

TRIBO-CORROSION PROPERTIES OF A NiTi DENTAL WIRE

TRIBOKOROZIJSKE LASTNOSTI DENTALNE ŽICE NiTi

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NiTi-alloy archwires are used in dental medicine for tooth positioning. Failures are reported during the mounting and operation. It is supposed that these difficulties are results of a simultaneous presence of corrosion and mechanical wear. First, a corrosive medium was examined in order to simulate the conditions in the mouth. Different simulated body fluids were compared with natural saliva using electrochemical methods. The corrosion properties of the NiTi dental wire in the as-received state and without the surface oxide film were studied with electrochemical impedance spectroscopy. Tribo-corrosion tests of NiTi in artificial saliva were performed and a relation between the chemical and mechanical wear was studied. After the experiment, the surface was spectroscopically examined. The relation between the chemical and mechanical wear was determined.

Keywords: NiTi, simulated saliva, passive film, tribo-corrosion, electrochemical impedance spectroscopy

Žice zlitine NiTi se uporabljajo v dentalni medicini za oblikovanje zobnega loka. Med namestitvijo in uporabo se večkrat pojavijo pretrgi. Domneva se, da je vzrok sočasna korozija in mehanska obraba. Raziskava je bila najprej usmerjena v iskanje primerne korozivnega medija, ki nadomešča razmere v ustih. Z elektrokemijskimi metodami smo primerjali več različnih sintetičnih slin z vzorcem naravne sline. Korozijski preizkusi dentalne žice NiTi z oksidno plastjo (dostavljen vzorec) v primerjavi z žico brez oksidne plasti so bili izvršeni z elektrokemijsko impedančno spektroskopijo. Tribokorozijski preizkusi v umetni slini so pokazali odnos med kemijskim in mehanskim prispevkom obrabe. Po eksperimentu je bila površina spektroskopsko pregledana. Določena je bila odvisnost med kemijsko in mehansko obrabo.

Ključne besede: NiTi, umetna slina, pasivna plast, tribokorozija, elektrokemijska impedančna spektroskopija

1 INTRODUCTION

A NiTi alloy is known as a shape-memory alloy. It is able to change its shape from a deformed to its original shape if it is heated or cooled in a certain temperature range. In general, the atomic composition of the alloy is 50 % Ni and 50 % Ti. A dental NiTi alloy wire is subjected to the mechanical and corrosive wear, known as tribo-corrosion processes. Tribo-corrosion is a complex process and its parameters include corrosion, deformation, friction and mechanical wear. The total wear of a material within a tribo-corrosion system is a combination of all these factors. Destructive effects of one factor on another one cannot be controlled and they are difficult to predict. The corrosion environment of dental wires includes several factors (saliva, food, drink), and, occasionally, also chemical abrasives (toothpaste, gels and mouthwashes). It is difficult to include all the factors and influences in the electrochemical experiments, so the research has been limited to the factor that is constantly present – the saliva.

In most cases the studies on a NiTi alloy are electrochemical researches.¹⁻⁵ There are some researches that investigate different surface finishes^{4,6-9} with the aim to improve the surface since nickel is known to be a potentially allergenic material. There are some studies that investigate the problems of pitting¹ and crevice corrosion^{2,3,6} on the NiTi alloy.

Since the NiTi alloy is primarily used for biomedical purposes, the electrochemical research of the material properties often uses a variety of simulated human fluids. For the studies of the biomaterial properties in the body, different simulated body fluids are used like: simulated body fluid (SBF),⁷ Hank's solution^{1,3,4,8} and solutions of NaCl with different concentrations.^{2,9} For the corrosion studies of dental materials, several different artificial salivas were used such as the artificial salivas according to Fusayama^{5,10,11} and Duffo et al.¹²

There are very few studies of the NiTi alloy with an emphasis on tribo-corrosion. Only tribological properties of NiTi alloys are reported.^{13,14} Zhang and Farhat¹³ found that the NiTi-alloy wear resistance is about 30 times greater than that of pure titanium, and about 10 times greater than that of pure nickel. Abedini and colleagues¹⁴ tested the tribological behaviour of a NiTi alloy in the austenitic and martensitic phase forms. They noted that plastic deformation dominates in the martensitic phase and fatigue wear dominates in the austenite phase.

