.

2.4. Barrier and corrosion properties of calcium phosphate coatings formed by the electrochemically assisted deposition method

The barrier properties and corrosion resistance of coated Nitinol samples were tested in the Hanks' solution using electrochemical impedance spectroscopy (EIS). The corrosion behavior of coated Nitinol substrates was studied in the Hanks' solution at 37 °C performed at the open circuit potential, E_{OCP} in the frequency range from 10⁵ to 10⁻³ Hz with an *ac* voltage amplitude of ±5 mV using a Solartron frequency response analyzer SI 1255 and Solartron electrochemical interface 1287. Impedance measurements were performed after 1 h of stabilization at E_{OCP} . The experimental data were fitted using the complex non-linear least squares (CNLS) fit analysis [34] software ZView®, and values of the elements of the proposed equivalent circuit were derived with χ^2 values less than 2 × 10⁻³ and relative error values below 5%.

3. Results and discussion

The HA coatings were deposited on Nitinol substrates by the electrochemically assisted method. A first step was cathodic

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