Comparative Electrochemical Behaviour of Uncoated and Coated NiTi for Dental Orthodontic Wires

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The electrochemical characteristics of polytetrafluoroethylene (PTFE) coating produced on NiTi orthodontic wires were investigated. Electrochemical impedance spectroscopy (EIS) and linear potentiodynamic polarization (LPP) techniques in the conventional three-electrode configuration was employed to test the PTFE-coated NiTi wire during their exposure to artificial saliva. For comparative purpose the same electrochemical measurements were performed on uncoated NiTi wire. In addition, scanning electron microscopy (SEM) was employed to observe the surface morphology of both uncoated and PTFE-coated NiTi wires after LPP in artificial saliva. It was found that the PTFE-coated NiTi wire had a lower corrosion rate (corrosion and passive current density), about one order of magnitude lower than the uncoated NiTi substrates. The NiTi substrate was actually passive in these experimental conditions. The EIS interpretation was performed in two-layer model of the coated sample. The corrosion mechanism for the PTFE-coated NiTi wires arises from electrolyte penetration in the pore of the PTFE deposits.

Keywords: PTFE-coated NiTi wire, artificial saliva, EIS, LPP, SEM

Titanium and its alloys represent one of the most widely studied and used metallic biomaterials due their good mechanical properties, high corrosion resistance and good biocompatibility [1-5]. Since the 1970s, the NiTi is intensely used for dental orthodontic applications due to its shape memory effect, superelasticity and good biocompatibility [6-8].

The biocompatibility of metallic materials is closely related to their corrosion behaviour. NiTi wire has a protective TiO_2 based passive film which is also formed on Ti and Ti alloys [9, 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 [12-14]. Ni-ion releases, due to the NiTi alloy corrosion process, are generally harmful for human health, may lead to allergenicity and toxicity [15].

Surface modification used to improve the corrosion resistance of NiTi alloy seems attractive.

This work presents the electrochemical study for polytetrafluoroethylene (PTFE) coated NiTi orthodontic wires in contact with artficial saliva. The initial *p*H was 5.6 and was adjusted to 4 by addition of lactic acid. The lactic acid exists naturally in human oral cavity [8].

Taking into account this overall research area, in order to obtain and characterize biocompatible coated PTFE NiTi orthodontic wires, several on-line (EIS - electrochemical impedance spectroscopy, LPP - linear potentiodynamic polarization) and off-line (SEM - scanning electrons microscopy) diagnosis tools have been improved.

Experimental part

Materials and methods

Both PTFE-coated and uncoated equiatomic NiTi orthodontic wires were provided by USA.

In figure 1, SEM micrograph of a covered NiTi wires with a layer of polytetrafluoroethylene (PTFE) is presented. Some properties of polymer layer (e.g. smoothness and porous aspect) can be observed.

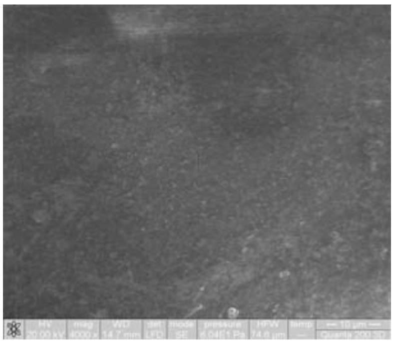

Fig. 1. SEM figure of NiTi wire covered with polytetrafluoroethylene (PTFE) layer

The uncoated NiTi wire was mirror-polished (with 400-2500 grit emery paper and alumina suspension), washed with bidistilled water, ultrasonically degreased in ethanol, and dried in air.

The solution used for electrochemical test consisted of Fusayama artificial saliva [16]. The initial *p*H was 5.6 and was adjusted to 4 by addition of lactic acid.

