



Influence of preparation methods on the properties of self-assembled films of octadecylphosphonate on Nitinol: XPS and EIS studies

Ingrid Milošev^{a,*}, Mirjana Metikoš-Huković^b, Željka Petrović^b

^a Jožef Stefan Institute, Department of Physical and Organic Chemistry, Jamova 39, SI-1000 Ljubljana, Slovenia

^b Faculty of Chemistry and Chemical Technology, Department of Electrochemistry, Savska 16, 10000 Zagreb, Croatia

ARTICLE INFO

Article history:

Received 2 April 2012

Received in revised form 12 July 2012

Accepted 7 August 2012

Available online 18 August 2012

Keywords:

Nitinol

Octadecylphosphonic acid

Self-assembling

X-ray photoelectron spectroscopy

Simulated physiological solution

ABSTRACT

The NiTi alloy (Nitinol), with its favorable micro-structured properties and self-passivity (resembling that of pure Ti) is used as an implant material for arterial stents and orthodontic wires. During the long term contact of the alloy with aggressive environment of human body, corrosion by releasing Ni²⁺ ions can occur. Thus, the usefulness of such material can be dramatically enhanced if its interface structure and surface chemistry are controlled. The octadecylphosphonate interface (ODP) synthesis, which involves a self-assembled covalently (monodentate type) bonded film of octadecylphosphonic acid (ODPA) on the oxide covered NiTi surface, produces stable and corrosion resistant interfaces. This paper introduces integrated approach to the characterization of the NiTi/ODP interfacial architecture as well as the structure of the electrified ODP/solution interface using high-resolution XPS and in situ EIS measurements. The main focus of this work was to determine the influence of the ODPA deposition method (spray and immersion) on the depth-dependent structural characteristics and orientation of ODPA molecules in the surface film by means of angle resolved XPS. Mechanically strong and chemically stable NiTi/phosphonate interfaces have the potential for their successful implementation in stent technologies.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Nitinol (NiTi) is a nearly equiatomic nickel–titanium alloy with favorable material properties such as shape memory, superelasticity (the martensite–austenite crystal structure change) and favorable biocompatibility [1–3]. The martensite form of NiTi is soft and easily deformable, which makes it a valuable implant material for production of arterial stents and orthodontic wires [1].

The successful use of NiTi and other metal alloys as implant materials is crucially dependant on its corrosion resistance to body fluids [4]. Generally, corrosion processes, which occur on the implant material surface in direct contact with body fluids, are responsible for limited biocompatibility and an appearance of undesirable reactions in implant-adjacent tissues. One of the possible consequences of corrosion processes on the NiTi surface is a release of Ni ions from the bulk material into surrounding tissues that can cause harmful local and systemic effects. Ni ions are well known sources of allergy and toxicity for human body [3,5,6]. Therefore, there is a need for a detailed understanding of electrochemical (corrosion) processes occurring at the NiTi/physiological solution interface as well as developing corrosion resistant interfaces for further bonding of biomolecules.

Self-assembly of organic molecules on metal and inorganic substrates is a powerful approach for modifying their surface chemistry [7]. The well accepted standard interface is the gold/thiolate [8] and copper/thiolate interfaces [9]. Interfaces of self-assembled long-chain carboxylic and phosphonic acid films on metals and oxide covered metals are mechanically and chemically stable under ambient conditions [10]. Additionally, phosphonic acid-based films offer high hydrolytic stability under aggressive physiological conditions providing long-term corrosion resistance [11]. Phosphonic acids are known for low toxicity in mammals [12] and are routinely used in the treatment for metabolic disorders of the bone (Paget's disease) and tumor induced hypocalcaemia [13]. The assembly process is quite practical as the phosphonic acid adsorption occurs on oxide/hydroxide covered metal surfaces (TiO₂ [14–16], SiO₂ [17], α-Al₂O₃ [18,19], NiO [20]) via an acid–base condensation mechanism [17]. The adhesion of a phosphonic acid film on metal and metal alloys is greatly enhanced by the conversion of surface-adsorbed phosphonic acid to surface-bond phosphonate during thermal annealing following self-assembled film formation [17].

