

# Evaluation of Corrosion Resistance of NiTiNb Orthodontic Wires in Tomato Juice

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*An investigation about corrosion resistance of NiTiNb orthodontic wires in tomato juice at 37°C have been carried out by using electrochemical techniques. For comparison, NiTi orthodontic wires have also been evaluated. Both samples were examined using electrochemical techniques: open circuit potential, linear potentiodynamic polarization (LPP) and electrochemical impedance spectroscopy (EIS) in tomato juice. The electrochemical corrosion properties of NiTiNb and NiTi orthodontic wires were measured in terms of zero current potential (ZCP) and corrosion current density ( $j_{cor}$ ). EIS technique was applied to study the nature of the passive film formed on both samples at 10 minutes and 1 hour immersed time in tomato juice. From EIS data, an equivalent circuit (EC) with one time constant was modeled.*

**Keywords:** NiTiNb, orthodontic wires, tomato juice, cyclic polarization, EIS, SEM

Titanium and its alloys represent one of the most attractive biomaterials due their better corrosion resistance, mechanical properties, and good biocompatibility [1-6]. Since the 1970s, the NiTi alloy is intensely used for dental orthodontic applications due to their shape memory effect, superelasticity and good biocompatibility [7-9].

The biocompatibility of metallic materials is closely related to their corrosion behaviour. NiTi wire has a protective TiO<sub>2</sub> based passive film which is also formed on NiTi alloys [10]. The potential of this passive film breakdown, sometimes very low for NiTi alloy, is leading to active dissolution processes. It has been found that NiTi alloy exhibits poor resistance to localized corrosion in chloride-containing environments, with arguably low pitting potential values [11].

Some studies have shown that NiTi alloy exhibits excellent resistance against corrosion in physiological media, others have shown that it exhibits poor resistance [12, 13]. Ni-ion releases, due to the NiTi alloy corrosion process, are generally harmful for human health, may lead to allergenicity and toxicity [14].

Third alloying element was added to NiTi alloy to enhance its mechanical or corrosion properties [15, 16].

The prevalence of dental corrosion in the mouth has increased in the few decades as a result of increasing consumption of commercial juice [17].

The aim of this study was to characterize the corrosion resistance of NiTiNb orthodontic wires compared to the NiTi orthodontic wires in tomato juice.

## Experimental part

### Materials and methods

A NiTiNb alloy produced by National Institute of Research & Development for Non-ferrous and Rare Metals, Bucharest,

Romania, was used for the study: with the following chemical composition (% by weight): Ti = 37.8, Nb = 14.5, and Ni = balance. An equiatomic NiTi alloy produced by the same supplier was used in some tests as reference material. Both alloys were synthesized by electron beam melting technique and the chemical compositions were according to the data providing by the manufacturer. The samples were ground with SiC abrasive paper up to 2000 grit, final polishing was done with 1 mm alumina suspension. Then, the samples were degreased with ethyl alcohol followed by ultrasonic cleaning with deionized water and dried under an air stream.

### Electrochemical Tests. The Electrochemical Media

a. Fresh Fusayama artificial saliva [18] was selected as it has been shown to produce results that were consistent with the clinical experience of dental alloys. The pH of this artificial saliva was 5.6.

b. Juice sample was prepared from fresh tomatoes (*Lycopersicon esculentum*) fruits (harvested in the Ia<sup>o</sup>i - Agronomical and Veterinary Medicine University experimental greenhouses) using an electric tomato juicer and following classic technological process steps [19], like concentration (85°C for 5 min), canning and pasteurization (118°C for 60 s). The main biochemical characteristics of tomato juice were determined in the Biochemistry Laboratory from Agronomical and Veterinary Medicine University- Ia<sup>o</sup>i, using standard analysis procedures based on official methods [20, 21]. The quality of the tomato juice used as an electrochemical media was according with the Codex General Standard regulations for fruit juices and certain similar products intended for human consumption [22, 23], having: 91% moisture content, 13% total soluble solids, 1.4% NaCl content, 4.06 (mg/100g) ascorbic acid

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content, 0.54 titrable acidity (g citric acid/100g) and  $pH = 4.6$ .