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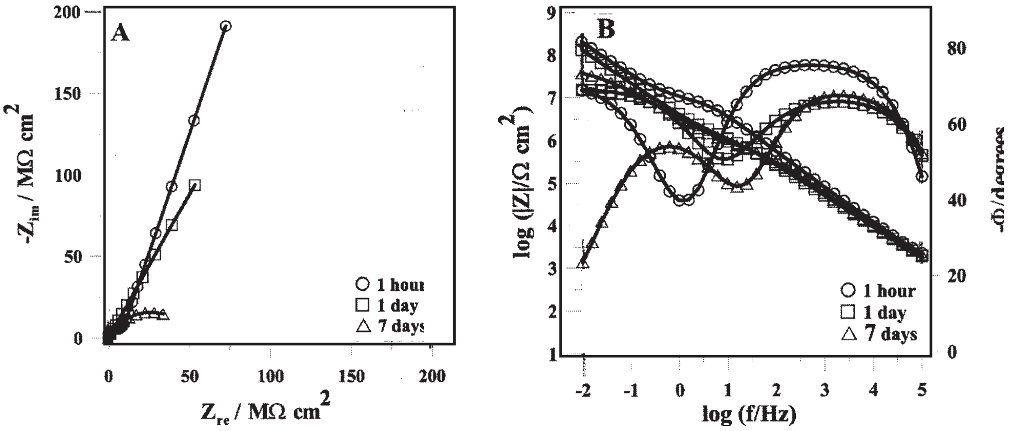

Fig. 2. Nyquist plot (A) and Bode plot (B) recorded for PTFE-coated NiTi wire after different immersion times in artificial saliva (*p*H = 4), at 37°C measured at open circuit potential

Electrochemical tests

Both uncoated and PTFE-coated NiTi wires were placed in a glass corrosion flow cell kit (C145/170, Radiometer, France), which was filled with artificial saliva (*p*H = 4). A saturated calomel electrode was used as the reference electrode, and a platinum coil as the counter electrode. In this paper, the potentials are reported versus the saturated calomel electrode (SCE). The temperature of the electrochemical cell was maintained at 37 ± 1°C.

Electrochemical measurements were performed using a potentiostat model PARSTAT 4000 (Princeton Applied Research, NJ, USA). The instrument was controlled via a personal computer and *VersaStudio* software.

Electrochemical impedance spectra (EIS) were measured over a frequency range extending from 10^5 Hz to 10^{-2} Hz using a 10 mV amplitude AC voltage signal. The EIS tests were recorded at the open circuit potential developed by the samples after 1-hour, 1-day, and 7-days of immersion in test solution. Analysis of the spectra was performed in terms of equivalent circuit (EC) fitting using *ZSimpWin* version 3.22 software.

Linear potentiodynamic polarization (LPP) test were also carried out in artificial saliva, after 7-days immersion time, at 37 ± 1 °C. These measurements were conducted by stepping the potential using a scanning rate of 0.5 mV/s from - 0.8 V to + 1 V. All the polarization experiments were performed three times, to the reproducibility of the results obtained.

SEM analysis of corroded surfaces

The surface morphology of both uncoated and PTFE-coated NiTi orthodontic wires after LPP test were assessed using scanning electron microscopy (Quanta 3D, FEI, Hillsboro, OR, USA).

Results and discussions

Electrochemical impedance spectroscopy

The EIS results are presented in the form of Nyquist plots in which the imaginary impedance (Z_{im}) is plotted against the real impedance (Z_{re}). Figure 2A shows the Nyquist plots obtained for PTFE-coated NiTi wire, at open circuit potential, after 1-hour, 1-day and 7-days of immersion in artificial saliva. All three Nyquist diagram indicates that the results describe two depressed, capacitive-like semicircles, one at high frequencies and another at lower frequency values. Also, the Bode phase spectra (fig. 2B) correspond to systems exhibiting two time constants as revealed by the presence of two maxima in these diagrams. That is, they can be divided into two distinct frequency ranges: the time constant in the high frequency part, which arises from uncompensated ohmic resistance resulting from the penetration of the electrolyte through a porous coating layer, and the low frequency part accounting for the processes taking place at the substrate/electrolyte interface.

