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Effect of pH, fluoride and hydrofluoric acid concentration on ion release from NiTi wires with various coatings

Visnja KATIC¹, Lidija CURKOVIC², Magdalena UJEVIC BOSNJAK³, Kristina PEROS⁴, Davor MANDIC⁵ and Stjepan SPALJ¹

¹ Department of Orthodontics, Faculty of Medicine, University of Rijeka, Kresimirova 40, 51000 Rijeka, Croatia

² Department of Materials, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, I. Lucica 5, 10000 Zagreb, Croatia

³ Water Safety Department, Croatian National Institute of Public Health, Rockefellerova 7, 10000 Zagreb, Croatia

⁴ Department of Pharmacology, School of Dental Medicine, University of Zagreb, Gundulićeva 5, 10000 Zagreb, Croatia

⁵ Research Center for Metals in the Region of Istria—METRIS, Zagrebacka 30, 52100 Pula, Croatia

Corresponding author, Visnja KATIC; E-mail: visnja.katic@medri.uniri.hr

Aim was to determine effect of pH, fluoride (F⁻) and hydrofluoric acid concentration (HF) on dynamic of nickel (Ni²⁺) and titanium (Ti⁴⁺) ions release. Nickel-titanium wires with untreated surface (NiTi), rhodium (RhNiTi) and nitride (NNiTi) coating were immersed once a week for five min in remineralizing agents, followed by immersion to artificial saliva. Ion release was recorded after 3, 7, 14, 21 and 28 days. Pearson correlations and linear regression were used for statistical analysis. Release of Ni²⁺ from NiTi and NNiTi wires correlated highly linearly positively with HF (r=0.948 and 0.940, respectively); for RhNiTi the correlation was lower and negative (r=-0.605; p<0.05). The prediction of Ti⁴⁺ release was significant for NiTi (r=0.797) and NNiTi (r=0.788; p<0.05) wire. Association with F⁻ was lower; for pH it was not significant. HF predicts the release of ions from the NiTi wires better than the pH and F⁻ of the prophylactic agents.

Keywords: Topical fluoride, Mass spectrometry, Nickel-titanium alloy, Orthodontic wires, Surface properties

INTRODUCTION

Various modifications of the surface of NiTi archwires are being introduced in attempt to keep wires' excellent working properties while improving their aesthetic appearance and reducing susceptibility to corrosion^{1,2}. Nitrogen ion implantation leads to surface composition changes from NiTi to TiN (titanium nitride), replacing known allergen nickel with inert nitrogen. Improvement of the corrosion resistance of NiTi wire with nitrified surface compared to the uncoated NiTi wire was confirmed in previous electrochemical researches performed in artificial saliva and fluoride mouth rinse solution^{1,3,4}. Rhodium is a noble metal with white reflective appearance and excellent anti-corrosion properties⁵, but in the commercially available wires it was noted that this aesthetic feature diminishes fast within oral cavity^{6,7}. Also, it was found that this surface coating was uneven and non-homogeneous, which caused susceptibility to corrosion in artificial saliva, due to formation of galvanic coupling of underlying NiTi to noble metals in the surface coating²⁻⁴. There are no data available regarding the interaction between the rhodium coating and fluoride solutions.

Design of fixed orthodontic appliance enables retention of plaque which reflects in rapid change in microbial composition; with increase in acidogenic Streptococcus and Lactobacillus species^{8,9}. Lactic acid is the metabolic product that keeps the pH of the plaque low (in 24 h plaque pH is 4.8)^{9,10}; also, during longer inactive periods (e.g. sleeping) the pH of saliva is below 5, as well as after food intake (increase in bacterial

metabolism also causes drop of the pH of saliva below 5)^{11,12}.

Prophylactic agents are being used as adjuvant therapy during an orthodontic treatment to combat increased incidence of white spot lesions¹³. Adjuvant fluorides and calcium are being used for surface and subsurface remineralization¹⁴, and repeated administration of adjuvant prophylactic agents is recommended and necessary for maintenance of intact tooth surface in conditions of challenged oral hygiene¹⁵. Fluorides interact with the nickel-titanium (NiTi) orthodontic archwires, where protective titanium-oxide (TiO₂) layer on surface of the wires forms complexes with fluorides, and leads to surface corrosion, releasing nickel (Ni²⁺) and titanium (Ti⁴⁺) into adjacent tissue and saliva¹⁶. The metal forming more stable corrosion products corrodes slower; therefrom the Ni²⁺ ions are being released into the environment more than the Ti⁴⁺ ions¹⁷.