The aim of the present study is to investigate the electrochemical properties of a NiTi alloy in an artificial saliva to learn about the corrosion properties of a dental wire and to define the effect of the wear on the corrosion properties of the dental wire.

2 EXPERIMENTAL WORK

The following types on the NiTi alloy were used in the study:

- a NiTi dental alloy (a 3M orthodontic wire, super-elastic, 0.48 mm × 0.64 mm, Orthoform III Ovoid, Upper) for EIS (electrochemical impedance spectroscopy) and tribo-corrosion;
- a NiTi sheet (alloy BB NiTi, 2 mm sheet, super-elastic, flat annealed, surface-oxide free (pickled), Memry GMBH) for the basic electrochemical study.

NiTi dental-wire samples were investigated for two different surface finishes, first in the as-received state (with the suppliers' finish) and later the surface was abraded with the 1200-grid SiC paper.

Before measuring, the samples were ultrasonically cleaned in ethanol, washed with distilled water and then well dried. For the selection of the most appropriate simulated saliva, natural saliva was compared to six different compositions of simulated saliva proposed by various authors. Duffo¹² (0.6 g/L NaCl, 0.72 g/L KCl, 0.22 g/L CaCl₂·2H₂O, 0.68 g/L KH₂PO₄, 0.856 g/L Na₂HPO₄·2H₂O, 0.06 g/L KSCN, 1.50 g/L KHCO₃, 0.03 g/L citric acid); Ericsson¹² (0.584 g/L NaCl, 0.34 g/L KH₂PO₄, 1.50 g/L KHCO₃, 0.029 g/L citric acid, 0.34 g/L Na₂HPO₄, 0.166 g/L CaCl₂, 0.014 g/L MgCl₂); Hank¹² (8.0 g/L NaCl, 0.4 g/L KCl, 0.6 g/L KH₂PO₄, 0.06 g/L Na₂HPO₄·12H₂O, 0.10 g/L MgCl₂·6H₂O, 0.35 g/L NaHCO₃, 0.06 g/L MgSO₄·7H₂O, 1.0 g/L glucose, 0.60 g/L Na₂HPO₄, 0.14 g/L CaCl₂); Fusayama¹¹ (0.4 g/L NaCl, 0.4 g/L KCl, 0.906 g/L CaCl₂·2H₂O, 0.69 g/L KH₂PO₄, 0.05 g/L Na₂S·9H₂O); simulated body fluid (SBF)¹⁵ (8.18 g/L NaCl, 0.22 g/L KCl, 0.13 g/L KH₂PO₄, 0.07 g/L Na₂SO₄, 0.35 g/L NaHCO₃, 0.36 g/L CaCl₂, 0.30 g/L MgCl₂); NaCl + lactic acid¹² (5.844 g/L NaCl, 9.008 g/L lactic acid).

The natural-saliva collection was conducted in two consecutive days. During collecting the saliva was stored in a refrigerator at 2 °C. The donor of the saliva did not eat any food or drink for 1 h before, and during the collection. The procedure took place more than 1 h after the last teeth cleaning. To stimulate the saliva secretion, the donor was asked to chew a parafilm and drink only water.

The electrochemical testing was executed in a three-electrode corrosion cell with a SCE reference electrode and a graphite counting electrode. After 2 h stabilization at the open-circuit potential (OCP) potentiodynamic measurements were performed starting at -0.25 V vs. the OCP and progressing up to +2.0 V at the scan rate of 1 mV/s. A Gamry Instruments potentiostat/galvanostat (ZRA Reference 600, USA, 2006) was used.

