# ELECTROCHEMICAL STUDY ON CORROSION RESISTANCE IN PHYSIOLOGICAL MEDIA OF NITINOL WIRE USED AS BIOIMPLANT

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The characterization of Nitinol (NiTi) wire corroded in some physiological media is discussed according to electrochemical measurements, such as: potentiodinamic curves, Tafel polarization and polarization resistance technique. The morphology of the surface was examined using microscopic images. All the experimental data show that the physiological serum (PS) has a more pronounced corrosive character as compared to 5 % glucose solution and 10 % Aminosteril solution. The results obtained through polarization curves indicate that the potential of corrosion in pitting ($E_{cp}$) decrease from 1045 mV in aminosteril to 440 mV in glucose and 216 mV in physiological serum. Moreover, for the NiTi tested in Aminosteril, corrosion current density ($i_{corr}$) significantly decreases and polarization resistance ($R_p$) increases in a considerable manner as compared to their values which were obtained in PS and glucose. These results were discussed according to the formation of passive films; their stability strongly depends on the corrosive action of the artificial physiological media in the order: Physiological serum (PS) < 5% Glucose solution <<10 % Aminosteril solution.

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## 1. Introduction

The corrosion of bioimplants implies the interaction between an implant (a metal or an alloy) and the physiological medium, and is influenced both by the metal properties and the environment. From a thermodynamic and kinetic point of view, the theory of corrosion in liquid mediums implies the principles of electrochemistry, of diffusion and dissolution. Various forms of corrosion are met which can be appreciated and interpreted depending on certain factors such as: the pH of the medium, the nature of the bioimplant and temperature [1-12].

As a result of the electrochemical reactions on the metallic surface, certain elements in the alloy pass from the metallic form into an ionic form [6-12]. These materials must be biocompatible and resistant to biological fluids. They must not produce adverse reactions in the human body and must not degrade while being used [1-6].

Nitinol (Nickel Titanium Naval Ordinance Laboratory) is an alloy of an almost equal mixture of nickel and titanium. It was invented in the late 1960s and it belongs to a group of materials referred to as “smart materials” because of their unique physical properties that make

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Nitinol so remarkable: shape-memory and super-elasticity. The most important shape memory alloy used in biomedical applications, Nitinol is able to fulfill functional requirements related not only to their mechanical reliability, but also to its chemical reliability and its biological reliability [13,14]. Nitinol offers the possibility of designing and fabricating orthopaedic implants with great advantages such as high biocompatibility, superelasticity, the memory shape effect, resistance to corrosion and wear, resistance to torsion, invariable stress effects, dynamic interference, fatigue resistance and MRI compatibility. Nitinol's extraordinary ability to accommodate large strains, fatigue life and the ability to be electrically heated for shape recovery coupled with its physiological and chemical compatibility with the human body have made it one of the most commonly used materials in medical device engineering and design. In the last years, NiTi technology has contributed to significant improvements in orthopaedics and orthodontics. Its use is now overcoming the limits in designing smaller, more efficient minimally invasive tools and devices [13-20].

NiTi applications in orthopedics currently include internal fixation by the use of fixatives, compression bone stables used in osteotomy and fracture fixation, rods for the correction of scoliosis, shape memory expansion staples used in cervical surgery, staples in small bone surgery, and fixation systems for suturing tissue in minimal invasive surgery [13-20].

Although several studies have demonstrated the good corrosion resistance and biocompatibility of NiTi, the high nickel content of the alloy (55 weight % Ni) and its possible dissolution by corrosion still remains a concern [19, 20]. Tissues in the human body contain water, dissolved oxygen, proteins and various ions, such as chloride and hydroxide, and they present an aggressive environment to metals or alloys used for implantation [21, 22]. Corrosion resistance of a metallic implant is thus an important aspect of its biocompatibility [21]. In addition to the release of ions in the physiological environment, the corrosion process will also result in the deterioration of dimensional parameters of the corroding body. NiTi corrosion behaviour can be significantly improved after specific surface treatments such as electropolishing.