Previous research recorded the highest Ni²⁺ ion release from fixed orthodontic appliances during the first week of immersion in artificial saliva, and significant retardation in the Ni²⁺ ion release with prolonged immersion time^{18,19}. The titanium tends to form passive oxide layer on the surface, it was not established whether repeated application of fluoride containing agents reduces capability to restore TiO₂ protective layer on the NiTi wires, and affects the wire's corrosion susceptibility. Furthermore, if the protective ceramic or metallic coatings are non-homogeneous or contain micro cracks, there is a potential for formation of the localised corrosion within the underlying alloy due to

the invasion of the corrosive agent²⁰. Damaged surface layers increase the nickel ion release from the NiTi wire and consequently reduce the wire's biocompatibility, which can manifest as the hypertrophic gingival tissue and hypersensitivity reactions^{16,21}.

The fluoride concentration (F^-) and the pH of the solution influence the corrosion susceptibility of the NiTi wires^{1,22,23}, where the acidic fluoride environment favours the formation of the hydrofluoric acid (HF) which destroys the TiO_2 ²⁴. The influence of regular weekly application of remineralizing agents on wire's corrosion resistance and the dynamic of the release of ions from NiTi wires have not been established. Also, the influence of the type of coating on ion release from NiTi wires during regular use of remineralizing agents was not determined. Commercially available fluoride containing agents have many adjuvant ingredients, in range from phosphoric acid (used to decrease the pH of the agent) to various aromas (to improve flavour). Because of all this co-founding factors, this research tried to single out the most important contributors, which are common to various prophylactic re-mineralizing agents. The data on F^- and pH are easily available from the data sheet for every commercial prophylactic re-mineralizing agent, while the HF can be calculated from the F^- and pH. Therefore, this study aims to determine effect of pH, F^- and HF concentration on dynamic of the release of nickel (Ni^{2+}) and titanium (Ti^{4+}) ions from NiTi wires with various coatings induced by repeated weekly use of the fluoridated remineralizing agents.

MATERIALS AND METHODS

Materials

Preformed NiTi orthodontic archwires in dimensions 0.508×0.508 mm BioForce Sentalloy (Dentsply GAC, NY, USA) were used in this study. The wire types used were: 1) NiTi with untreated surface; 2) rhodium coated NiTi (High Aesthetic); 3) nitride coated NiTi (IonGuard). Their chemical composition (titanium 49–50 wt%, nickel 50–51 wt%) was determined with the help of the atomic absorption spectrometry on Atomic Absorption Spectrophotometer, type AA 6800 (Shimadzu, Kyoto, Japan). The wire specimens for the AAS were dissolved in the concentrated acids' mixture of hydrofluoric acid (HF), hydrochloric acid (HCl), and nitric acid (HNO_3) (ratio HCl:HF: HNO_3 ; 2:1:1; v/v/v). The operating parameters were: wave length (364.3 nm (Ti); 232 nm (Ni)); slit (0.5 nm (Ti); 0.2 nm (Ni)); and gas/oxidant (C_2H_2/N_2O (Ti); C_2H_2 /air (Ni)). Calibration specimens were prepared from standard solutions (1,000 mg/L (Ti); 100 mg/L (Ni)).

Commercial fluoride agents were used: 1) Elmex gelée (Gaba, Lörrach, Germany); 2) Mirafleur-k-gel (Hager&Werken, Duisburg, Germany); 3) MI Paste Plus (GC, Tokyo, Japan). These prophylactic agents are usually applied once a week on teeth, as recommended by manufacturers. Testing media were heated in a water bath at 37°C, and their pH value was recorded with the pH meter MP 220 (Mettler Toledo, Greifensee,

Switzerland). The pH values were: Mirafleur-k-gel 5.1; Elmex gelée 5.5; MI Paste Plus 6.6. The F^- was measured with fluoride-ion selective electrode on Expandable Ion Analyzer EA 940 (Orion Research, Beverly, MA, USA). Average F^- was: 1) Elmex gelée 11273.3 ppm; 2) Mirafleur-k-gel 6171.1 ppm; 3) MI Paste Plus 816.4 ppm. The HF was calculated from the F^- , the pH of the remineralizing agents and the HF acid dissociation constant ($pK_a=3.17$) according to the equation: $[HF]=[F^-]/10^{pH-pK_a}$ ²⁵. The HF used for further analysis were: 1) MI Paste Plus 0.32 ppm; 2) Elmex gelée 53.88 ppm; 3) Mirafleur 71.31 ppm.

Artificial saliva solution was prepared from 1.5 g/L KCl, 1.5 g/L $NaHCO_3$, 0.5 g/L $NaH_2PO_4-H_2O$, 0.5 g/L KSCN, 0.9 g/L lactic acid, pH value 4.8, as used in previous research^{3,4,26,27}. The artificial saliva with the pH of 4.8 was used as imitation of more aggressive environment, which can be found in persons susceptible to caries; in such cases the prescription of adjuvant prophylactic agents would be recommended^{15,28,29}.