For EIS measurements an Autolab PGSTAT100 potentiostat/galvanostat, with a NOVA 1.6 module was used. The frequency scan ranged from 65 kHz to 1 mHz at 10 points per decade with an AC amplitude of ± 10 mV. The absolute impedance and phase angle were

measured at each frequency. The impedance measurements were carried out at the open-circuit potential (OCP) at different times of the immersion (2, 8, 24 and 72) h in the electrolyte. All the measurements were conducted in a Duffo simulated saliva. The impedance data were interpreted on the basis of the equivalent electrical circuits, using the Zview (Scribner) program for fitting the experimental data.

The tribo-corrosion tests were performed with a reciprocal tribometer (Tribotechnic, a pin-on-disc and reciprocating tribometer, 2009, France) in a Teflon cell with a platinum wire as the counter electrode and Ag/AgCl as the reference electrode. The counter body was a Al₂O₃ ball 6 mm. The length of the wear track was 10 mm, the sliding speed was 5 mm/s and the loads were 1 N and 2 N.

3 RESULTS AND DISCUSSION

3.1 Selection of an appropriate corrosion media

Figure 1 shows a potentiodynamic measurement of a NiTi alloy in different artificial saliva solutions and in natural saliva. The corrosion potential, E_{corr} , and the current density, j_{corr} , were defined by adjusting the tangents of the anodic and cathodic parts of the potentiodynamic curve in the Tafel region. The corrosion current density of the NiTi alloys in natural saliva was $46 \cdot 10^{-9} \text{ A cm}^{-2}$. The most similar result was obtained for the saliva proposed by Duffo,¹² where the current density was $70 \cdot 10^{-9} \text{ A cm}^{-2}$. Higher corrosion current densities were obtained for the other artificial salivas (**Table 1**). The current densities in the passive regions were similar in all the tested solutions, being approximately $3 \cdot 10^{-6} \text{ A cm}^{-2}$.

The breakdown potential value, E_b , was the same in Duffo's solution and in natural saliva, 1.1 V. The width of the passive area for the NiTi samples in natural saliva and in Duffo's solution were similar, 1.08 V for natural saliva and 1.06 V for Duffo's solution. All the other investigated solutions had their breakdown potentials at higher potential values and their widths of the passive areas differed from the values obtained in natural saliva. The highest values of the breakdown potential were measured in the solution of lactic acid with an addition of NaCl ($E_b = 1.40 \text{ V}$) and in Fusayama's artificial saliva ($E_b = 1.28 \text{ V}$).

After comparing the measurement results for the NiTi alloy in natural saliva with the results obtained in the artificial salivas, it is evident that the artificial saliva solution proposed by G. S. Duffo¹² shows the greatest similarity to natural saliva. The artificial saliva prepared with Duffo's procedure was used for further electrochemical measurements.

3.2 Electrochemical impedance spectroscopy

The electrochemical-impedance-spectroscopy results for the NiTi dental wire in a simulated saliva solution at

