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Electrochemical behavior of Ni-Ti alloy after surface modification

M. Kaczmarek [a,*], W. Simka [b], A. Baron [a], J. Szewczenko [a], J. Marciniak [a]
[a] Division of, Biomedical Engineering
Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
[b] Division of, Chemistry and Inorganic Technology, Silesian University of Technology, 44-100 Gliwice, Poland
* Corresponding author: E-mail address: marcin.kaczmarek@polsl.pl

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Materials

ABSTRACT

Purpose: The shape memory effect and superelasticity make the nickel-titanium alloy an interesting material for medical applications. But the biocompatibility has been questioned due to conflicting results in the literature. The latest research has shown that this situation may be caused by a variation in NiTi surface treatment. The appropriate surface treatment increases the corrosion resistance. The paper presents the electrochemical behavior of NiTi alloy after surface modification with the use of various techniques.
Design/methodology/approach: The evaluation of the electrochemical behavior of NiTi alloy was realized both by recording of anodic polarization curves with the use of the potentiodynamic method and by an electrochemical impedance spectroscopy technique (EIS).
Findings: Surface condition of metallic biomaterial determines its corrosion resistance. In the course of the work it was observed that the lowest values of corrosion current were recorded for the sterilized and the thermally passivated samples. The highest values of corrosion current were recorded for the ground samples. These samples obviously had also the highest corrosion rate.
Research limitations/implications: The obtained results are the basis for the optimization of physicochemical properties of the metallic biomaterial. The future research should be focused on selected specific implants specially with respect to their application features.
Practical implications: On the basis of the obtained results it can be stated that the suggested surface treatment can be applicable for medical implants due to the increase of the corrosion resistance and in consequence the increase of biocompatibility.
Originality/value: The paper presents the influence of various methods of the surface treatment on corrosion resistance of the NiTi alloy. The suggested methods can be applied in treatment of the material intended for medical applications especially in cases where the surface roughness plays important role.
Keywords: Metallic alloys; Biomaterials; Corrosion; Tyrode's physiological solution

1. Introduction

Shape memory alloys are now widely recognized and accepted in medicine. Due to biocompatibility issues the choice of alloy system for medical applications is that based around the equiatomic NiTi system or what is often referred to as 'Nitinol' (Nickel Titanium Naval Ordnance Laboratory). Essentially nitinol is an alloy containing approximately 50 at.% nickel and 50 at.% titanium. Small compositional changes around this 50:50 ratio

make significant changes in the operating characteristics of the alloy. Slightly nickel rich alloys result in the effect known as 'superelasticity' and it is this phenomenon that is utilized in the vast majority of medical applications. Superelastic nitinol exhibits comparatively large fully recoverable strains. The unique mechanical behavior of nitinol and apparent biocompatibility has resulted in a number of interesting and often unique medical applications [1]. Nitinol and other metallic materials have been used for implants in orthopedics (cambers, intramedullary nails and devices for the treatment of scoliosis) and orthodontics (orthodontic archwires in which superelastic properties are used) [2÷7]. 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 [2÷8].

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 response between the tissue 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, 9]. The two main factors that determine 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 over both these issues in the case of Nitinol. Dissolution of Ni ions and the possibility of inducing allergic [10, 11], toxic [12] and carcinogenic [13, 14] 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 a property directly related to their surface conditions. 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 [15]. But first of all it should be mentioned that appropriate surface conditions influence the corrosion resistance of metallic biomaterial. Since corrosion resistance, with the exception of noble metals, relies rather on protective oxide films than on intrinsic unreactivity, surface oxide film formation is of great importance for Nitinol corrosion performance [15].

2. Material and methods

The corrosion resistance of NiTi alloy intended for implants was tested. The tests were carried out on samples in the form of a flat bar (length l = 21 mm, width w = 16 mm and thickness equal to 1 mm). The tests were carried out on samples of the following surfaces: ground – average roughness R_a = 0,31 μm; electropolished – average roughness R_a = 0,12 μm; boiled in water by 1 hour – average roughness R_a = 0,11 μm; sterilized in steam at the temperature of 136^{O}C and pressure p = 3 bar – average roughness R_a = 0,12 μm; thermally passivated at the temperature of 450 ^{O}C by 1 hour – average roughness R_a = 0,13 μm. In order to measure the roughness the Surtronic 3+ surface analyzer was applied. The pitting corrosion tests were performed by recording of anodic polarization curves. The Eco Chemie B.V PGSTAT30 system with accompanying software FRA (Frequency Response Analyzer System) for electrochemical tests was applied – fig. 1. The saturated calomel electrode (SCE) was applied as the reference electrode. The tests were carried out in Tyrode's physiological solution (pH = 6,8 ÷ 7,4) – table 1. The exposed area of the specimen was equal to 1 cm^2; reversal of the scanning direction was done when the anodic current density reached 100 μA/cm^2.