Methods

The wire specimens, each 10 cm long and 2 cm² in surface, were immersed in 10 mL of artificial saliva and kept in a heated water bath at 37°C. At one week intervals, the wires were taken out of the artificial saliva, and immersed in MI Paste Plus, Mirafleur-k-gel and Elmex gelée for five min at 37°C. Afterwards, the wire specimens were rinsed with distilled water and immersed to fresh artificial saliva. The Ni^{2+} and Ti^{4+} ion release was recorded after 3, 7, 14, 21 and 28 days of immersion. Released Ni^{2+} and Ti^{4+} ions were measured by inductively coupled plasma-optical emission spectroscopy on Thermo Elemental "IRIS Intrepid II" XSP, Duo, (Thermo Electron, Austin, TX, USA). The average daily nickel release during the observed period was calculated for two wires (for upper and lower dental arch), in order to translate the results to clinical setting and address the aspect of biocompatibility³⁰. All experiments were done in triplicate.

Surface characterization was employed to demonstrate and help clarify corrosion processes, as they primarily occur on the wire's surface. Upon completion of the ion release immersion protocol, one wire from every experimental group was taken for surface analysis to record surface changes related to ion release. Visual inspection of the surface was done with the scanning electron microscopy (SEM) FEG QUANTA 250 (FEI Company, Eindhoven, The Netherlands) at magnification ×2,000. The analysis of the chemical composition of the surface and near surface areas (four different spots on one wire from every experimental group, both bright and dark areas) was done with the use of energy-dispersive spectroscopy (EDS) QUANTAX EDS (Bruker, Karlsruhe, Germany).

Statistical methods

The sample size was based on a priori power analysis. For the expected correlation coefficient $r=0.75$, the statistical power $\beta=80\%$ and significance level $\alpha=95\%$,

the needed minimum sample size for testing of correlations and the regression analysis describing ion release influenced by the HF concentration equals 11, for every wire type (MedCalc 14.8.1, MedCalc Software, Ostend, Belgium). Pearson correlation and linear regression were used to explore influence of the pH value, total fluoride concentration and HF concentration in prophylactic agents on the ion release from the orthodontic wires. Effect sizes *i.e.* the magnitude of relationship was estimated by using r and R^2 . The SPSS 10.0 (SPSS, Chicago, IL, USA) was used for all analysis, statistical significance was pre-set to $p < 0.05$.

Previously published results from wires' immersion to the artificial saliva alone were used for comparison³⁾.

RESULTS

Release of Ni^{2+} and Ti^{4+} ions

The release of Ni^{2+} and Ti^{4+} ions from the three wire types combined with various remineralizing agents is shown in columns (for measured time intervals), and as lines (total amount) over time in Fig. 1. The NiTi and NNiTi wires showed similar behaviour in remineralizing agents, with most of the ions released after immersion to the media with the highest HF concentration. The

RhNiTi wire released most of the ions in combination with the media with the lowest HF concentration.

Correlation between the pH, F^- and HF concentration in remineralizing agents and the release of Ni^{2+} and Ti^{4+} ions

Table 1 shows the correlations between the release of the Ni^{2+} and Ti^{4+} ions from the tested wires and the pH value, F^- and HF in remineralizing agents determined with the Pearsons correlations. The HF from the remineralizing agents exhibited the highest correlation with the release of the ions from the NiTi wires. The release of the Ni^{2+} ions from the NiTi and NNiTi wires increased with the increase in the HF of the remineralizing agent. Contrary, the increase in the HF caused decrease in the release of the Ni^{2+} ions from the RhNiTi wires.

The linear regression models for prediction of the release of Ni^{2+} ions from the HF concentration were significant for all three wire types (Table 2). Prediction was strong for the NiTi ($r=0.948$) and the NNiTi ($r=0.940$), but moderate for the RhNiTi ($r=-0.605$; $p < 0.05$). Increase of the HF concentration for 1 ppm causes increase of the Ni^{2+} ion release for $0.582 \mu\text{g}/\text{cm}^2$ for the NiTi, and $0.622 \mu\text{g}/\text{cm}^2$ for the NNiTi wire (Table 2). Contrary, the increase of the HF concentration for