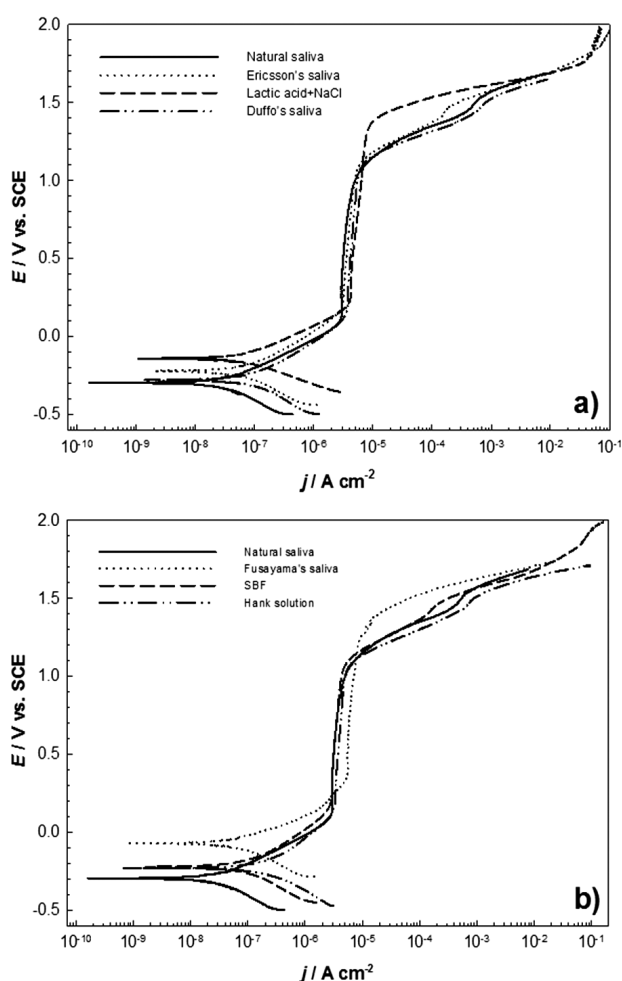


Figure 1: Potentiodynamic curves for the NiTi alloy in different simulated body solutions: a) Fusayama's saliva, SBF and Hank's solution compared to natural saliva, b) Ericsson's saliva, NaCl with the lactic acid and Duffo's saliva compared to natural saliva, at a scan rate 1 mV/s

Slika 1: Potenciodinamične krivulje za zlitino NiTi v različnih umetnih slinah: a) slina Fusayama, SBF in Hank primerjava z naravno slino, b) slina Ericsson, NaCl z mlečno kislino in Duffo-slina, primerjava z naravno slino, hitrost preleta 1 mV/s

Table 1: Electrochemical parameters for the NiTi alloy in different simulated saliva solutions compared with natural saliva

Tabela 1: Elektrokemijski parametri za zlitino NiTi v različnih raztopinah umetne sline v primerjavi z naravno slino

	$E_{\text{corr}} / \text{V}$	$j_{\text{corr}} / (\text{A cm}^{-2})$	E_b / V	$\Delta(E_b - E_{\text{pp}}) / \text{V}$
Natural saliva	-0.30	$46 \cdot 10^{-9}$	1.10	1.08
Fusayama's saliva	-0.13	$78 \cdot 10^{-9}$	1.28	1.00
Ericsson's saliva	-0.21	$114 \cdot 10^{-9}$	1.10	0.90
SBF	-0.25	$81 \cdot 10^{-9}$	1.15	1.04
Hank's solution	-0.23	$147 \cdot 10^{-9}$	1.15	1.03
Lactic acid + NaCl	-0.16	$124 \cdot 10^{-9}$	1.40	1.20
Duffo's saliva	-0.32	$71 \cdot 10^{-9}$	1.10	1.06

different immersion times are presented as Nyquist plots and Bode diagrams in **Figures 2 and 3**.

The impedance spectra consist of a high-frequency intercept with the abscise axis and the main-frequency

semicircle. It can be seen at different immersion times on **Figures 2 and 3** that the impedance response increases with the time. There is a small difference in the profiles of the high- and medium- frequency regions, but a great difference in the responses at the lower frequencies.

The impedance spectra were fitted with the Randles equivalent circuit, as presented in **Figure 3**. The equivalent circuit consists of the resistance and capacitance elements due to the oxide film (RC) that are in the series with R_e , representing the electrolyte resistance.

R and Q represent the properties of the outer porous and passive film/solution interface reactions. The Q symbol signifies the possibility of a non-ideal capacitance (a constant-phase element, CPE) with n varying from 0.939 to 0.952 for the impedance data at different immersion times. The impedance of the CPE is given by:¹⁶

$$Q = Z_{CPE}(\omega) = [C(j\omega)^n]^{-1} \quad (1)$$

For $n = 1$, the Q element is reduced to a capacitor with the C capacitance and for $n = 0$, to a simple resistor.

The values of the fitted parameters of the equivalent circuit at four different immersion times and different potentials are presented in **Table 2**.