### Electrochemical Setup

A glass corrosion flow cell kit (C145/170, Radiometer, France) with a platinum counter-electrode and a freely adjustable Luggin capillary containing a saturated calomel reference electrode (SCE) was employed to perform the electrochemical measurements [24].

Electrochemical measurements were carried out in aerated solution at  $37 \pm 1^\circ\text{C}$  using a PAR (Princeton Applied Research, USA) 4000 potentiostat controlled by a personal computer and specific software (ElectrochemistryPower Suite, PAR). All potentials referred to in this article are with respect to SCE.

The following sequence of electrochemical experiments was adopted (step by step):

- open circuit potential measurement ( $E_{oc}$ ) versus time for 1 hour in artificial saliva;
- open circuit potential measurement versus time for 10 minutes in tomato juice;
- electrochemical Impedance Spectroscopy (EIS) measurement at open circuit potential, in tomato juice after 10 min immersed;
- open circuit potential measurement versus time for 1 hour in tomato juice;
- EIS measurement at open circuit potential, in tomato juice after 1 hour immersed;
- linear potentiodynamic polarization (LPP) from -0.4 to 0.5 V with 0.5 mV/s potential sweep rate. Using an automatic data acquisition system, the LPP curves were plotted and both corrosion current density ( $j_{corr}$ ) and zero current potential (ZCP) were estimated by using both anodic and cathodic branches.

The Electrochemical Impedance Spectroscopy (EIS) spectra were recorded in the  $10^{-2}$  to  $10^5$  Hz frequency range. The applied alternating potential signal had amplitude of 10 mV. In order to supply quantitative support for discussions of these experimental EIS results, an appropriate model (ZSimpWin-PAR, USA) for equivalent circuit (EC) quantification has also been used. Since the measured capacitive response is not generally ideal due to certain heterogeneity of the electrode surface a constant phase element (CPE) was introduced for fitting the spectra, instead of an ideal capacitance element [25].

### Scanning Electron Microscopy (SEM) of corroded surfaces

In order to observe the occurrence of the surface effects of the corrosion after LPP treatment, all corroded surfaces were observed by SEM. To perform this Quanta 200 3D scanning electron microscope, was used.

### Results and discussion

The open circuit potential ( $E_{oc}$ ) is used as a criterion for the corrosion behaviour. Generally, materials with large

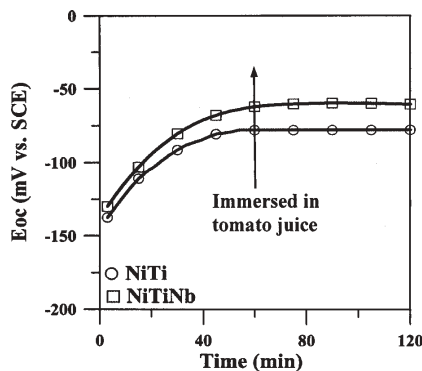


Fig.1. Variation of open circuit potential ( $E_{oc}$ ) with time for dental orthodontic wires maintained 1 hour in artificial saliva and after 1 hour immersed in tomato juice

negative potential values are more reactive whilst those with large positive values are far less reactive [26]. The  $E_{oc}$  of a metal varies as function of the time. In figure 1 the variation of  $E_{oc}$  with time for both orthodontic wires in artificial saliva and in tomato juice is shown. These results are based on the orthodontic wires studied after 1 h of immersion in artificial saliva and 1 hour of immersion in tomato juice.

