Microstructural Analysis of Ti-Based Shape Memory Alloys Following the Electrochemical Corrosion in Artificial Saliva

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Abstract. The investigations carried out aimed to highlight the structural modifications occurred in the Ti-based shape memory alloys subject to electrocorrosion in Afnor artificial saliva. The behavior to corrosion was highlighted by fast electrochemical tests, mainly by dynamic potentiometry. From the microstructural analysis we noticed that the specimens of the two Ti-based shape memory alloys show traces of “pitting” corrosion on their surface of diverse sizes, a fact that will raise issues in terms of cytotoxicity due to the corrosion products released.

1. Introduction

NiTi (NiTiinol) alloy shows the SME (shape memory effect) where its shape and rigidity is thermally controlled as it is a material capable to sense the external temperature modifications and to be transformed into a pre-programmed shape in elastic and plastic deformation energies [1].

The superelastic NiTi orthodontic wires allow the increase, transmission and control of light and continuous forces necessary for dental shifts [1-3]. Due to the specificity of the orthodontic fixed appliances many authors suggest the inclusion of some constraint elements on the model assemblies so as to reproduce the clinical reality [4-6] as opposed to ISO 15841: 2006 methodology [7].

The beta-titanium (β-Ti) wires are titanium molybdenum alloys. Goldberg and Burstone envisioned this alloy for orthodontic use after recognizing such advantages as elastic modulus below stainless steel and near to nickel-titanium (NiTi) conventional alloy, excellent formability, weld-ability, and low potential for hypersensitivity [8].

Corrosion consists in the degradation of a material under the chemical or electrochemical action of the environment where it is located.

Due to the high content of nickel of the NiTi alloy, there is the possibility that the Ni in the alloy might dissolve due to corrosion with a carcinogenic potential on the body [9].
The specialized studies have shown that the corrosion products of the dental alloys solubilized in the gum tissues depend on the alloy composition which influences the resistance to corrosion by the structure formed during casting and the subsequent processing protocols.

2. Paper goal
The goal of this study consists in the determination of the structural modifications occurred in two shape memory alloys intended for orthodontic fixed appliances following electrocorrosion in Afnor artificial saliva.

3. Materials and methods
We used two types of orthodontic wires from Ti-based alloys supplied by the same manufacturer, namely Nitinol Clasic-3M and Beta III Titanium-3M.

For the electrocorrosion tests we used a solution of Afnor artificial saliva having pH=8.2 and a chemical composition very close to the natural saliva.

The behavior to corrosion was studied by fast electrochemical tests, mainly through dynamic potentiometry. The potential measurements within open circuit and potentiodynamic polarizations were carried out on a VoltaLab 21 (PGP201 - Radiometer Copenhagen) potentiostat equipped with VoltaMaster 4 software for data acquisition and processing. The linear polarization curves were registered for a scanning speed of the potential of 1mV/s, within a potential interval close to the corrosion potential. To verify the susceptibility to corrosion in points and the main parameters of the corrosion process in case of some high overpotentials, the cyclical polarization curves were registered for the speed of 100 mV/s, for the -500 ... +1500 mV potential range. All measurements were performed at 25°C in naturally aired solution. For I=0 corrosion current we determined, by means of Volta Master 4 software, the shape of branches (b_a and b_c) of Tafel diagram, the polarization resistance R_p, the density of the corrosion current J_cor and the corrosion speed V_cor.

The microstructural analysis was performed by electronic microscopy for different powers of amplification of the image depending on the structural details identified on the surface. We studied the main characteristics of the surface before and after the electrocorrosion resistance tests.

4. Results and discussions
Through the corrosion tests we obtained Tafel diagram (figure 1a) and the cyclical diagram (figure 1b) characterizing the electrocorrosion behavior of the Nitinol Clasic-3M alloy.

![Figure 1. Polarization curves of Nitinol Clasic-3M alloy in Afnor artificial solution. a- linear and b- cyclical.](image-url)
The results registered during the electrocorrosion process in solution of Afnor artificial saliva indicate an adequate behavior of Nitinol Clasic-3M material characterized by a polarization resistance of 152.09 kohm.cm and a corrosion speed per year of 15.04 µm/Y (table 1).