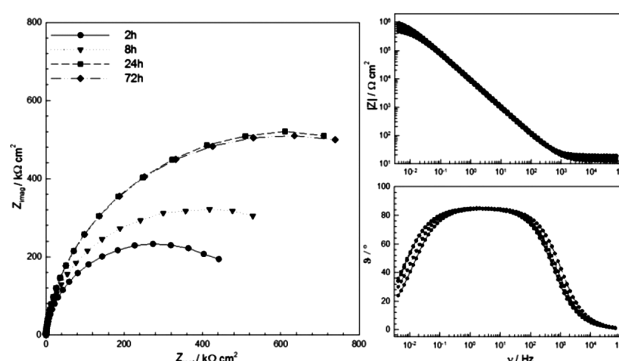


Figure 2: Nyquist and Bode plots for the NiTi dental wire in the as-received state at the OCP for different immersion times in the simulated saliva

Slika 2: Nyquistov in Bodejev diagram za dentalno žico NiTi v dostavljenem stanju pri OCP po različnih časih namakanja v umetni slini

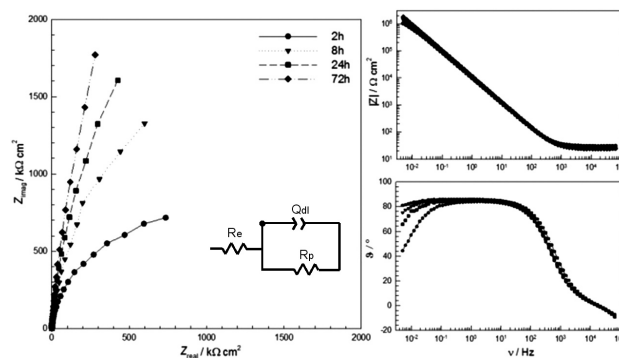


Figure 3: Nyquist and Bode plots for the NiTi dental wire without an oxide film at the OCP for different immersion times in the simulated saliva

Slika 3: Nyquistov in Bodejev diagram za dentalno žico NiTi brez oksidne plasti pri OCP po različnih časih namakanja v umetni slini

Table 2: Values of the fitted parameters of the equivalent circuit as a function of the applied potential at different immersion times**Tabela 2:** Vrednosti prilagojenih parametrov nadomestnega vezja v odvisnosti od uporabljenega potenciala pri različnih časih namakanja

NiTi wire in the as-received state	<i>CPE</i>	<i>n</i>	<i>R_p</i> / (kΩ cm ²)	<i>C</i> / (F cm ⁻²)
2 h	$2.25 \cdot 10^{-5}$	0.939	517	$2.64 \cdot 10^{-5}$
8 h	$2.10 \cdot 10^{-5}$	0.941	704	$2.49 \cdot 10^{-5}$
24 h	$1.91 \cdot 10^{-5}$	0.941	1104	$2.31 \cdot 10^{-5}$
72 h	$1.65 \cdot 10^{-5}$	0.943	11250	$1.99 \cdot 10^{-5}$
NiTi without the oxide film	<i>CPE</i>	<i>n</i>	<i>R_p</i> / (kΩ cm ²)	<i>C</i> / (F cm ⁻²)
2 h	$1.79 \cdot 10^{-5}$	0.938	1470	$2.22 \cdot 10^{-5}$
8 h	$1.64 \cdot 10^{-5}$	0.947	4470	$2.09 \cdot 10^{-5}$
24 h	$1.57 \cdot 10^{-5}$	0.951	9330	$2.03 \cdot 10^{-5}$
72 h	$1.50 \cdot 10^{-5}$	0.952	20400	$2.00 \cdot 10^{-5}$

The R_e parameter has a value from $15 \Omega \text{ cm}^2$ to $24 \Omega \text{ cm}^2$ and it is ascribed to the electrolyte resistance. The R values are increasing with the immersion time, showing that the oxide film on the NiTi alloy has an increasing resistance. The CPE , denoted as Q , was recalculated using equation¹⁷ $C = [R^{1-n} Q]^{1/n}$ in order to compare the capacitance values for the NiTi dental alloy at different immersion times.