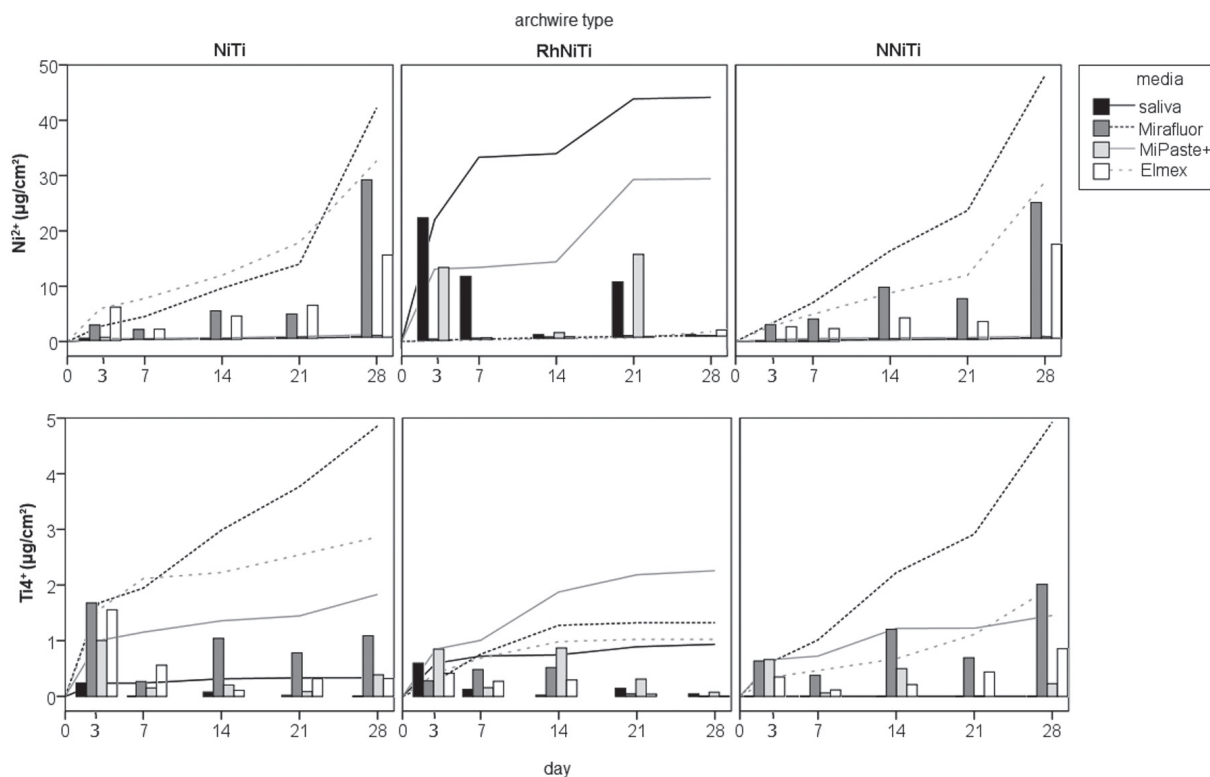


Fig. 1 The release of nickel (Ni^{2+}) and titanium (Ti^{4+}) ions over time from the uncoated (NiTi), rhodium coated (RhNiTi) and nitride coated (NNiTi) nickel-titanium wires is shown in columns (for measured time intervals), and as lines (total amount). Samples marked as “saliva” were exposed only to artificial saliva; “MiPaste+, Elmex; Mirafluor” were exposed to the artificial saliva and prophylactic agents MI Paste Plus; Elmex gelée; Mirafluor-k-gel, respectively.

Table 1 Correlation between nickel (Ni^{2+}) and titanium (Ti^{4+}) ion release from the uncoated (NiTi), rhodium coated (RhNiTi) and nitrified (NNiTi) wires and the pH, fluoride (F^-) concentration and hydrofluoric acid (HF) concentration determined with the Pearsons correlations

Wire type		Ti^{4+} ($\mu\text{g}/\text{cm}^2$)	pH	F^- (ppm)	HF (ppm)
NiTi	Ni^{2+} ($\mu\text{g}/\text{cm}^2$)	0.873*	-0.302	0.752*	0.948*
	Ti^{4+} ($\mu\text{g}/\text{cm}^2$)	—	-0.302	0.506	0.797*
	pH	—	—	-0.108	-0.325
	F^- (ppm)	—	—	—	0.787*
RhNiTi	Ni^{2+} ($\mu\text{g}/\text{cm}^2$)	0.394	0.130	-0.555	-0.605*
	Ti^{4+} ($\mu\text{g}/\text{cm}^2$)	—	0.481	-0.207	-0.187
	pH	—	—	-0.108	-0.325
	F^- (ppm)	—	—	—	0.787*
NNiTi	Ni^{2+} ($\mu\text{g}/\text{cm}^2$)	0.850*	-0.324	0.652*	0.940*
	Ti^{4+} ($\mu\text{g}/\text{cm}^2$)	—	-0.070	0.396	0.788*
	pH	—	—	-0.108	-0.325
	F^- (ppm)	—	—	—	0.787*