Analysis of Bode spectra in terms of an equivalent circuit (EC) allowed obtaining the values of the impedance parameters. The EIS spectrum measured for PTFE-coated NiTi wire in artificial saliva, at 37 °C, could be acceptably fitted with the model presented in figure 3A. The EC is based on the consideration of a two-layer model for the surface and represents the electrochemical behaviour of a metal covered with an unsealed porous layer [17-19]. The experimental data show good fitting and an error smaller than 5%.

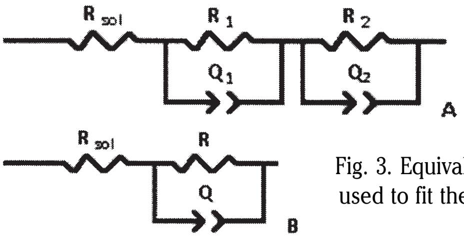

Fig. 3. Equivalent circuits (ECs) used to fit the impedance data

Table 1 shows the results of the curve fits.

For fitting the spectra, a constant phase element (CPE) was used instead of a pure capacitance due to the distributed relaxation feature of the coated layer due to surface non-homogeneities present at the microscopic level [20]. The impedance representation of CPE is given by:

$$Z_{(CPE)} = \frac{1}{Y_0(j\omega)^n} \qquad (1)$$

where ω is the angular frequency and Y_0 is a constant, and the value of the exponent n indicates the deviation from ideal capacitive behaviour (e.g., when n = 1).

The parameter R_{sol} represents the resistance of solution occurring between the sample and the reference electrode. It has a value around 80 ± 3 Ω cm² in artificial saliva, and is not listed in table 1.

Table 1

ELECTROCHEMICAL PARAMETERS OBTAINED FROM EIS SPECTRA USING THE SELECTED EC FOR THE PTFE-COATED NiTi WIRE AFTER DIFFERENT IMMERSION TIME IN ARTIFICIAL SALIVA (*p*H = 4), AT 37 °C

Time	Q_1 (μS cm^{-2} s^n)	n_1	R_1 (kΩ cm^2)	Q_2 (μS cm^{-2} s^n)	n_2	R_2 (MΩ cm^2)
1-hour	14	0.89	310	5.3	0.85	205
1-day	14	0.88	275	5.9	0.85	113
7-days	15	0.86	160	6.8	0.84	64

Table 2

ELECTROCHEMICAL PARAMETERS (AVERAGE (STANDARD DEVIATION)) DETERMINED FROM LINEAR POTENTIODYNAMIC POLARIZATION CURVES MEASURED FOR BOTH PTFE-COATED AND UNCOATED NiTi ORTHODONTIC WIRES IN ARTIFICIAL SALIVA (pH = 4), AT 37 °C

NiTi wire	ZCP (mV vs. SCE)	j_{corr} (nA cm^{-2})	j_{pass} (μA cm^{-2})	E_{bd} (mV vs. SCE)
PTFE-coated	-620 (21)	110 (8)	0.7 (0.1)	-
Uncoated	-380 (12)	930 (23)	7.5 (0.4)	650 (7)

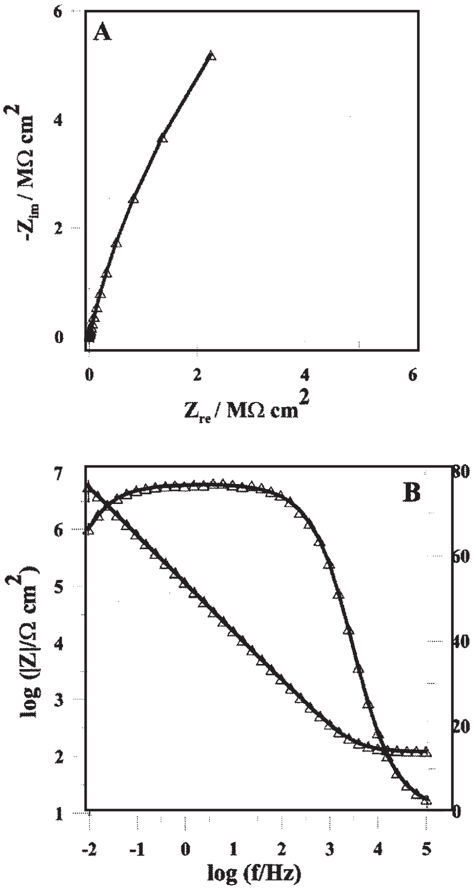

Fig. 4. Nyquist plot (A) and Bode plot (B) recorded for uncoated NiTi wire after different immersion times in artificial saliva (pH = 4), at 37 °C, measured at open circuit potential