Upon immersion, the corresponding  $E_{oc}$  values shifted rapidly towards more positive potential values, as observed in figure 1. After approximately 40 min., the rate of variation of  $E_{oc}$  values decayed quite significantly, though monotonously shifting in the positive direction suggesting the growth of an oxide film onto the both orthodontic wires.  $E_{oc}$  for experimental NiTiNb orthodontic wires in artificial saliva is more positive than NiTi orthodontic wires, probable due to the positive contribution of the Nb alloying element in the formation of oxide film. Tomato juice had no significant influence on the  $E_{oc}$ . This behaviour can be essentially attributed to the presence of the oxide film. The open circuit potential of the NiTiNb sample was stabilized at -61 mV vs. SCE, whereas the NiTi sample adopted a more negative potential at -106 mV vs. SCE in the tomato juice.

Bode spectra recorded at open circuit potential, with the NiTiNb and NiTi alloys immersed in tomato juice Bode spectra recorded at open circuit potential, with the NiTiNb and NiTi alloys immersed in tomato juice for a different period of time immersion, are shown in figures 2(A-B) and 3(A-B).

Both the impedance modulus of NiTiNb and NiTi alloys show that in the higher region  $\log / Z /$  tends to become constant. This is a typical response for the resistive behavior and correspond the solution resistance,  $R_{sol}$ . For the medium frequency range, a linear relationship between  $\log / Z /$  and  $\log f$  is observed all cases, through with relatively different slopes (always less than -1), whereas the maxima in the phase angle plots are smaller than  $-90^\circ$ , indicating that the passive films were not completely capacitive.

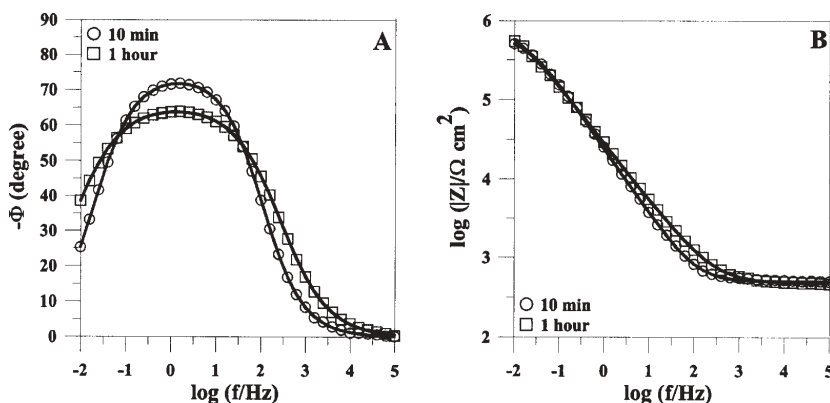


Fig. 2. Measured (discrete points) and fitted (solid lines) Bode impedance modulus versus frequency diagrams (A) and phase angle versus frequency diagrams (B) for NiTiNb alloy maintained 10 min and 1 hour in aerated tomato juice at open circuit potential at  $37^\circ\text{C}$  temperature

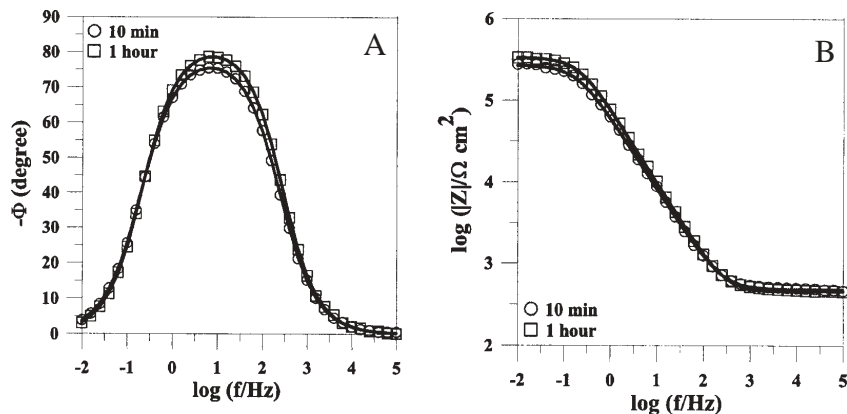


Fig. 3. Measured (discrete points) and fitted (solid lines) Bode impedance modulus versus frequency diagrams (A) and phase angle versus frequency diagrams (B) for NiTi alloy maintained 10 min and 1 hour in aerated tomato juice at open circuit potential at 37°C temperature