Furthermore, the electrochemical behavior of the investigated alloy was extended by an electrochemical impedance spectroscopy technique (EIS) in third electrode cell. The auxiliary electrode was a platinum foil and the saturated calomel electrode was the reference. The electrochemical impedance measurements were made at open circuit potential with the perturbing a.c. signal amplitude of ±0.05 V in the frequency range between 50 kHz and 0.1 Hz.

Macroscopic observations of samples' surfaces were carried out both before and after the electrochemical tests. The observations were realized with the use of the Hitachi S4200N scanning microscope.

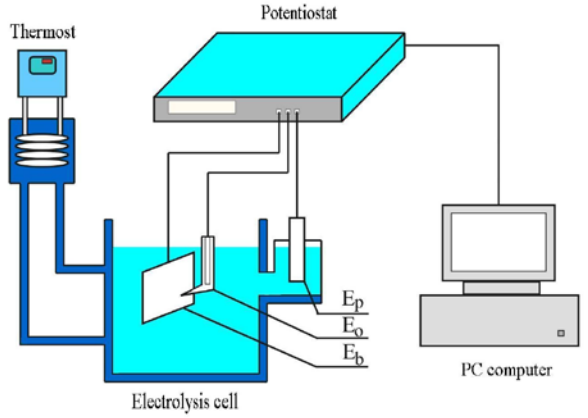

Fig. 1. Diagram of the corrosion resistance set

Table 1.
Tyrode's physiological solution - PN – EN ISO 10993-[15]

ingredients	g/l distiled water
NaCl	8,000
$CaCl_2$	0,200
KCl	0,220
$NaHCO_3$	1,000
Na_2HPO_4	0,050
$MgCl_2$	0,200

3. Results

3.1. Pitting corrosion resistance results in the Tyrode's physiological solution

Results of electrochemical tests have revealed the influence of surface preparation of the Ni-Ti alloy on the corrosion resistance

– table 2. For the ground samples, the corrosion potential was equal to E_{corr} = - 317 mV and the anodic current was equal to $3{,}24 \cdot 10^{-5}$ A/cm^2. Polarization of samples caused the rapid increase of anodic current for the potential E_B = + 490 mV. The average polarization resistance of the samples was equal to $R_{p\,av} = 3{,}49\ 10^3$ Ω. The average corrosion rate of the ground samples was equal to $3{,}07 * 10^{-1}$ mm/year.

For the electropolished samples, the corrosion potential was equal to E_{corr} = - 311 mV, and the anodic current was equal to $1{,}01 \cdot 10^{-6}$ A/cm^2. Polarization of samples caused the rapid increase of anodic current for the potential E_B = + 1398 mV. The average polarization resistance of the samples was equal to $R_{p\,av} = 1{,}27 \cdot 10^5$ Ω. The average corrosion rate of the electropolished samples was equal to $1{,}03 \cdot 10^{-2}$ mm/year.

The corrosion potential of the boiled samples was equal to E_{corr} = - 246 mV. The anodic current was equal to $1{,}49 \cdot 10^{7}$ A/cm^2. The average polarization resistance of the samples was equal to $R_{p\ av} = 1{,}74 \cdot 10^5$ Ω. The average corrosion rate of the boiled samples was equal to $1{,}41 \cdot 10^{-3}$ mm/year.

For the sterilized samples, the corrosion potential was equal to E_{corr} = - 234 mV, and the anodic current was equal to $8{,}31 \cdot 10^{-8}$ A/cm^2. The average polarization resistance of the samples was equal to $R_{p\ av} = 1{,}87 \cdot 10^6$ Ω. The average corrosion rate of the sterilized samples was equal to $7{,}86 \cdot 10^{-4}$ mm/year.

The corrosion potential of the thermally passivated samples was equal to E_{corr} = - 218 mV. The anodic current was equal to $7{,}45 \cdot 10^{-8}$ A/cm^2. Polarization of samples caused the rapid increase of anodic current for the potential E_B = + 1365 mV. The average polarization resistance of the samples was equal to $R_{p\,av} = 9{,}84 \cdot 10^4$ Ω. The average corrosion rate of the boiled samples was equal to $7{,}04 \cdot 10^{-4}$ mm/year.