* $p < 0.05$

Table 2 Linear regression models for prediction of nickel ion release from the uncoated (NiTi), rhodium coated (RhNiTi) and nitrified (NNiTi) wires in correlation with the hydrofluoric acid (HF) concentration

Model		Unstandardized coefficient B	Std. Error	Standardized coefficient Beta	p
NiTi	Constant	0.970	2.757	—	—
	HF (ppm)	0.582	0.062	0.948	<0.001
RhNiTi	Constant	36.266	10.170	—	—
	HF (ppm)	-0.547	0.228	-0.605	0.037
NNiTi	Constant	0.110	3.180	—	—
	HF (ppm)	0.622	0.071	0.940	<0.001

NiTi: $R=0.948$; $R^2=0.899$; Adj. $R^2=0.889$

RhNiTi: $R=0.605$; $R^2=0.366$; Adj. $R^2=0.303$

NNiTi: $R=0.940$; $R^2=0.884$; Adj. $R^2=0.873$

Table 3 Linear regression models for prediction of titanium ion release from the uncoated (NiTi), rhodium coated (RhNiTi) and nitrified (NNiTi) wires in correlation with the hydrofluoric acid (HF) concentration

Model		Unstandardized coefficient B	Std. Error	Standardized coefficient Beta	p
NiTi	Constant	0.992	0.505	—	—
	HF (ppm)	0.047	0.011	0.797	0.002
RhNiTi	Constant	1.568	0.433	—	—
	HF (ppm)	-0.006	0.010	-0.187	0.561
NNiTi	Constant	0.570	0.533	—	—
	HF (ppm)	0.048	0.012	0.788	0.002

NiTi: $R=0.797$; $R^2=0.636$; Adj. $R^2=0.599$

RhNiTi: $R=0.187$; $R^2=0.035$; Adj. $R^2=0.062$

NNiTi: $R=0.788$; $R^2=0.622$; Adj. $R^2=0.584$

Table 4 Average daily nickel (Ni^{2+}) ion release from the three types of orthodontic wires immersed in different media through periods of time (Ni^{2+} $\mu\text{g}/\text{day}$)

Wire type	Media type	Ni^{2+} $\mu\text{g}/\text{day}$				
		1st–3rd day	4th–7th day	8th–14th day	15th–21st day	22nd–28th day
NiTi	AS+MiPaste	1.13	0	0.11	0.21	0.30
	AS+Elmex	12.32	2.82	3.70	5.23	13.05
	AS+Mirafuor	5.69	2.74	4.52	3.86	25.00
RhNiTi	AS+MiPaste	27.04	0.46	0.90	13.17	0.11
	AS+Elmex	0.22	0.25	0.25	0.11	0.98
	AS+Mirafuor	0.48	0.33	0.20	0.25	0.13
NNiTi	AS+MiPaste	0.73	0.28	0.13	0.04	0.22
	AS+Elmex	5.44	3.56	3.41	2.83	14.94
	AS+Mirafuor	6.24	6.23	8.28	6.44	21.58

NiTi, uncoated nickel-titanium wire; RhNiTi, rhodium coated nickel-titanium wire; NNiTi, nitrified nickel-titanium wire; AS, artificial saliva; Mi Paste, MI Paste Plus; Elmex, Elmex gelée; Mirafuor, Mirafuor-k-gel.

1 ppm causes decrease of the Ni^{2+} ion release for $0.547 \mu\text{g}/\text{cm}^{-2}$ for the RhNiTi wire (Table 2).

The linear regression models for prediction of the release of Ti^{4+} ions from the HF concentration are significant for the NiTi ($r=0.797$) and the NNiTi ($r=0.788$; $p<0.05$) wire, but not for the RhNiTi wire (Table 3). Association with F^- was lower; for the pH it was not significant. Increase of the HF concentration for 1 ppm causes increase of the Ti^{4+} ion release for $0.047 \mu\text{g}/\text{cm}^{-2}$ for the NiTi, and $0.048 \mu\text{g}/\text{cm}^{-2}$ for the NNiTi wire (Table 3).

Average daily Ni^{2+} ions release

Average daily Ni^{2+} ions release during the observed period was calculated for two wires (for upper and lower dental arch), for all three wire types and three prophylactic agents (Table 4).

RhNiTi wire had highest average daily Ni^{2+} ions release during the first three days after immersion to the prophylactic agent with low HF concentration, followed by the third week, after immersion to the same agent. After immersion to the prophylactic agents with high HF concentration there was very low average daily Ni^{2+} ions release through all time periods.