Following the line of investigations of phosphonate self-assembled layers on TiO₂ covered Ti [14,21] and Ti-alloy surfaces [22,23] in the present work octadecylphosphonic acid (ODPA) was assembled on the oxide surface of NiTi. It is noteworthy to stress that although NiTi is near-equiatomic nickel–titanium alloy, the surface natural film (spontaneously formed in air or aqueous solution) consists mainly of TiO₂ because oxidation of Ti is thermodynamically more

* Corresponding author at: Jožef Stefan Institute, Department of Physical and Organic Chemistry, Jamova c. 31, SI-1000 Ljubljana, Slovenia. Tel.: +386 1 4773 452; fax: +386 1 4773 822.

E-mail address: ingrid.milosev@ijs.si (I. Milošev).

favorable than that of Ni [2,4]. Spontaneously formed oxide is chemically resistant, however, in long term contact with aggressive body fluids Nitinol alloy may corrode. Thus, NiTi surfaces were modified with self-assembled films of ODPA via two different methods: (i) aerosol spraying and (ii) the immersion method in order to improve the corrosion resistance to enhance biocompatibility of this material under physiological conditions.

It was our goal to reveal the depth structure, thickness and composition of self-assembled octadecylphosphonate (ODP) film in dependence of deposition method. Structural and chemical characteristics of the interfaces in the system NiTi/surface film/physiological solution were investigated using high-resolution angle resolved X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) measurements.

2. Material and methods

2.1. Material, preparation and treatment

The following chemicals were used as received: octadecylphosphonic acid (ODPA, Alfa Aesar, 95%), tetrahydrofuran (THF, J. T. Baker, p.a.), and isopropyl alcohol (Fluka, p.a.). Nitinol foil (NiTi, Alfa Aesar, wt.% Ni 55.82, Ti balance, C \leq 0.05, O \leq 0.05, total all others metal impurities \leq 0.20) was cut into 0.38 mm-thick discs 13 mm in diameter.

Circular shape NiTi samples were polished using 240–1200 grit SiC paper followed by an alumina suspensions (particle size: 1, 0.3 and 0.05 μm). Samples were ultrasonically cleaned with acetone and redistilled water and degreased in isopropyl alcohol. Freshly prepared samples were subsequently stored in a regular air-convection oven at 90 °C for 30 min to produce a hydroxylated oxide surface [24].

Self-assembled ODP films, from 0.5 mM solution in dry THF, on the oxide surface of NiTi were effected by two simple and reliable procedures so called “aerosol spray method” and “immersion method”. In the first case a nonaqueous solution of ODPA was aerosol sprayed (using TLC sprayer, Nalgene®) onto NiTi samples, while in the second case NiTi samples were dipped in the same nonaqueous solution of ODPA for 24 h at ambient temperature and pressure. However, adhesion of ODPA films to the substrate was weak and the surface films were easily removed by solvent rinse. Heating the material, at 120 °C in a regular air-convection oven for 5.5 and 24 h, transforms the phosphonic acid intermediate to a phosphonate one, which is strongly chemically bonded on the surface and resists removal by solvent washing and mechanical “peel” test [24,25]. The modified NiTi samples by octadecylphosphonate are termed in the text as NiTi/ODP_{imm} and NiTi/ODP_{spray}, respectively.

2.2. Electrochemical measurements

All measurements were performed in simulated physiological solution with the following composition: 8 g/L NaCl, 0.4 g/L KCl, 0.25 g/L NaH₂PO₄·2H₂O, 0.35 g/L NaHCO₃, 0.06 g/L Na₂HPO₄·2H₂O, 0.19 g/L CaCl₂·2H₂O, 0.4 g/L MgCl₂·6H₂O, 0.06 g/L MgSO₄·7H₂O, and 1 g/L glucose. This solution is known as Hanks balanced salt solution. Measurements were carried out in a standard three electrode cell (PAR, Corrosion Cell System, Model K47) at the room temperature using a Solartron Potentiostat/Galvanostat (Model 1287) with FRA 1260. The counter electrode consisted of two graphite rods. The reference electrode, to which all potentials in the paper are referred, was an Ag/AgCl, 3.0 mol dm⁻³ KCl ($E = 0.210$ V vs. standard hydrogen electrode (SHE)). The NiTi substrates modified with ODP films served as working electrodes; the area exposed to the electrolyte was 1 cm². Impedance measurements were performed at open circuit potential with an a.c. voltage amplitude of ± 5 mV in the frequency range 1×10^4 – 5×10^{-3} Hz. After 1 h of stabilization in Hanks solution, impedance data were collected and fitted using the complex non-linear least squares (CNLS) fit analysis [26] utilizing commercial

ZView® software. The fitting quality was evaluated by chi-squared and relative error values of calculated EEC parameters, which were of the order of 10^{-4} and below 5%, respectively, indicating that the data adjusted well to the proposed equivalent circuit.