Table 2.
Corrosion resistance of NiTi alloy in the Tyrode's solution

Surface	Corrosion potential E_{corr}, mV	Corrosion current I_{corr}, A/cm^2	Polarization resistance $R_{p\,av}$, Ω	Corrosion rate V, mm/year
Ground	-317	$3{,}24 \cdot 10^{-5}$	$3{,}49 \cdot 10^3$	$3{,}07 \cdot 10^{-1}$
Electropolished	-311	$1{,}01 \cdot 10^{-6}$	$1{,}27 \cdot 10^5$	$1{,}03 \cdot 10^{-2}$
Boiled	-246	$1{,}49 \cdot 10^{-7}$	$1{,}74 \cdot 10^5$	$1{,}41 \cdot 10^{-3}$
Sterilized	-234	$8{,}31 \cdot 10^{-8}$	$1{,}87 \cdot 10^6$	$7{,}86 \cdot 10^{-4}$
Thermally passivated	-218	$7{,}45 \cdot 10^{-8}$	$9{,}84 \cdot 10^4$	$7{,}04 \cdot 10^{-4}$

Impedance spectra have been presented as Bode phase and Bode magnitude plots in fig. 2 for ground and sterilized samples and in fig. 3 impedance spectra for electropolished, boiled and thermally passivated samples. Bode plots are used because it has been argued that they are more informative than the conventionally popular Nyquist plots [16].

In common to study the oxide film on a passive metal using a two – layer model consisting of an inner layer which is compact and the barrier type, and outer layer which is porous [17]. The inner barrier layer dominates the impedance spectra at higher and intermediate frequencies while the outer layer dominates at low frequencies.

From the impedance spectra (Fig. 2) recorded at the open circuit potential can obtained three frequency regions referring to the high, intermediate and low frequency values. The first time constant (from 50 kHz to 15 Hz) corresponds to capative behavior of the electrode. It is related to the inner surface layer at the alloy surface. The low frequency less than 15 Hz time constant describes the relaxation effects inside the pores of the outer porous part of the layer and probably diffusion inside the pores and through the layer.

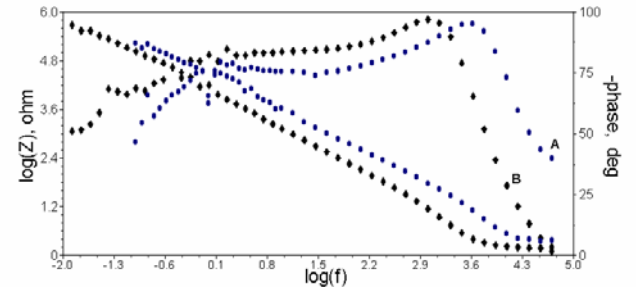

Fig. 2. Bode plots of impedance spectra for boiled (A) and ground (B) samples recorded in Tyrode's solution

The absence of more than one sloping segments in the Body plot indicates that the time constants that might be present were close together and unresolvable (Fig. 3). In the high frequency value the Bode magnitude plots exhibited constant log $|Z|$ values vs. log (f) with a phase angle near 0°. The high frequency plateau of the magnitude of the impedancy $|Z|$ was due to response of the electrode ohmic resistance, which includes: electrolyte resistance, cell geometry, impedance of the conductors and the reference electrode. The spectra displayed a linear slope of about – 1 in the middle frequency range. This is a characteristic response of a capacitive behavior of surface film. In the low frequency value phase angle is close to 90°, this idictative of film acquiring pure capacitive behavior [18]. A certain degree of deviation from ideal capacitive behavior can be observed from the Bode – phase plots in which the maximum phase angle reached was approximately 10° below 90°. Such a deviation has also been reported by others for films on Ti alloys [19, 20].

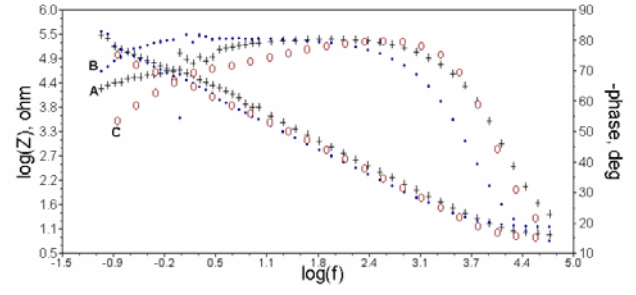

Fig. 3. Bode plots of impedance spectra for electropolished (A) sterilized (B) and thermally passivated (C) samples

The changes in the passive film resistance of the materials can be attributed to structural changes in the film or changes in the ionic or electrical conductivity of the film. As it can be seen the chemical composition and microstructural properties of the treated surface of Nitinol exhibit a direct influence on the electrochemical properties. Increased corrosion stability of the electropolished, sterilized and thermally passivated in spite of ground and boiled observed due to changes in roughness of the surface.

4. Conclusions

To sum up the performed corrosion tests of the Ni-Ti alloy intended for medical applications it can be stated that surface treatment increases corrosion resistance in the physiological fluid. Similar study should be performed for other media simulating body fluids in order to better understand corrosion phenomena on Ni-Ti surface.

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