Table 1

VALUES OF FITTED PARAMETERS OF THE EC AS FUNCTION OF IMMERSION TIME OF BOTH ORTHODONTIC WIRES IN TOMATO JUICE

Samples	Immersion time	$10^3 Q_p$ S cm <sup>-2</sup> s <sup>n</sup>	n	$10^{-3} R_p$ Ω cm <sup>2</sup>
NiTiNb	10 min	1.6	0.85	2.8
	1 hour	1.5	0.86	3.2
NiTi	10 min	1.3	0.88	5.1
	1 hour	1.2	0.89	5.8

According to the impedance diagram, the Bode-phase plots are in agreement with an EC with one time constant (fig. 4).

The impedance spectra were fitted using the ZSimpWin software and the resultant EIS parameters are given in Table 1. The fitting quality of EIS data was estimated by both the chi-square ( $\chi^2$ ) test (between  $10^{-4}$  and  $10^{-5}$ ) values and the comparison between error distribution versus frequency values ( $\pm 5\%$  for the whole frequency range) corresponding to experimental and simulated data. In this EC,  $R_{sol}$  is the ohmic resistance of the electrolyte (around  $160 \pm 10 \Omega \text{ cm}^2$ ),  $R_p$  represents the polarization resistance and  $Q$  is the impedance related to a constant phase element (CPE). The more will increase the value of polarization resistance, the more will resist the sample to corrosion.

From Stern-Geary equation [27],

$$j_{\text{corr}} = B / R_p$$

with  $B$  constant determined by Tafel slope tests, it follows that the higher the  $R_p$ , the lower is the corrosion rate.

For both samples, the EIS spectra indicate that the formed film is not affected by the tomato juice of immersion time, as suggested by the slowly increase of polarization resistance ( $R_p$ ) values. The  $R_p$  values are higher than of NiTiNb sample, showing that the formed film on this sample is more resistant to corrosion than the one formed on NiTi sample.

The  $Q$  values decrease by increasing the immersion time assuming values characteristics of the electric double layer.

The values of the parameters ( $R_p$ ,  $Q$ ) obtained with the fitting procedure are reported in table 1.

Oxide layer can block the access of electrochemically active species to the electrode surface, restricting ion diffusion to the surface, and thus reducing the overall corrosion rate which can explain the increase in  $R_p$  with increasing immersion time.



Fig. 4 - Equivalent circuit (EC) used for fitting the measured impedance spectra

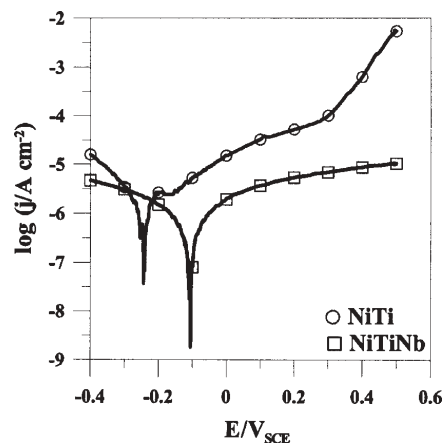


Fig. 5. Linear potentiodynamic polarization curves for NiTiNb and NiTi orthodontic wires tested in tomato juice, on semi-logarithmic axes; 0.5 mV/s, 37°C temperature

The linear potentiodynamic polarization (LPP) tests were performed 1 hour after immersion in artificial saliva and 1 h after immersion in tomato juice at open circuit potential. The LPP curves of both samples in tomato juice are shown in figure 5.

The polarization curves for both samples can be divided into three potential domains. The cathodic domain includes potentials where the current is determined by the oxygen reduction. The second domain includes the transition from cathodic to anodic current at the zero current potential (ZCP). Third domain corresponds to the passive plateau where the current density is, approximately, constant. Finally, the four domains are characterized, only to NiTi alloy by the increase in current due to breakdown ( $+ 0.3 \text{ V vs SCE}$ ) of the passive layer. In the case of NiTiNb alloy no breakdown of the passive layer occurs in the range of potential test (up to  $+ 0.5 \text{ V vs SCE}$ ). This indicates that the oxide layer formed on the surface of NiTiNb alloy is integral and protective.