The R_1 and Q_1 parameters describe the processes occurring at electrolyte/coating layer: R_1 is the pore resistance due to penetration of and Q_1 corresponds to the constant phase elements of the coating layer. The parameter R_2 coupled with Q_2 describes the processes at the electrolyte/substrate layer interface: R_2 is the charge transfer resistance at the electrolyte/substrate interface in the pores and Q_2 to the constant phase element at the electrolyte/substrate layer interface.

From the fitted values of table 2, some differences between the characteristics of coated layer are observed. In fact, both resistances R_1 and R_2 values of PTFE-coated NiTi wire decreases with immersion times. However, the values of R_2 were three orders of magnitude larger than R_1 at all exposures, thus revealing that substrate layer interface provides most of the corrosion protection to the material. As immersion time increases from 1-hour to 7-days, the resistance R_2 decreases from 205 M Ω cm^2 to 64 M Ω cm^2.

Despite the protecting effect of PTFE in the coating for the protection of the NiTi wire for more extended period of time, the poor sealing capacity of the coating is responsible for the later deterioration of the electrochemical behaviour of the system. In fact, new ionic pathways are developed through the coatings that probably lead to the exposure of the underlying NiTi wire to the artificial saliva [21].

For highly corrosion resistant materials, Mansfeld [22] indicated that the polarization resistance may even reach 10^6 Ω cm^2. This indicates that the PTFE-coated NiTi wire maintained 7 days in artificial saliva (pH = 4) are highly resistant to corrosion.

For the sake of comparison, Nyquist diagram (fig. 4A) and Bode spectra (fig. 4B) of the uncoated NiTi wire in artificial saliva after 7-days immersion times was also recorded.

The Nyquist plot of uncoated NiTi wire shows one capacitive arc in the high and intermediate frequency. In this case of uncoated NiTi alloy the Bode phase plots are in agreement with an EC with one time constant. The EC (fig. 3B) is characterized by one parallel combination term (RQ) in series with the resistance of the solution (R_{sql}). The R and Q describe the electrochemical characteristics of the passive oxide layer on the surface of the uncoated NiTi wire: R and Q are the resistance and constant phase element of passive layer of the uncoated NiTi wire. For the uncoated NiTi wire, the resistance of the passive layer was approximately 5 M Ωcm^2. However, charge transfer resistance at the electrolyte/substrate interface, R_2 for PTFE-coated NiTi wire, was one order of magnitude larger than resistance of the passive layer of the uncoated NiTi wire after 7-days immersion times.

Figure5 displays the experimental linear potentiodynamic polarization curves, after 7-days immersion time in artificial saliva (pH = 4) at 37 °C, for the uncoated and PTFE-coated NiTi wires

Figure 5 clearly proves that PTFE-coated NiTi wire had a better corrosion resistance than that of uncoated NiTi wire. In the case of HA-coated NiTi wire, one distinct region can be identified in the anodic branches of the polarization curves. In this region, the dissolution of HA-coated NiTi wire was under kinetic control, and the anodic current density increased very slowly with potential in the positive direction, characteristic of a passive behaviour. In contrast, the uncoated NiTi wire presents two regions. In the second region, the rapid increase in the current value is due to breakdown of the passive film. Breakdown potential (E_{bd}) of the passive film is clearly around 650 mV. Passive current density (i_{pass}) was determined from the potentiodynamic anodic branch and was taken approximately at the middle of passive range. Also, the zero current potential (ZCP) and corrosion current density (j_{corr}) values were determined by Tafel analysis for a range of ± 100 mV around of ZCP. The