NiTi wire had highest average daily Ni^{2+} ions release during the fourth week of use of Mirafuor-k-gel, followed by the fourth week and the first three days of usage of Elmex gelée. The MI Paste Plus caused highest average daily Ni^{2+} ions release during the first three days, and still it was lower than through any other period of time for the agents with high HF concentration.

NNiTi wire exhibited average daily Ni^{2+} ions release in trends similar to those of NiTi wires (Table 4).

Surface characterization

Micromorphology of the wires' surface showed the most pronounced surface irregularities for specimens immersed to the media that caused low ion release (Figs.

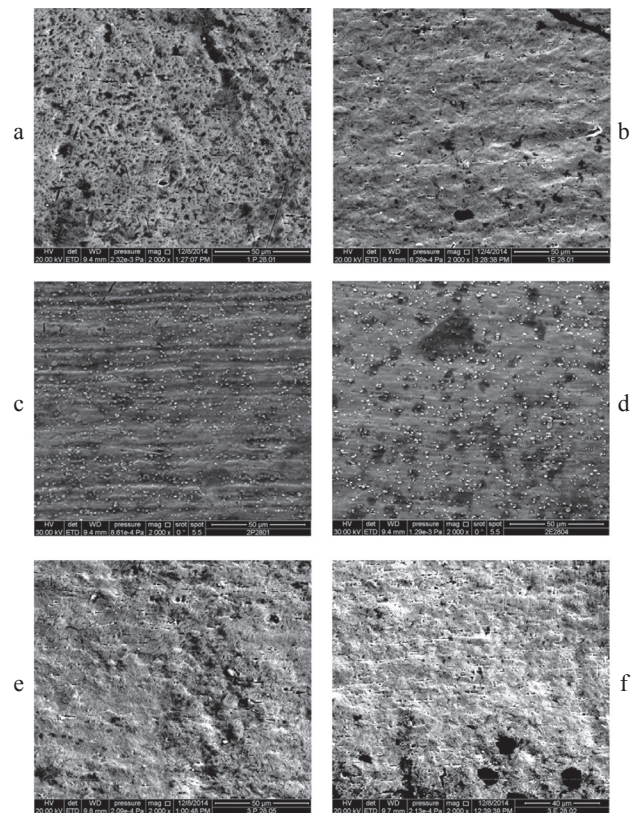


Fig. 2 Scanning electron microscope images ($2,000\times$ magnification) of the uncoated (a, b), rhodium coated (c, d) and nitride coated (e, f) nickel-titanium wires after immersion to artificial saliva (AS)+MI Paste Plus (a, c, e) and AS+Elmex gelée (b, d, f).

2 a, d, e), when compared to the media which caused high ion release (Figs. 2 b, c, f).

Table 5 Chemical composition of three types of orthodontic wires immersed in different media determined with the energy-dispersive spectroscopy analysis

Wire type	Media	Chemical composition, wt%					
		Nickel	Titanium	Rhodium	Gold	Carbon	Oxygen
NiTi	AS	52.84	44.23	—	—	2.71	0.22
	AS+Mirafleur	51.85	43.53	—	—	4.28	0.34
	AS+MIPaste	52.98	43.04	—	—	3.98	—
	AS+Elmex	54.38	43.97	—	—	1.65	—
RhNiTi	AS	12.21	5.63	28.40	46.19	5.47	2.1
	AS+Mirafleur	5.53	0	35.76	55.21	—	3.5
	AS+MIPaste	10.31	6.22	32.99	43.3	5.58	1.6
	AS+Elmex	9.01	5.57	29.08	50.5	4.47	1.37
NNiTi	AS	51.74	44.51	—	—	3.75	—
	AS+Mirafleur	49.96	42.68	—	—	7.36	—
	AS+MIPaste	52.04	44.74	—	—	3.22	—
	AS+Elmex	49.71	41.81	—	—	7.29	1.19

NiTi, uncoated nickel-titanium wire; RhNiTi, rhodium coated nickel-titanium wire; NNiTi, nitrified nickel-titanium wire; AS, artificial saliva; Mi Paste, MI Paste Plus; Elmex, Elmex gelée; Mirafleur, Mirafleur-k-gel.

Table 5 showed distribution of surface and subsurface elements, with more of the nickel being present, when compared to titanium. Also, the coating on RhNiTi wire showed notable presence of gold, but also nickel and titanium.

DISCUSSION

Concentration of the HF is the best predictor of the influence of various remineralizing agents on the release of Ni²⁺ and Ti⁴⁺ ions from the uncoated NiTi, as well as rhodium coated and nitride coated NiTi wires. The pH and the F⁻ of the prophylactic remineralizing agents influence the corrosion of the various dental materials^{24,31,32}, but the HF concentration should be used to give more accurate prediction for the release of ions from the NiTi alloys.

