Electrochimica Acta 55 (2010) 2437–2441

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electropolishing and passivation of NiTi shape memory alloy

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ARTICLE INFO

Article history:
Received 27 October 2009
Received in revised form
25 November 2009
Accepted 28 November 2009
Available online 4 December 2009

Keywords:
NiTi
Biomaterials
Corrosion
Electropolishing
Passivation
Electrochemical impedance spectroscopy

ABSTRACT

Electropolishing of NiTi alloy has been investigated. The influence of polishing bath composition and the operating conditions instead of the conditions of the process on the quality of the surface, evaluated by AFM and SEM methods, was established. Morphologically uniform surfaces were obtained only in the case of solutions containing hydrofluoric and sulfuric acids. Electropolished samples were sterilized and thermally passivated, then their corrosion resistance was measured in Tyrode's physiological solution. It was established that already after the electropolishing the corrosion resistance of NiTi alloy increases due to the spontaneously formed TiO_2 layer. The increase of the thickness of the layer during sterilization and thermal passivation causes further increase in the corrosion resistance.

1. Introduction

Nitinol and other metallic materials have been used for implants in orthopedics (cambers, intramedullar nails and devices for the treatment of scoliosis) in orthodontics (orthodontic archwires for which superelastic properties play important role) and in cardiology [1–4]. This alloy is also rapidly becoming the material of choice for self-expanding stents, graft support systems, filters, baskets and various other devices for minimally invasive interventional procedures [5]. The wide spectrum of application in implantology imposes special requirements on the biocompatibility of Nitinol. Biocompatibility tends to be associated with materials that are inert in the human body, i.e. where there is no interaction between the tissues and the foreign material. In many cases this definition is too restrictive. Biocompatibility has been recently redefined as '*the ability to perform with an appropriate host response in a specific application*' [1,6]. Two main factors determining the biocompatibility of a material are: the host reaction induced by the material and the degradation of the material in the body environment. Much concern exists about both issues in the case of Nitinol. Dissolution of Ni ions and the possibility of inducing allergic [7,8], toxic [9] and carcinogenic [10,11] effects associated with the biological properties of Ni is the greatest problem that can be faced after Nitinol implantation. The biological response to implant materials is directly related to their surface properties. There are many parameters that characterize a surface. Chemical composition, crystallinity and heterogeneity, roughness and wettability, all of them are of great importance for biological response [12]. But first of all it should be mentioned that the surface properties influence the corrosion resistance of metallic material. Since corrosion resistance, with the exception of noble metals, relies rather on protective oxide films than on inherent inertness, surface oxide film formation is of great importance for Nitinol corrosion performance [13]. Corrosion resistance of a metal depends strongly on the structure of the metal and the state of the surface, so the proper electrochemical treatment of the metal surface may significantly improve its corrosion resistance. Electropolishing exerts very beneficial influence, because it removes the outermost surface layer of the metal created during mechanical working. Such a surface layer usually has a deformed structure and different from the core of the metal physicochemical properties and contains a lot of structural defects and other imperfections, which is the reason of increased electrochemical activity of the surface and its decreased corrosion resistance. Another factor that exerts beneficial influence on the slowing down the corrosion processes is the formation of protective passive layer. Quality and properties of that layer influence positively the corrosion resistance of the implant so its biocompatibility. The electrochemical properties of NiTi alloy are well recognized, however the investigations

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doi:10.1016/j.electacta.2009.11.097

of electropolishing of this alloy were in only few papers [14–18]. That process was conducted mainly in the methanolic solutions of sulfuric acid.

The aim of this paper was to determine the influence of the electropolishing parameters on the quality of the surface of NiTi alloy as well as the influence of electropolishing and passivation on its corrosion resistance.

2. Materials and methods

The investigations were carried out on NiTi alloy intended for implants. The chemical composition of the alloy (Ni – 55.5%, Ti – balance) met the requirements of the ASTM 2063 standard. Samples have the shape of a piece of a foil of the dimensions: 1 mm × 10 mm × 15 mm. Electropolishing was conducted in the electrolyzer (made of PP). The cathode was made of stainless steel. Following baths were used:

K1 – containing sulfuric acid, nitric acid and hydrofluoric acid [19],
K2 – containing sulfuric acid, hydrochloric acid and methanol [19],
K3 – containing sulfuric acid, hydrofluoric acid and ethylene glycol [20,21].

Before electropolishing all samples were mechanically polished on emery paper grade 600.

The mean roughness factor R_a of the surface was measured using profilometer Surtronic 3+ (Taylor Hobson) whereas the morphology of the sample surfaces was investigated using Hitachi S-3400N scanning electron microscope and AFM NanoScope E (Digital Instruments) atomic force microscope.