In this study the behavior of Nitinol (NiTi) in physiological serum (PS), glucose and aminosteril solutions is discussed according to electrochemical measurements and microscopic images related to morphology of surfaces before and after corrosion tests.

## 2. Experimental

The Nitinol used had the following composition (wt. %): 50 % Ni and 50 % Ti. Before corrosion the samples were degreased with acetone and dried. Physiological serum (0.9 % NaCl), 5 % glucose and 10 % aminosteril were used as aggressive media for corrosion tests. All the mentioned solutions were bought from pharmacy, being used as perfusion solutions in medical treatment. The composition of 10 % Aminosteril containing amino acids and other electrolytes is shown in Table 1.

For electrochemical measurements a standard cell has been used with a working electrode (surface 0.314 $cm^2$) made of NiTi wire, a platinum auxiliary electrode (surface 1 $cm^2$) and a Ag/AgCl reference electrode. The electrode made of NiTi was polished with metalographic paper, washed in distilled water, degreased in acetone and dried in warm air. The potentiodinamic polarization was conducted with a scan rate of 1 $mV.s^{-1}$, in an electrochemical system, VoltaLab 40, with a personal computer and VoltaMaster 4 software. The immersion time of the plates in the respective media was 4 minutes in open circuit, at room temperature.

The morphology of the Nitinol surface before and after treatment in the above mentioned solutions was examined using a metallographic microscope Euromex, with Canon camera and included software.

*Table 1. Composition of 10 % Aminosteril solution.*

| Electrolyte | Concentration (g/L) |
|---|---|
| L-isoleucine | 4.67 |
| L-leucine | 7.06 |
| L-lysine | 5.97 |
| L-lysine (monohydrochloride) | 7.46 |
| L-methionine | 4.10 |
| L-phenylalanine | 4.82 |
| L-threonine | 4.21 |
| L-thryptophan | 1.82 |
| L-valine | 5.92 |
| L-arginine | 10.64 |
| L-histidine | 2.88 |
| L-alanine | 15.00 |
| L-proline | 15.00 |
| L-malic acid | 8.08 |
| Glycine | 15.95 |
| NaOH | 1.200 |
| KCl | 0.683 |
| KOH 85% | 0.716 |
| $MgCl_2 \cdot 6H_2O$ | 1.017 |

## 3. Results and discussion

### Potentiodynamic curves

The polarization curves of Nitinol in physiological serum (PS) and glucose are presented in Fig.1a. The study of the response given by Nitinol polarization in physiological serum (PS) and glucose solutions, simulating the body fluid conditions indicate that the critical potential in pitting ($E_{cp}$) is shifted to higher value, when the corrosion process of Nitinol carried out in glucose. It has also been observed that the critical potential in pitting ($E_{cp}$) decreases from 440 mV in glucose to 216 mV in physiological serum. Polarization curve of nitinol in aminosteril solution is shown in Fig.1b. Note that, in this case, the corrosion process occurs at low current densities, of the order of microamps, and $E_{cp}$ reaches a high value of 1045 mV. Thus, we can say that in aminosteril, Nitinol corrosion occurs more slowly than in PS or glucose. This can be explained according to the composition of aminosteril solution, which contains aminoacids and bases (NaOH and KOH) that favor spontaneous passivation of nitinol, up to a potential of 1045 mV.