Findings from the EDS indicate that the surface coating on RhNiTi is not homogenous, because the presence of both surface and subsurface elements was noted. The degree of corrosion of the basic material under protective coating is determined by the quantity and size of the surface defects, as well as the coating thickness³³. The release of the Ni²⁺ and Ti⁴⁺ ions should be attributed to the pores found in disrupted surface coating^{2,3}, and the variability in ion release should be attributed to greater variations in surface coating thickness and homogeneity between the specimens. The TiN coating on NiTi wire is resistant to corrosion in the low HF concentration agent, but repeated administration of the remineralizing agents with high HF causes deterioration of the wire's corrosion resistance, even if the contact between the wire and the remineralizing agent lasts only five min a week. The

TiO₂ coating on the uncoated NiTi wire behaves in the similar fashion. In the high HF concentration groups, the highest release of ions was during the fourth week of the experiment for both NiTi and NNiTi wire. This indicates the progressive degradation of the protective surface layer, caused by the repeated application of the remineralizing agents. Contrary, in artificial saliva alone the release of ions from uncoated NiTi decreases with the prolonged time of immersion, because the protective oxide layer remains stable^{3,18,19}.

The daily dosage of 5 µg of nickel which induce epithelial proliferation³⁴, was observed for the NiTi wire during the first three days, and during the third week when using prophylactic agents with high HF concentration. For the NNiTi wire, epithelial proliferation could be expected during the first three days, and during the first three weeks when using prophylactic agents with high HF concentration. More than 10 µg of nickel a day have cytotoxic effect³⁵, and such cytotoxic daily dosage was observed for the NiTi wire during the first three days and later during the fourth week when using prophylactic agents with high HF concentration. For the NNiTi wire, cytotoxic daily dosage of nickel could be achieved during the fourth week of application of the prophylactic agents with high HF concentration. Cytotoxic effect of nickel could also be expressed during the first three days and through the third week when the RhNiTi wire is in weekly contact with the prophylactic agent with low HF concentration. Previous researches confirm the importance of the nickel concentration and time of exposure on influence on the cell growth^{35,36}.

Nickel can be found in the environment (water, food, jewellery, kitchen appliances, money coins, wire

musical instruments)³⁷, as well as in the components of the edgewise appliance (brackets, rings, tubes, springs, coils)¹⁶. Estimated average daily nickel intake from food, water and supplements is around 260 µg³⁸. The lower limit of threshold values associated with nickel-induced allergic reactions (300–600 µg of nickel)³⁸ was not met when using various prophylactic agents. The risk for the onset of the hypersensitivity reactions could be lowered if the release of the Ni²⁺ ions from known sources would be as low as possible. It was noted that an early orthodontic treatment accompanied by prolonged low release of nickel has protective effect on the risk of nickel sensitization, commonly caused by ear piercing^{21,39}, although those low values of nickel release were not precisely determined nor stated. Present study contributes to the determination of the expected average nickel ion release for three different NiTi wire types in interaction with regular weekly application of the three prophylactic agents.

Still unexplored are the hypersensitivity reactions caused by titanium⁴⁰. Future research should clarify the role and dosage of titanium that could pose hazard to human health. The timing of increased titanium uptake and preceding, concurrent or following hypersensitivity reactions should be further investigated.

The SEM images show the smoother surface in specimens with higher ion release, similar to previously observed uniform corrosion of the surfaces caused by the fluoride ions in bare NiTi wires¹⁷. Surface layer characterization of the NiTi indicates that prophylactic remineralizing agents with high HF concentration cause similar corrosion pattern on nitride coating, as on the bare NiTi wires. Rhodium coating on commercially available orthodontic wires appears to be uneven, with dross visible all over the surface, which also probably contributes to diminishing of aesthetic appearance, which was documented after clinical use^{6,7}.

Previous researches found increase in nickel ion release under bending stress⁴¹, which should be taken into account together with other intraoral conditions that modify experimental findings, *i.e.* organic components in saliva⁴². Future research should include more sensitive instrumental technique to explain the interaction between the RhNiTi and the fluoridated remineralizing agents.

CONCLUSIONS

1. Concentration of the HF predicts the release of Ni²⁺ and Ti⁴⁺ ions from the uncoated, rhodium coated and nitride coated NiTi wires better than the pH and the F⁻ concentration of the fluoridated remineralizing agents.
2. The corrosion properties of the coated wires are also influenced by the composition and homogeneity of the coating. In the prophylactic remineralizing agents with the high HF concentration, the ion release increases for the uncoated and nitrified NiTi wires and decreases for the rhodium coated NiTi wires.