A decrease in the C value can be attributed to the thickening of the oxide layer. The thickening effect is larger in the case of the as-received oxide film than in the case of the oxide film naturally grown during the immersion in the simulated saliva. A similar effect was already observed in^{18–20}.

Based on equation:

$$d = (\epsilon) (\epsilon_0) (A) / C \quad (2)$$

where ϵ is the value for the dielectric constant, d is the thickness of the film, ϵ_0 is $8.85 \cdot 10^{-14} \text{ F/cm}$ and A is the surface area (cm^2), the thickness of the oxide layer can be estimated. The decrease in capacitance points occurs with the increase in the thickness of the passive layer. This thickness growth is larger at the early immersion times at the OCP.

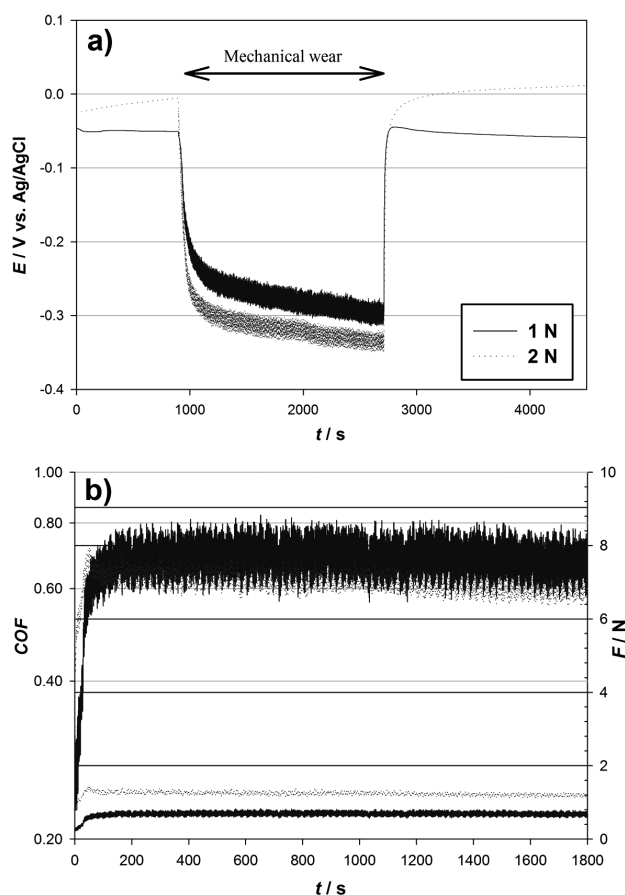
Assuming the value of 48 for the dielectric constant,²¹ the thickness determined with EIS can be calculated. The calculated thickness of the oxide film on the NiTi wire is approximately 1 nm and in the case when the oxide film was abraded during the 2 h immersion, the thickness is 2 nm.

The measured impedance spectra and the recalculated values show that the polarization resistance of the oxide films, immersed in a simulated saliva increases with the time of immersion. It is larger for the freshly polished oxide films on the NiTi wires than in the case of the as-received NiTi wires. Also, the impedance results show that the former oxide layer might be thinner and less protective than the oxide film formed during the immersion in a simulated saliva solution.

Even if the oxide layer on the NiTi wire is damaged, a quick repassivation is expected.

3.3 Tribo-corrosion

Due to a slightly more demanding form of the wire (the wire width of 0.64 mm) and the width of the wear track made with the 2 N force, which was up to 0.6 mm, the experiments with higher loads were not conducted. **Figure 4** shows a tribo-corrosion experiment on the dental NiTi wire worn by the 1 N and 2 N forces. The coefficients of friction (COF) were high, ≈ 0.7 , and the increase was intense in the first 50 s; after that the value of the COF was fairly constant. Near the end of the rubbing period, the COF value was registered and it was 0.75 for the load of 1 N and 0.65 for the load of 2 N. The COF fluctuations were smaller when the load of 2 N was applied. During the mechanical wear with 2 N load, the recorded potential was lower by 0.08 V than in the case of the test with the 1 N load. It was found that during the mechanical wear the potential and the coefficients of friction were stable and the fluctuation window was fairly narrow. These findings can also be attributed to the homogeneous surface. After the mechanical wear in the tribo-corrosion tests, the repassivation was fast, appro-