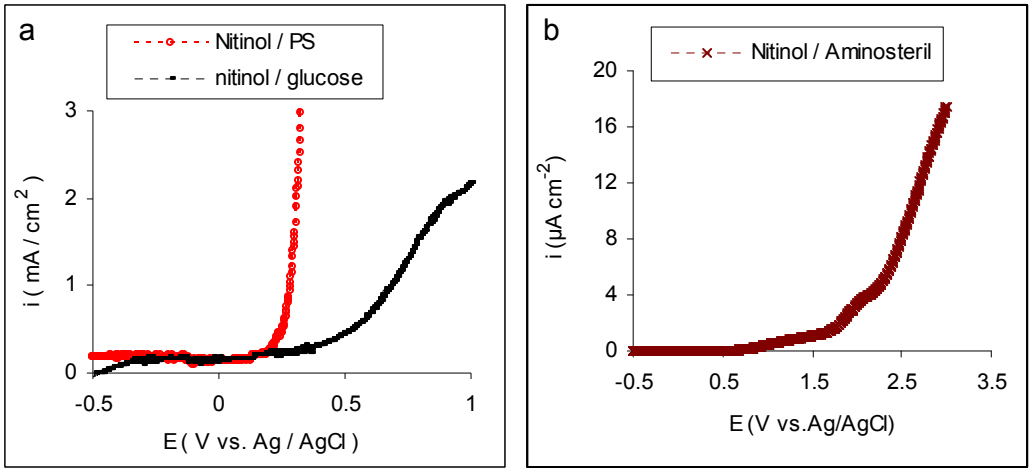


*Fig. 1. Potentiodynamic curves of NiTi obtained in different artificial physiological media: a – physiological serum (PS) and glucose solutions; b – aminosteril solution*

*Tafel polarization*

Corrosion currents ($i_{corr}$) were calculated by extrapolation of anodic and cathodic Tafel lines to the corrosion potential (see Fig.2, Tafel Diagram).

The polarization curves presented in Fig.2 show that:

(i) for NiTi corroded in glucose solution, the corrosion potential ($E_{corr}$) was shifted in the positive direction; (ii) to the potential of -270 mV, the anodic process of NiTi corroded in glucose solution is significantly modified than that of nitinol corroded in PS; (iii) from

-270 mV to the critical pitting potential ($E_{cp}$), anodic polarization curves overlap, indicating in both cases, the formation of passive film on the surface; over $E_{cp}$, NiTi becomes active, indicating the beginning of passive film destruction, this phenomenon being more pronounced in PS; (iv) from Fig.2 it can be seen that the polarization curves of nitinol in aminosteril solution were shifted in the area of very low currents, less than 50 µA, as compared to those of nitinol corroded in PS or glucose; this can be associated with a significant decrease of corrosion current.

The corrosion currents (µA $cm^{-2}$) were obtained using VoltaMaster 4 software and these are presented in Fig.4.

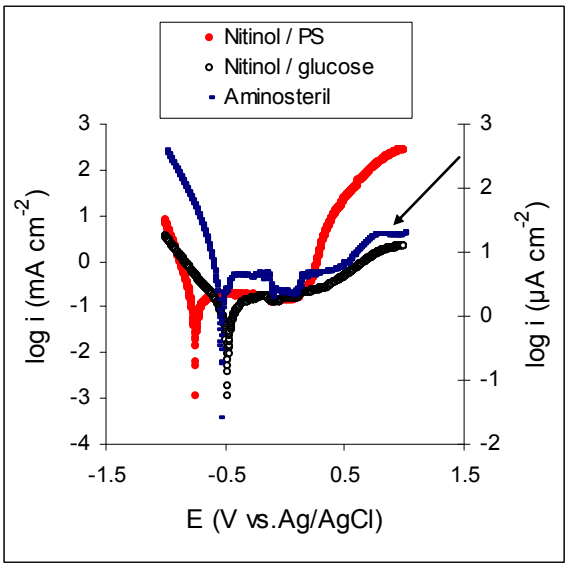


*Fig. 2. Tafel diagram of NiTi coroded in various artificial physiological media*

*Polarization resistance technique*

Using the polarization resistance technique the corrosion resistance of NiTi was evaluated in this media simulating body fluids. Various composition of environments ($Cl^-$ ions, glucose and aminoacids) affected the corrosion resistance of NiTi. The results showed that the aminosteril solution is the least corrosive medium for Nitinol, and because of high $Cl^-$ ions content, PS is the most corrosive one. The polarization curves obtained in the potential ranges near to corrosion potentials were recorded with a scan rate of 1 mV $s^{-1}$. The linearization was accomplished in the domain of over-voltages values ± 10 mV (Fig.3). The slopes $(di/dE)_{E\to Ecorr}$ of the lines from Fig.3 represent the polarization conductance. Polarization resistances ($R_p$ - Ω $cm^2$) were calculated using relation 1 and these are presented in Fig.4.