**Table 1.** Parameters of electrocorrosion process in Afnor artificial solution for Nitinol Clasic-3M alloy.

| Parameter      | Value         |
|----------------|---------------|
| \(E(I=0)\)    | -426.8 mV     |
| \(J_{cor}\)   | 1.2865 µA/cm  |
| \(R_p\)       | 152.09 kohm.cm|
| Corrosion rate | 15.04 µm/Y    |

The analysis of the cyclical diagram of corrosion highlights the “pitting” effect through corrosion, as it is of hysteresis type with the return branch on the exterior. The “pitting” type of corrosion represents a deficient way of behavior of the material at the interaction with the exterior environment due to the quantity of material transferred to the electrolyte environment (in our case Afnor artificial saliva).

In figure 2 we presented Tafel diagram (figure 2a) and the cyclical diagram (figure 2b) characterizing the electrocorrosion behavior of Beta III Titanium-3M alloy.

![Tafel diagram](image)

**Figure 2.** Polarization curves of Beta III Titanium-3M alloy in Afnor artificial solution a- linear and b- cyclical.

The results registered for the corrosion in solution of Afnor artificial saliva are given in table 2. We may notice a superior behavior of Beta III Titanium-3M material characterized by a high polarization resistance of 160.77kohm.cm and a corrosion rate per year of 6.114 µm/Y.

**Table 2.** Parameters of electrocorrosion process in Afnor artificial solution for Beta III Titanium-3M alloy.

| Parameter      | Value         |
|----------------|---------------|
| \(E(I=0)\)    | -459.8 mV     |
| \(J_{cor}\)   | 0.5228 µA/cm  |
| \(R_p\)       | 160.77 kohm.cm|
| Corrosion rate | 6.114 µm/Y    |
In figure 3, we presented the electronic microscopy images for the surface of Nitinol Clasic-3M alloy at different amplification scales. The surface of the material shows “pitting” traces characterized by pits appearing on the surface of the specimens.

![Image](image_url)

**Figure 3.** Nitinol Clasic-3M at different amplification scales: a) 100:1 amplification scale, b) 1000:1 amplification scale, c) 2000:1 amplification scale and d) 3000:1 amplification scale.

At low amplification powers (figure 3a) the traces of the electrocorrosion test are not visible. Figures 3b-3d clearly highlight the traces of the corrosion process, material dislocations measuring between 1 and 10 µm and having an orderly character. In figure 3d, we may also notice the formation of some corrosion compounds on the surface of material grouped around the corrosion points.

The connection between the manner of grouping of the reaction compounds and the orderly arrangement of the craters on the surface of the material is determined by the interaction between compounds and the phasic constitution of NiTi alloy. Being still separate, the craters do not affect at this moment the functionality of nitinol smart alloy.

Beta III Titanium-3M alloy corroded on the direction of mechanical processing (figure 4a-4c) through the formation of some crevices on the surface of the material with widths of 1-3 µm and lengths up to 40 µm.

In figure 4c, we may notice the existence of corrosion compounds at the level of the surface of the smart metal material. Compounds are 5-15 µm wide and 20-30 µm long.
Figure 4. Electronic microscopies of the surface of Beta III Titanium-3M alloy at different amplification scales: a) 500:1 amplification scale, b) 1000:1 amplification scale, c) 2000:1 amplification scale.

The surface of Beta III Titanium-3M alloy is totally corroded, the corrosion formations being unified and making a long line of corrosion. These “crevices” will affect both the mechanical stability of the smart material and the special properties characteristic to the shape memory alloys.

5. Conclusions
To define the behavior to corrosion of the dental alloys we used the linear polarization method and the cyclical polarization method.

By the linear polarization method we obtained corrosion potentials providing information about the tendency towards corrosion of the alloy in the corrosion environment (for example Afnor artificial saliva).

The results registered during the electrocorrosion process indicate a superior behavior of Beta III Titanium-3M material characterized by a high polarization resistance and a lower corrosion speed per year.

The microstructural analysis of the surface of the two nitinol alloys after the electrocorrosion resistance test in Afnor artificial solution was performed through SEM electronic microscopy by using a SE secondary electron detector. Both alloys show “pitting” traces of diverse sizes. Although both materials corroded through the dislocation of material from the superficial layer, they had different behaviors through the formation of distinct craters having an orderly arrangement (Nitinol Classic-3M alloy), and by the unification of craters and the formation of crevices (Beta III Titanium-3M),
respectively. Both forms of manifestation of electrocorrosion effects in Afnor artificial saliva will negatively influence both the mechanical properties and the special properties of the two shape memory alloys.

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