**Figure 4:** Monitoring of the: a) electrochemical potential, b) coefficient of friction and force vs. time during the tribo-corrosion test on the dental NiTi wire in a Duffo solution

Slika 4: Spremljanje: a) elektrokemijskega potenciala, b) koeficienta sile trenja v odvisnosti od trajanja tribokorozijskega preizkusa žice NiTi v Duffo-raztopini

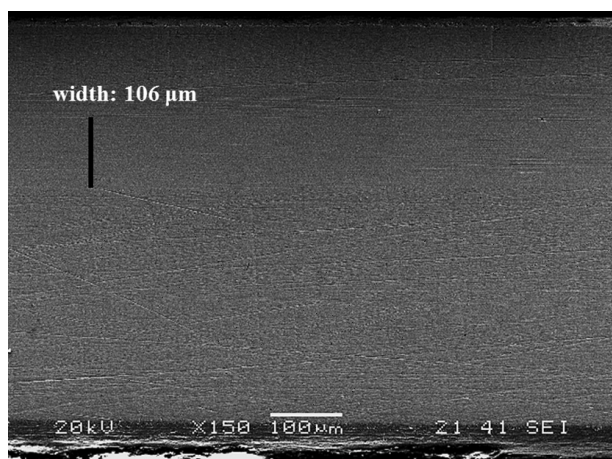


Figure 5: SEM image of the wear track of the NiTi dental wire after the tribo-corrosion test with the normal load of 1 N

Slika 5: SEM-posnetek sledi obrabe na dentalni žici NiTi po tribo-korozijskem preizkusu z obtežbo 1 N

ximately 30 s, showing fairly good repassivation properties of the NiTi dental alloy.

In **Figure 5**, a SEM image presents the wear track on the NiTi alloy after the tribo-corrosion test with the load of 1 N. The wear track is hardly visible, most likely due to the homogeneous surface and the large hardness of the NiTi alloy.¹³ The hardness of the NiTi dental alloy in the wear track was about 400 HV. The width of the wear track depending on the normal load was 106 μm for the 1 N load. In the case of the higher load of 2 N (not shown) the width of the wear track was about 135 μm.

We tried to define the prevailing wear mechanism by observing the characteristic changes in the surface topography and the microstructure of the thin zone below the rubbing surface. The wear particles were not found during the mechanical wear of the dental alloy. The wear track was smoothly worn, as already indicated by the small changes in the coefficient of friction. The SEM image did not give any additional information on the possible wear-mechanism properties. Since a considerable electrochemical change was detected by measuring the corrosion potential, one can assume that an oxidative wear as a tribo-corrosion phenomenon took place, combining the mechanical wear and oxidation.

4 CONCLUSIONS

A comparison between different solutions and natural saliva was made to study and determine realistic conditions. Furthermore, the corrosion and tribo-corrosion properties of a NiTi dental alloy in artificial saliva were studied.

Different solutions simulating the body fluids were tested with electrochemical techniques in order to find a solution that most closely represents the appropriate effects of natural saliva on the electrochemical properties of the NiTi alloy.

From the electrochemical impedance spectroscopy results it was clear that a NiTi-alloy archwire has a good corrosion resistance. By comparing two samples with different surfaces it could be concluded that the wire without the oxide film has better corrosion properties than the wire in the as-received state.

In the tribo-corrosion study it was found that the effect of the mechanical wear is fairly strong and the coefficients of friction are high. Heavy pressures on the surface accelerate the corrosion of the NiTi dental wire.

It can be concluded that the mechanical wear also has a great effect on the NiTi dental wire used in realistic conditions. It was evidenced that the NiTi alloy has good repassivation abilities.

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