The anodic polarization curves were recorded on NiTi electrodes covered with spontaneously formed oxide and ODP film in the potential range between -0.1 and 1.3 V with the sweep rate 10 mV/s.

2.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed with a TFA Physical Electronics Inc. spectrometer using non- and monochromatized Al K α radiation (1486.6 eV) and a hemispherical analyzer. Monochromatized radiation used for high-resolution spectra yielded a resolution of 0.6 eV, as measured on an Ag 3d_{5/2} peak. These spectra were used for differentiation between various species, i.e. to study the chemical environment, whereas spectra obtained using non-monochromatized variation were used for the quantification of chemical composition. The energy resolution was 0.5 eV. Survey scan spectra were recorded at a pass energy of 187.85 eV, whereas individual high-resolution spectra were taken at a pass energy of 23.5 eV with an energy step of 0.1 eV. The analyzed area during XPS analysis was 0.4 mm². The energy scale was calibrated by referencing the main hydrocarbon peak set at a binding energy of 285.0 eV. Depth profiling was performed for the NiTi/ODP_{spray} sample. An Ar⁺ ion beam with an energy level of 3 keV and a raster of 4 mm \times 4 mm was used for sputtering. This resulted in a sputtering rate of 1.7 nm/min relative to the SiO₂ standard [27].

Angle-resolved XPS (AR-XPS) measurements were conducted at different take-off angles (detection angles), namely 15, 30, 45, 60 and 75° with respect to the surface plain to obtain depth-dependent information on the composition and structure of the layers. The analyzed depth, defined as the depth from which 90% of the XPS signal is originating, increases with increasing angle. Thus at small angles the information closer to the surface (outer interface) is provided, whereas at large angles the information closer to the bulk (inner interface) is provided [28,29]. The analyzed depth was up to 10 nm. XPS spectra were background subtracted, using the non-linear, iterative Shirley method [28,29]. The fitting procedure allowed signals to be evaluated by determining the peak position, height, width and Gaussian/Lorentzian ratio [30]. For fixed border conditions, during deconvolution procedure all peak parameters except height were kept constant, i.e. within defined limits.

The spectra recorded on NiTi electrode covered with ODP layers prepared by immersion or by spraying were evaluated using parameters of standard peaks (Table 1) [31–33]. During the deconvolution of the spectra, all peak parameters, except height, were kept constant. Border conditions were also kept constant (Table 1). The parameters for metal peaks (Ti and Ni) were recorded on sputter-cleaned substrates (no oxide present). The Ti 2p_{3/2} peak for metal state is centered at 454.4 eV, and that for Ni metal shows a main 2p_{3/2} peak at 852.9 eV and a satellite (sat.) \sim 6.5 eV above it [31–33]. As a standard for TiO₂, XPS spectrum for Ti thermally oxidized for 1 h in an oxygen atmosphere at 450 °C was recorded [32]. Ti-suboxides (TiO and Ti₂O₃) were fitted using synthetic spectra obtained as the difference between standard spectra recorded for thermally oxidized substrates and spectra recorded for electrode covered with ODP layers [32]. Ni(II) oxide shows a complex structure including three peaks in the 2p_{3/2} region at 854.6, 856.3, and 861.5 eV [34]. The former two peaks have been attributed to multiplet splitting (m.s.), whereas the latter peak has been explained by monopole charge transfer (c.t.) processes accompanying ionization of the Ni 2p electrons [35].

The high-resolution spectra of oxygen, carbon and phosphorus were deconvoluted using component peaks in a way to reflect possible bonding of the ODP layer with the oxide layer formed at the metal surface and the orientation of species within the ODP layer.

Download English Version:

<https://daneshyari.com/en/article/10615042>

Download Persian Version:

<https://daneshyari.com/article/10615042>

[Daneshyari.com](https://daneshyari.com)