After electropolishing selected samples were subjected to sterilization and passivation. Samples were sterilized in the steam atmosphere in an autoclave ($t = 136\,^{\circ}\mathrm{C}$, $p = 3$ bar). Passivation was performed in air at the temperature of 450 °C during 1 h. Corrosion resistance of the NiTi alloy after electropolishing, sterilization and passivation was investigated using potentiodynamic method and the electrochemical impedance spectroscopy. Measurements were conducted at the temperature of 37 °C in the Tyrode solution of the composition: NaCl – 8.00 g dm^{-3}, $CaCl_2$ – 0.20 g dm^{-3}, KCl – 0.20 g dm^{-3}, $MgCl_2$ – 0.05 g dm^{-3}, $NaHCO_3$ – 1.00 g dm^{-3}, Na_2HPO_4 – 0.05 g dm^{-3} of pH = 6.9 at the free access of air. AutoLab PGSTAT 30 (EcoChemie) and typical electrochemical cell in three-electrode configuration with saturated calomel electrode as the reference electrode and platinum gauge as a counter electrode were used in the electrochemical measurements. Analytical reagent grade chemicals produced by POCh S.A. (Poland) and Millipore water were used for preparation of the solutions.

3. Results and discussion

Basing on visual inspection it was established that effective electropolishing is possible with the use of K3 bath. In the baths K1 and K2 etching of the samples occurred and the surface became rough and irregular. K3 bath was selected to further studies – smoothing and brightening of the sample surface occurred when this bath (Fig. 1) was used in electropolishing. Depending on the process parameters, either an increase or a decrease of the surface roughness factor in comparison to mechanically polished sample ($R_a = 0.18\,\mu\mathrm{m}$) occurred. Real surface area of the polished sample, calculated from AFM data, was higher than its geometrical area by 12.4%. After the electropolishing the real surface area was higher than the geometric area by only about 2.5% (Fig. 2). For the polished samples the mean surface roughness factor, calculated from AFM data was 54.6 nm whereas for those that were electropolished only 9.5 nm. Samples after electropolishing in K3 bath at the high current density (50 A dm^{-2}) were subjected to sterilization and thermal passivation. After sterilization and thermal passivation there was no practical change in morphology of the samples surface (Fig. 3).

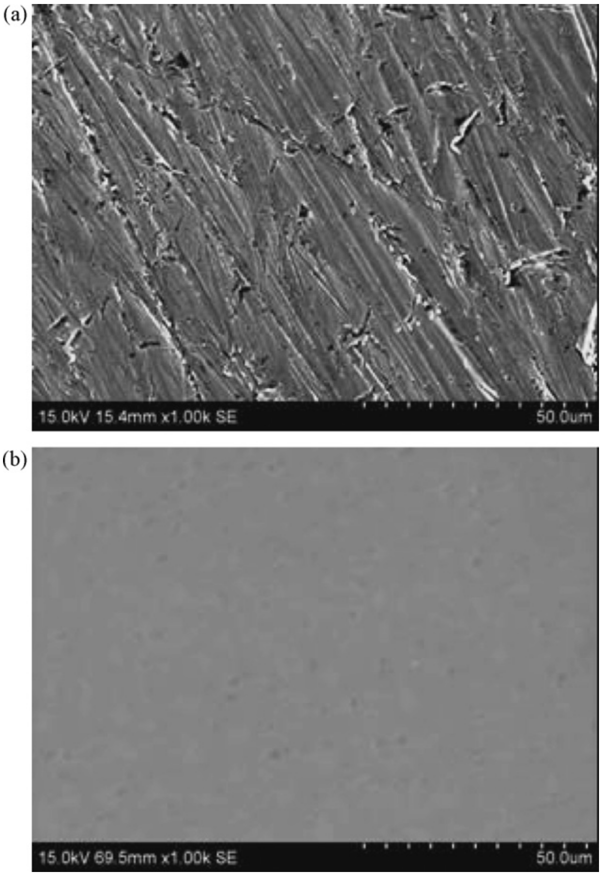

Fig. 1. SEM images of the surface of ground (a) and electropolished ($R_a = 0.07\,\mu\mathrm{m}$) (b) samples.

It was established, basing on the electrochemical investigations of the corrosion resistance of NiTi alloy in physiological Tyrode's solution that electropolishing improves its corrosion resistance. Corrosion potential moves to the value of −311 mV and polarization resistance increases practically to the value of 1.3×10^2 kΩ cm^2 (Table 1, Fig. 4). Sterilization or thermal passivation caused a further increase of the corrosion resistance. The corrosion potential moved to approximately −180 mV (after sterilization) or to approximately −130 mV (after thermal passivation). Corrosion current density decreased to 8×10^{-5} and 7×10^{-5} mA cm^{-2}, respectively. In the case of samples that were not subjected to electropolishing and passivation pitting and the evolution of gases started at the potential of approximately 1300 mV (Fig. 4), whereas in the case of samples after electropolishing and sterilization pitting started at the potential of approximately 1500 mV. That is due to both the transpassive dissolution of NiTi and the oxygen evolution, taking place heterogeneously on the surface. The pit on a ground sample after corrosion test is presented in Fig. 5. No pitting was observed in the case of samples subjected to electropolishing and passivation (Fig. 5).

Impedance spectra have been presented as Bode phase and Bode modulus plots in Figs. 6–9. Bode plots were used rather than popular Nyquist plots because it has been argued that they are more informative [22]. It is common when studying the oxide films on passive metals to use a two-layer model consisting of an inner layer which is compact and of the barrier type, and outer layer which is porous [23]. The inner barrier layer dominates the impedance