Electropolishing of Nitinol Wires and Its Influence on Corrosion Mechanisms

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Abstract. Nitinol is a superelastic and shape-memory alloy often used for the production of vascular stents and surgery implants. Electrochemical polishing is normally used at the preparation stage of stent production. The Electropolishing treatment was performed in 1M Sulfuric acid in 75% Methanol and 25% Glycerine for several treatment times. The corrosion behaviours of Nitinol wires in Hanks’ Balanced Salts Solution and in 3% NaCl at room temperature before and after the treatment were compared. It was found that Nitinol is less active in Hank’s solution that in Sodium Chloride. Tafel slopes built to polarization curves indicate that the mechanisms of corrosion of Nitinol in Hanks’ solution and in NaCl are different. On the other hand, total corrosion current densities are similar in both kinds of media. Plausible equivalent circuits hint that the surface layers formed in Hanks’ solution are not the same as in NaCl. Specimens after the Electrochemical Polishing do not show any differences in the equivalent circuits either in Tafel slopes.

1. Introduction
Nitinol, a Ni-Ti alloy in an almost equiatomic ratio, is a novel engineering material in the medical and aerospace industry. Nitinol is often used for biomedical applications such as dentistry and dental surgery, blood vessel stents, valves and others.[1][2] As one of production stages, Nitinol stents are normally electropolished [3–5] so that two main parameters are monitored: corrosion (and abrasion) resistance and nickel content in the surface layers.[6–9] To the best of our knowledge, there is no standard protocol of corrosion testing for electropolished Nitinol implants in terms of commonly accepted corrosive media, corrosion type and measurement procedure. Rather, pitting [7,10–14], fretting [8,15–17] or galvanic corrosion [6,7,15,18,19] are most often studied; artificial saliva [1,6,15], Ringer solution[7,15,20,21], Hank’s solution [12,21–23] and NaCl [7,12,18,24] are used and numerous electrochemical and other techniques are employed.

This article describes a peculiarity observed in a study of galvanic corrosion of Nitinol wire before and after electropolishing in the framework of a larger research project. Corrosion behavior of Nitinol wires was studied by several electrochemical techniques, namely OCP monitoring, Linear Polarization Resistance, Tafel slope extrapolation and Electrochemical Impedance Spectroscopy in two different corrosive media: balanced Hank’s solution and NaCl. An interesting change of the observed rate determining steps was observed: the corrosion of untreated Nitinol wires in Hank’s solution occurred under pronounced cathodic control, while the limiting stage of the corrosion of untreated Nitinol wires in NaCl was anodic. For electropolished specimens the control was anodic for both electrolytes.

2. Experimental
Nitinol wires OD = 0.3 mm (Johnson Matthey, $A_t = -16^\circ C$) were used as received from the manufacturer.
Electrical polishing was performed in 1M H$_2$SO$_4$ in methanol-glycerol 3:1 at 10V for 210 sec at 5°C (iced water bath). The average current of ~ 2A current was measured during the polishing process, and the solution became greenish at its end.

A wire was inserted into a three-electrode cell so that 10 -12 mm of the specimen were in the electrolyte. Platinum wires served as counter electrodes and Ag|AgCl electrodes in saturated KCl were used as reference electrodes. The temperature was 23 ± 1°C. All the electrochemical measurements were made using an IVIUM-n-STAT potentiostat.

Hank’s solution (H8262 from Sigma Aldrich) was stored refrigerated after opening. Solutions of 3% NaCl were prepared as usually.

Before electrochemical measurements each specimen was kept in the cell until a stable to less than ± 5 mV during 15 minutes OCP was reached (typically, 2 – 4 days).

### 3. Results

OCP values for untreated specimens in Hank’s solution (28 ± 8 mV) are nobler and less scattered than for untreated specimens in NaCl (~ 66 ± 65 mV). Electropolished specimens demonstrated OCPs of 35 ± 13 mV in Hank’s solution and ~ 33 ± 18 mV in NaCl. The following changes of pH are observed: in NaCl pH grows from ~7.2 to ~ 8.5; in Hank’s solution pH grows from ~7.2 to ~ 7.6 (Buffer effect of Hank’s solution). According to ICP, more nickel ions are present in the electrolyte after the completion of the tests in Hank’s solution than in NaCl. This effect is minimized by the electrical polishing.

Electrochemical Impedance spectra (10 kHz – 0.1 Hz, excitation pulses of 10 mV with respect to OCP) are best fitted to the R(QR) circuit for the corrosion in Hank’s solution both of untreated and electropolished specimens; in NaCl both kinds of specimens are best fitted to R(Q(R(QR))) circuit, cf. Figure 1.

