



Study of the formation process and the characteristics of tantalum layers electrodeposited on Nitinol plates in the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid

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ABSTRACT

Thanks to excellent mechanical and biochemical properties, the nickel–titanium shape memory alloy (Nitinol) constitutes an increasingly praised platform material in dental, cardiovascular and orthopedic biomedical devices. In order to strengthen their protective abilities toward corrosion, to reinforce their biocompatibility and to confer them specific osseointegrative capacities, Nitinol plates are covered with a thin tantalum layer by electrodeposition in the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid. XPS and SEM/EDX analyses highlight the chemical and morphological characteristics of the deposits: notably, these present an intrinsic dimpled nanometric structuration which is particularly remarkable considering the “soft” experimental conditions and very interesting for fundamental and applied bioactive perspectives. The present study investigates the specific and synergic effects of the Ni occurrence on the surface of the Nitinol substrates, the presence of fluorine species in the working bath, and the electrodeposition duration on the resulting formation process, morphology and chemical composition of the tantalum coating. Finally, samples are submitted to electrochemical characterizations and *in vitro* hydroxyapatite growth tests for a primary assessment of their corrosion resistance and osseoinductive features.

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1. Introduction

Among the numerous kinds of shape memory alloys developed during the last 80 years for their intrinsic mechanical properties (one- and two-way shape memory phenomena, superthermoelasticity, rubber-like effect, high-damping capacity) and the number of potential application fields, the particular case of the nickel–titanium alloy constitutes one of the most promising material [1,2]. Discovered in the early 1960s by Buehler *et al.* and further known as “Nitinol” – standing for nickel–titanium (composition) and the Naval Ordnance Laboratory of White Oak, Maryland (place of discovery) [3], this metallic alloy can nowadays be routinely prepared under various forms (wire, bar, tubing, sheet, ribbon, strip). Depending on initial stoichiometry of Ni and Ti, presence of impurities (oxygen, carbon, nitrogen) and thermal/mechanical processing conditions and treatments during casting and shape setting processes, it can present variable and highly specific mechanical, chemical and morphological characteristics [4]. Thanks to the wide

variety of its fundamental features and forces, Nitinol has quickly found an echo in numbers of advanced industrial domains – aeronautics, robotics, sensors and actuators, *etc.* – as well for many usual devices: cell-phone technology, watchmaking, sportive equipment, and even more common objects such as eyeglass frames or underwire bras [1]. But its main interest lies in the development of biomaterials for medical instruments (surgical scissors, graspers and pliers, probes) and implants in dentistry (wires, braces, screws), orthopedics (prostheses, pins, rods, plates) and cardiology (stents, heart valves) [1,2,5–8].

In this context, the main challenge concerns the biocompatibility of the nickel–titanium alloy: if titanium is widely recognized as highly biocompatible and resistant to corrosion (especially under its oxidized form TiO_2), nickel as element (usually present for ~55% in Nitinol) can easily corrode in Ni^+ and Ni^{2+} cations which have a potentially high level of toxicity, present an allergen nature and are often considered as possibly carcinogen [1,5,7,8]. The biomechanical performance of bare Nitinol, mainly dependent on the host reaction induced by the material and its degradation in the body environment, is thus subject to many investigations and assessments which turn out to be very controversial: while some authors praise its good biocompatibility and its protective nature against corrosion phenomena, others are more careful and point

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out problems of poor bioactivity (for instance weak osseointegrative properties of several orthopedic devices), nickel leakage in human body, and implant instability – not to say long-term loosening [1,2,5,7–11]. In any case, Nitinol surface stability is the central point of those issues, and its direct control is really crucial for its further exploitation as biomaterial. Different methodologies have been pursued with this aim: some direct modifications of the oxide surface layer through mechanical, chemical and electrochemical processes (etching, sandblasting, polishing, electropolishing, anodization), heat treatments (in boiling water, air, inert gases), and surface implantations (with Ar^+ , N^+ , oxygen, carbon, etc.) have proved to act positively on the corrosion resistance, the hindering of nickel release, and the promotion of interactions with body cells and proteins [12–24]. Another convenient approach consists in the covering of Nitinol surface with organic and inorganic coatings (organosilanes and organophosphonic acids SAMs, calcium phosphate and hydroxyapatite layers, polymers and polyelectrolyte films): this strategy implies thus the creation of a barrier interface protecting the material against the potentially aggressive external conditions and preventing its damaging in the form of a nickel release from the implant to the body environment [17,24–33].