The corresponding corrosion parameters obtained from the polarization curves of both tested samples are listed in table 2.

Tafel analysis of both the anodic and cathodic branches of the polarization curves delivered values for ZCP and corrosion current densities ( $j_{\text{corr}}$ ).

The corrosion current density of the NiTi orthodontic wires were about 2 times higher compared to the NiTiNb orthodontic wires showing that the NiTi orthodontic wires were quantitatively more susceptible to corrosion than the NiTiNb orthodontic wires.

It is also interesting to compare the values of ZCP derived from polarization curves with those of  $E_{\text{oc}}$  spontaneously

**Table 2**

ELECTROCHEMICAL PARAMETERS DETERMINED FROM THE POLARIZATION CURVES MEASURED FOR BOTH NiTiNb AND NiTi SAMPLES AFTER 1 h IMMERSION IN TOMATO JUICE

Alloy	ZCP, mV	$j_{\text{corr}}$ , $\mu\text{A}\cdot\text{cm}^{-2}$
NiTiNb	-78	0.7
NiTi	-241	1.3

attained by both samples (cf. fig.1). In both cases the values determined for the ZCP are more negative than those corresponding to  $E_{\text{oc}}$ . This variation is probably due to partial reduction of the spontaneously formed oxide layer on the surface of the samples while recording the cathodic branch of the polarization curves.

The surface morphologies of both samples polarized at +0.5 V in tomato juice were examined by scanning electrochemical microscopy (SEM).

SEM micrograph revealed that the uniform oxidation occurred on NiTiNb alloy after corrosion test in tomato juice, and did not show an obvious tendency of deterioration (fig. 6A).

The analyses of figure 6B indicate the appearance of selective corrosion at the surface of NiTi orthodontic wires.

## Conclusions

The results obtained in this work showed the electrochemical and corrosion behavior of NiTiNb orthodontic wires in tomato juice. For comparison, NiTi orthodontic wires have also been evaluated.

The electrochemical tests performed using LPP and EIS showed a good corrosion resistance of both orthodontic wires after immersion 1 h in artificial saliva and 1 h in commercial tomato juice. The high corrosion resistance of both orthodontic wires in tomato juice electrochemical media is due to the highly protective passive film that is the key factor for its biocompatibility.

Low corrosion and passive current densities, typical of passive materials, were obtained for NiTiNb alloy tested in tomato juice.

No passivation could be established with the NiTi orthodontic wires when polarized in tomato juice. After LPP, over the surface of NiTi alloy a selective corrosion appears.

The EIS results show that both orthodontic wires exhibit passivity at open circuit potential in tomato juice ( $R_p$  was around  $3\text{-}5 \times 10^5 \Omega\text{cm}^2$ ). Bode phase plots show one maxima of the immersed and polarized dental materials. The EIS spectra are best fitted using a simple EC characterized by one branches ( $Q, R_p$ ). This model is consistent with the model of a one layer structure for passive film.

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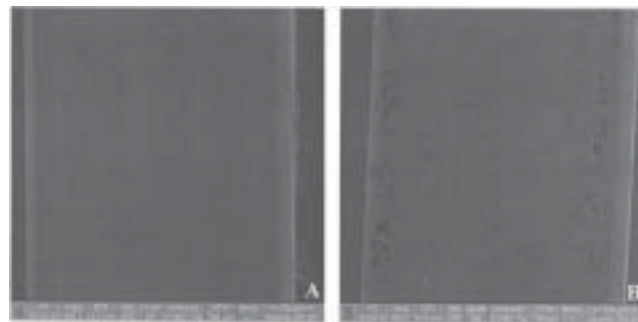


Fig. 6. Surface attack morphology: (A) NiTiNb, and (B) NiTi orthodontic wires

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