$$\left(\frac{di}{dE}\right)_{E\to E_{corr}} = \frac{1}{R_p} \qquad (1)$$

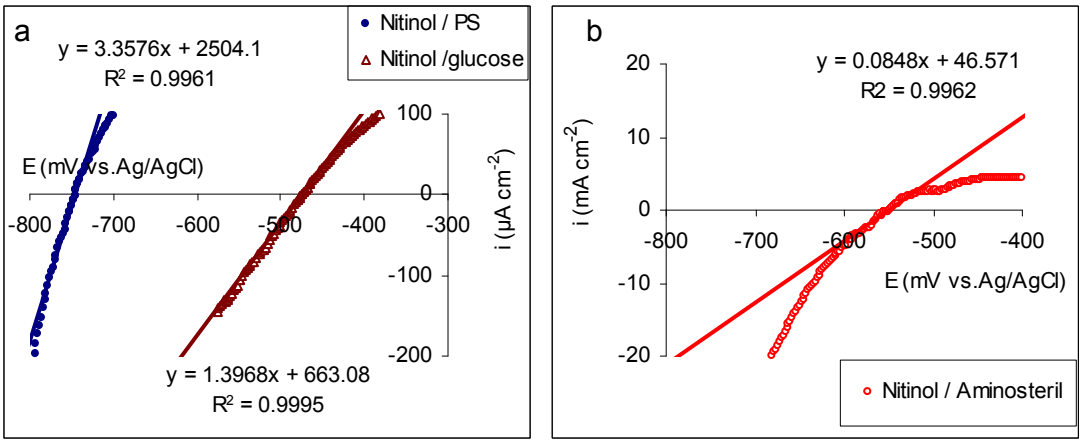


*Fig. 3. Potentiodynamic curves near $E_{corr}$ of NiTi obtained in different artificial physiological media: a – physiological serum (PS) and glucose solutions; b – aminosteril solution*

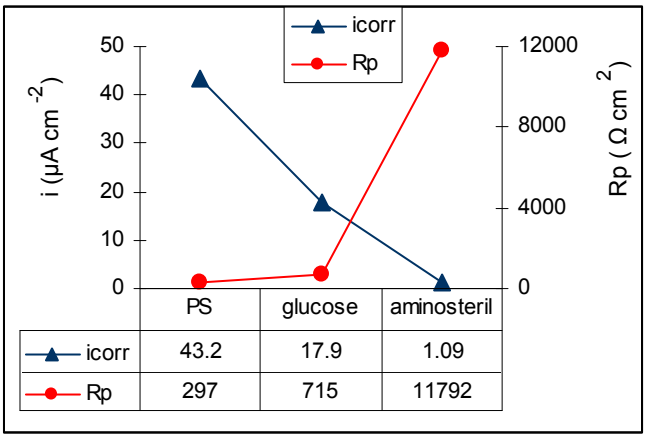


*Fig. 4. The numerical values of corrosion currents and polarization resistances obtained for NiTi in different artificial physiological media*

From Fig.4 it can be seen that for NiTi corroded in aminosteril, high polarization resistance was obtained, as compared to NiTi corroded in PS and glucose. This is probably due to

the inhibitory action of various aminosteril components. Thus, NiTi is passivated in aminosteril solution, forming a surface layer with better adherance and stability as compared to the passive films formed in PS and glucose. The corrosion current ($i_{corr}$) value of 1.09 μA obtained for NiTi in aminosteril confirms that a very slowly attack of aminoacids occured.

**Surface morfology**

The electrochemically-corroded NiTi samples in PS, glucose and aminosteril were also tested using the microscopic images, which indicate the formation of superficial film providing a passivation on the corroded electrode in these solutions. The microscopic images of NiTi surface before (Fig.5a) and after corrosion in PS (Fig.5b), in glucose (Fig.5c) and in aminosteril (Fig.5d) are presented. Uncorroded sample did not show any particular feature in microscopic imaging than small defects (Fig.5a).