![Figure 1. Electrochemical Impedance Spectra of untreated Nitinol samples in (a) Hank’s solution and (b) 3% NaCl](image)

Tafel slopes (Figure 2) demonstrate that for untreated Nitinol in Hank’s solution $b_a < b_c$, while for electropolished Nitinol in in Hank’s solution $b_a \sim b_c$. Nitinol in NaCl shows that $b_a > b_c$ both for untreated and electropolished samples.
Figure 2. Tafel slopes $b_a$ and $b_c$ built to a polarization curve of electropolished Nitinol in Hank’s solution

4. Discussion
The release of nickel observed for the corrosion of Nitinol in Hank’s solution hints that the corresponding oxidation process occurs relatively fast and easily:

$$Ni \rightarrow Ni^{2+} + 2e^- \quad (1)$$

The higher values of cathodic Tafel slopes evidence that the overall corrosion process is limited by a reduction process, which is probably:

$$H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad (2)$$

Nickel ions are leaving to the electrolyte and no layer of corrosion products is formed on the metal surface. This is why the best fit is to the equivalent circuit $R(QR)$, corresponding to the mostly bare, although not flat, metal surface.

Electropolishing lowers the surface concentration of nickel thus retarding reaction (1), which is manifested in the higher than for untreated Nitinol cathodic Tafel slopes.

In NaCl the oxidation occurs more preferably to titanium, resulting in the formation of titanium oxide layer on the metal surface. The oxide layer presents some difficulty for the metal oxidation and turns it into the rate determining step. The presence of the oxide layer might be the reason to the fact that the observed Impedance spectra are best fit by the equivalent circuit $R(C(R(CR)))$.

At this stage, we cannot explain why NaCl promotes the oxidation of titanium or, on the other hand, why Hank’s solution favors the oxidation of nickel.

5. Conclusions
Release of $Ni^{2+}$ to the electrolyte is more significant for Hank’s solution than for NaCl. This release decreased due to electrical polishing.

A layer of corrosion products is formed on the metal surface for NaCl, but not for Hank’s solution.

Cathodic reaction is the rate determining step for the corrosion in Hank’s solution. However, the corrosion in NaCl occurs under anodic control. Electrical polishing causes the cathodic process to proceed more easily.

References
[1] Duerig T, Pelton a and Stöckel D 1999 An overview of nitinol medical applications Mater. Sci. Eng. A 273–275 149–60
[2] A. V. Datye, M. Jaramillo K H W 2004 Corrosion Behaviour of Cardiovascular Stents Second LACCEI International Latin American and Caribbean Conference for Engineering and Technology (LACCEI’2004) “Challenges and Opportunities for Engineering Education, Research and Development” (Miami) pp 1–6
[3] Ma X Z, Zhang L, Cao G H, Lin Y and Tang J 2007 Electrochemical micromachining of nitinol by confined-etchant-layer technique Electrochim. Acta 52 4191–6

[4] Simka W, Kaczmarek M, Baron-Wiecheć A, Nawrat G, Marciniak J and Zak J 2010 Electropolishing and passivation of NiTi shape memory alloy Electrochim. Acta 55 2437–41

[5] Miao W D, Mi X J, Wang X L and Li H C 2006 Electropolishing parameters of NiTi alloy Trans. Nonferrous Met. Soc. China (English Ed. 16 0–2

[6] Venugopalan R, Trepanier C and Venugopalanli R 2000 Assessing the corrosion behaviour of Nitinol for minimally-invasive device design Minim. Invasive Ther. Allied Technol. 9 67–73

[7] Khalil-Allafi J, Amin-Ahmadi B and Zare M 2010 Biocompatibility and corrosion behavior of the shape memory NiTi alloy in the physiological environments simulated with body fluids for medical applications Mater. Sci. Eng. C 30 1112–7

[8] Trepanier C, Venugopalan R and Pelton A 2000 Corrosion Resistance and Biocompatibility of Passivated NiTi Shape Mem. Implant. SE - 3 35–45

[9] Bai Z and Rotermund H H 2011 The intrinsically high pitting corrosion resistance of mechanically polished nitinol in simulated physiological solutions J. Biomed. Mater. Res. - Part B Appl. Biomater. 99 B 1–13

[10] Riaz N, Wolden S L, Gelblum D Y and Eric J 2017 J Biomed Mater Res B Appl Biomater. 2017 August ; 105(6): 1330–1341. 105 6072–8

[11] Kazimierczak a., Podraza W, Lenart S, Wiernicki I and Gutowski P 2013 Electrical potentials between stent-grafts made from different metals induce negligible corrosion Eur. J. Vasc. Endovasc. Surg. 46 432–7
[24] Bolat G, Mareci D, Iacoban S, Cimpoesu N and Munteanu C 2013 The Estimation of Corrosion Behavior of NiTi and NiTiNb Alloys Using Dynamic Electrochemical Impedance Spectroscopy *J. Spectroscopy* **2103** 714920