In the particular framework of orthopedic metallic biomaterials, the design of corrosion protective and osseointegrative substrates must be achieved in a synergic way. For this purpose, surface modification of Nitinol by a thin tantalum layer constitutes one of the most promising and successful methodology lately developed. Tantalum (Ta) is known for many years as a very effective material for applied biomedical perspectives owing to its total inertia toward human body, its high chemical stability and corrosion resistance, its excellent global biocompatibility and bioactivity, and also its good radiopacity [34–37]. Its use has been reported in numerous dental applications, fractures, nerves and soft tissues repairing devices, and electrodes for pacemakers [34]. However, exploitation of Ta as bulk material is restricted due to its high density and cost. The preparation of (ultra) thin Ta coatings on platform materials is thus generally preferred, for which different methods can be considered: radio frequency sputtering, chemical vapor deposition, electrostatic spray deposition, ion implantation, sol-gel coating, and electrodeposition [38–45]. This last technique has been selected here as it permits a high level of control on the composition, thickness and morphology of the deposited layer.

Originally, electrodeposition of refractory metals such as Ta had to be performed in high temperature molten salts, but their utilization has been progressively limited because of strong economic and technical considerations. In the presence of oxide ions, a loss in the current efficiency of the electrolysis process was noticed because of the formation of oxyfluorides which are then reduced in unstable Ta subhalides, thus the working baths had to be completely free of oxygen contaminations to lead to current efficiencies close to unity. Moreover, corrosion problems on the substrates are known to occur quicker at very high temperatures – between 650 and 850 °C for Ta electrodeposition [46–48]. Recently, the use of ionic liquid media has been specifically pointed out for their advantages in terms of electrical conductivity, thermal stability, low vapor pressures and especially large electrochemical windows. In the framework of Ta electrodeposition, they also specifically allow a practical elaboration in more moderate conditions [48,49]. Several groups, including ours, have studied and commented the electrodeposition of tantalum from halide salts (TaCl_5 and mainly TaF_5) on platinum, gold, titanium, and Nitinol substrates, in various ionic liquids (generally imidazolium- and pyrrolidinium-based compounds) and at working temperatures between 25 and 200 °C [44,45,48,50–55]. Concerning the practical conditions of electrodeposition, different electrochemical parameters have been tested.

In previous papers, corresponding analyses performed with titanium substrates have shown that the Ta layers prepared by cyclic voltammetry and potentiostatic experiments were showing very poor adherence features. However, the use of a galvanostatic deposition method (at constant current) led to very thin, homogeneous and adherent Ta films. Effects of both current density and deposition time were studied and pointed out as very important in finding a compromise between a good homogeneity of the tantalum coating and a reasonable experimental duration. Optimal values of $-100 \mu\text{A}/\text{cm}^2$ and 1 h at ambient temperature were found to generate the best quality Ta layers in terms of adherence, homogeneity and barrier effect [45,52].

The present paper reports the preparation on Nitinol plates of tantalum electrodeposits at ambient temperature, using an ionic liquid as solvent. Experimental conditions of electrodeposition are taken back from our previous works on pure titanium substrates [45,52]. Their particular impact, and specifically the influence of the electrodeposition time on the coatings chemical composition and morphology, is analyzed and discussed considering the particular case of the Nitinol base platform with its high nickel ratio. An evaluation of the degree of passivation and protection against corrosion brought by the Ta layer on Nitinol is also assessed through electrochemical characterizations. Finally, *in vitro* growth of hydroxyapatite crystals (inorganic part of the bone matrix) is performed on the Ta-covered substrates as a primary evaluation of the result of the surface modification on the osseointegrative properties of the material. Techniques used for the different analyses are X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), peeling tests, free potential and polarization curves.

2. Experimental

2.1. Products and reagents

Following solvents and chemicals are used as received for the pretreatment of the Nitinol samples and the electrodeposition process of tantalum: absolute ethanol (VWR Prolabo), acetone (Chem-Lab, 99+%), ultra-pure water (18 M Ω cm), tantalum fluoride (Aldrich, 98%), and lithium fluoride (Sigma-Aldrich, $\geq 99\%$). Prior to its utilization, the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (IoLiTec, 99%) is dried overnight at 100 °C under 25 mbar in order to eliminate residual traces of water. The simulating body fluid (SBF) employed for the tests of *in vitro* growth of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is prepared with sodium chloride (Acros, 99.5%), potassium chloride (Aldrich, $\geq 99.0\%$), magnesium hexahydrate chloride (Acros, 99%), calcium dihydrate chloride (Merck, 99.5%), sodium hydrogenocarbonate (Acros, 99+%), potassium hydrogenophosphate (Acros, 99+%), and sodium sulfate (Jansen Chimica, 99%) [56].

2.2. Nitinol substrates preparation

Nitinol substrates considered in this study consist in inter-metallic compounds and are purchased from AMF under the form of rectangular-shaped plates (20 mm $\times$ 10 mm $\times$ 0.3 mm). They are constituted of Ni (56%) and Ti (balance). The coupons are first mechanically polished on a Buehler-Phoenix 4000 instrument using silicon carbide papers (P800, then P1200) and diamond pastes (9, 3, then 1 μm) from Struers. They are then cleaned in absolute ethanol under ultrasounds for 15 min, submitted to UV-ozone for 30 min (Jelight 42-220), and finally ultrasonically retreated in absolute ethanol for another 15 min. After being blown dried under nitrogen, the substrates are stored for further use or analysis.

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