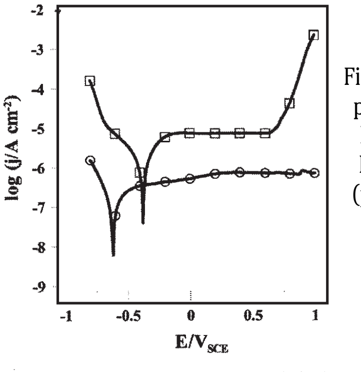

Fig. 5 Linear potentiodynamic polarization curves for both PTFE-coated and uncoated NiTi wire in artificial saliva (pH = 4), at 37 °C. Scan rate: 0.5 mV/s

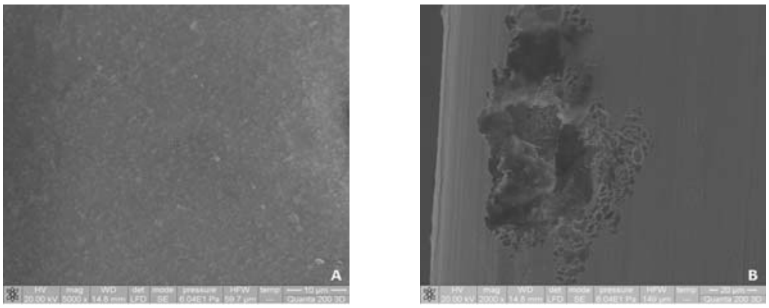

Fig. 6. (A) SEM images showing the surface of corroded: (A) PTFE-coated and (B) uncoated NiTi wire after LPP in artificial saliva (*p*H = 4), at 37 °C

average values of zero current potential (ZCP), corrosion current density (j_{corr}) and passive current density (i_{pass}) determined from the polarization curves are presented in table 2. The ZCP of the PTFE-coated NiTi wire was shifted towards a more negative potential, indicating a porous film formed on the surface [23-26]. The corrosion current density (j_{corr}) is characteristic for the degradation degree of the alloy. It is clear from figure 5 that there is a decrease of the corrosion current density of the PTFE-coated sample with respect to the uncoated sample. The corrosion and passive current density for uncoated NiTi wire is approximately ten times larger than in case of the PTFE-coated NiTi wire, when obtained in the same conditions. This demonstrates that the PTFE-coated sample has a greater corrosion resistance than the uncoated sample. The LPP observations confirm the trends presented above from EIS experiments.

SEM analysis of corroded surfaces

Figure 6A presents the SEM of PTFE-coated NiTi wire after LPP in HBSS at 37 °C. No obvious variation in the surface morphology of PTFE-coated NiTi wire was observed as result of the anodic polarization tests compared to its condition prior the testing.

A pitting corrosion of the uncoated NiTi surface wire was confirmed by SEM examination of the retrieved sample after completing the polarization tests (fig. 6B).

Conclusions

The electrochemical behaviour of uncoated and PTFE-coated NiTi orthodontic wires was evaluated by electrochemical impedance spectroscopy (EIS) and linear potentiodynamic polarization (LPP) in artificial saliva (*p*H = 4), at 37 °C. The corrosion current density for uncoated NiTi wire is approximately ten times larger than in case of the PTFE-coated NiTi wire. In case of uncoated NiTi wire, a breakdown of the passive layer was recorded. The SEM micrographs of corroded surfaces on uncoated NiTi wire confirm the pitting dissolution after LPP test. Two-layer model was used for EIS spectra considering an unsealed porous coated layer on the metallic substrate. Charge transfer values (R_2), obtained from equivalent circuit (EC), provide a quantitative basis for the corrosion monitoring of substrates covered by a polymer layer. EIS results confirm the experimental findings that coatings are not very dense. The resistance of PTFE coating decreases slowly after 7 days immersion in artificial saliva because the electrolyte advancing towards the substrate. However, the R_2 values were found to be bigger than 10^7 Ωcm^2 for the coating after exposure 7 days in artificial saliva; this indicates that the PTFE-coated NiTi wire is highly resistant to corrosion. PTFE effectively increase the corrosion resistance of the underlying NiTi substrate.

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