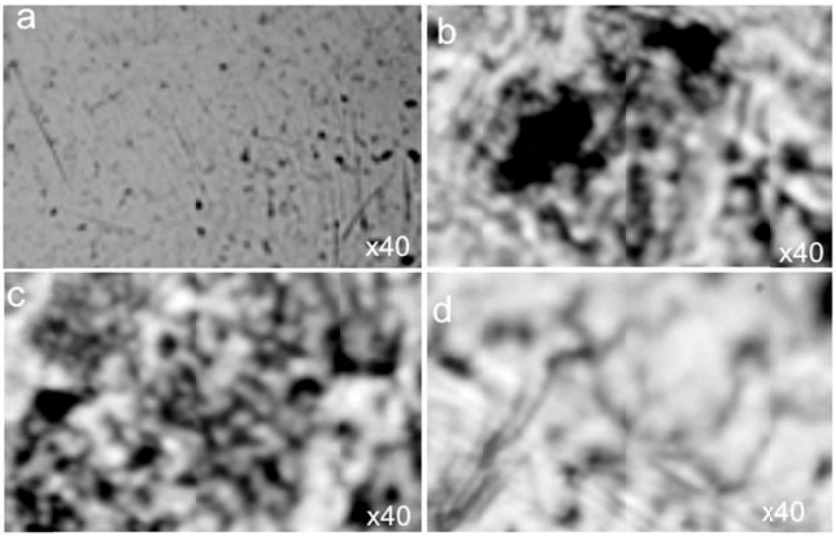


*Fig. 5. Microscopic images of NiTi surface: a – before corrosion; b – after corrosion in physiological serum; c – after corrosion in glucose; d – after corrosion in aminosteril*

The results of microscopy for corroded sample in physiological serum (PS), show evidence of corrosion spots, which affect the NiTi surface. Corrosion spots are much nuanced suggesting that the passive film formed on the surface was extensively damaged. In the presence of glucose the micrograph show evidence of corrosion spots less intense than those was shown in PS, but a non-uniform passive film is nuanced. Glucose interacts with NiTi surface sites, via labile bonds such as hydrogen bonding interactions, suggesting that at high potentials, the glucose desorption is facilitated and the passive film is partially destroyed. The formation of a uniform layer is evidenced in Fig.5d. providing a good passivation of NiTi surface. Together, adsorption and inhibitory effect of amino acids gives to NiTi high corrosion resistance in aminosteril.

## 4. Conclusions

While correlating the data obtained by the used electrochemical methods it has been observed that the used physiological serum has a quite high corrosive action.

It has also been observed that the potential of corrosion in pitting decrease from 1045 mV in aminosteril to 440 mV in glucose and 216 mV in physiological serum. These potentials cannot be reached in the human body under normal conditions, thus the material we have studied can be used as a bioimplant with no major risks.

In case of Niti corroded in aminosteril, corrosion current density significantly decreases and polarization resistance increases in a considerable manner as compared to their values which were obtained in PS and glucose. In this regard, when the Nitinol is immersed in PS solution, the

surface layer is not stable and the composition can be changed by incorporation of ions and molecules.

The results of microscopy for corroded sample in PS, show evidence of corrosion spots, and the formation of a non-uniform film on the Nitinol surface was observed. In the presence of glucose corrosion spots have a lower intensity, but passive film has an irregularly distribution on the surface. On microscopic image of NiTi corroded in aminosteril is observed a passive film which has an uniform distribution on the surface. The composition of passive film and inhibitory effect of amino acids provide a very high corrosion resistance of NiTi in aminosteril.

As a general conclusion, in this study, the results were discussed according to the formation of passive films; their stability strongly depends on the corrosive action of the artificial physiological media in the order: Physiological serum (PS) < 5% Glucose solution <<10 % Aminosteril solution.

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