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REFERENCES

- 1) Iijima M, Yuasa T, Endo K, Muguruma T, Ohno H, Mizoguchi I. Corrosion behavior of ion implanted nickel-titanium orthodontic wire in fluoride mouth rinse solutions. *Dent Mater J* 2010; 29: 53-58.
- 2) Iijima M, Muguruma T, Brantley W, Choe HC, Nakagaki S, Alapati SB, Mizoguchi I. Effect of coating on properties of esthetic orthodontic nickel-titanium wires. *Angle Orthod* 2012; 82: 319-325.
- 3) Katić V, Ćurković L, Ujević Bošnjak M, Špalj S. Determination of corrosion rate of orthodontic wires based on nickel-titanium alloy in artificial saliva. *Materialwiss Werkst* 2014; 45: 99-105.
- 4) Katić V, Otmacić Ćurković H, Semenski D, Baršić G, Marušić K, Špalj S. Influence of surface layer on mechanical and corrosion properties of nickel-titanium orthodontic wires. *Angle Orthod* 2014; 84: 1041-1048.
- 5) Weisberg AM. Rhodium plating. *Met Finish* 1999; 97: 297-301.
- 6) Bradley TG, Berzins DW, Valeri N, Pruszyński J, Eliades T, Katsaros C. An investigation into the mechanical and aesthetic properties of new generation coated nickel-titanium wires in the as-received state and after clinical use. *Eur J Orthod* 2014; 36: 290-296.
- 7) Rongo R, Ametrano G, Gloria A, Spagnuolo G, Galeotti A, Paduano S, Valletta R, D'Antò V. Effects of intraoral aging on surface properties of coated nickel-titanium archwires. *Angle Orthod* 2014; 84: 665-672.
- 8) van Gastel J, Quirynen M, Teughels W, Coucke W, Carels C. Longitudinal changes in microbiology and clinical periodontal variables after placement of fixed orthodontic appliances. *J Periodontol* 2008; 79: 2078-2086.
- 9) Arneberg P, Giertsen E, Emberland H, Ogaard B. Intra-oral variations in total plaque fluoride related to plaque pH. A study in orthodontic patients. *Caries Res* 1997; 31: 451-456.
- 10) Igarashi K, Hamada Y, Nishimaki H, Sakurai S, Kamiyama K. The acidogenic potential of plaque from sound enamel, white spot lesions, and cavities in children. *Pediatr Dent* 1987; 9: 212-215.
- 11) Law V, Seow WK, Townsend G. Factors influencing oral colonization of Mutans streptococci in young children. *Aust Dent J* 2007; 52: 93-100.
- 12) Dashper S, Reynolds E. pH regulation by *Streptococcus mutans*. *J Dent Res* 1992; 71: 1159-1165.
- 13) Heymann GC, Grauer D. A contemporary review of white spot lesions in orthodontics. *J Esthet Restor Dent* 2013; 25: 85-95.
- 14) Buzalaf MA, Pessan JP, Honório HM, ten Cate JM. Mechanisms of action of fluoride for caries control. *Monogr Oral Sci* 2011; 22: 97-114.
- 15) Marinho VC. Applying prescription-strength home-use and professionally applied topical fluoride products may benefit people at high risk for caries —the American Dental Association (ADA) 2013 clinical practice guideline recommendations. *J Evid Based Dent Pract* 2014; 14: 120-123.
- 16) Mikulewicz M, Chojnacka K. Trace metal release from orthodontic appliances by in vivo studies: a systematic literature review. *Biol Trace Elem Res* 2010; 137: 127-138.
- 17) Lee TH, Wang CC, Huang TK, Chen LK, Chou MY, Huang

- HH. Corrosion resistance of titanium-containing dental orthodontic wires in fluoride-containing artificial saliva. *J Alloys Compd* 2009; 488: 482-489.
- 18) Huang HH, Chiu YH, Lee TH, Wu SC, Yang HW, Su KH, Hsu CC. Ion release from NiTi orthodontic wires in artificial saliva with various acidities. *Biomaterials* 2003; 24: 3585-3592.
- 19) Kuhta M, Pavlin D, Slaj M, Varga S, Lapter-Varga M, Slaj M. Type of archwire and level of acidity: effects on the release of metal ions from orthodontic appliances. *Angle Orthod* 2009; 79: 102-110.
- 20) Liu C, Chu PK, Lin G, Yang D. Effects of Ti/TiN multilayer on corrosion resistance of nickel-titanium orthodontic brackets in artificial saliva. *Corros Sci* 2007; 49: 3783-3796.
- 21) Kolokitha OE, Kaklamanos EG, Papadopoulos MA. Prevalence of nickel hypersensitivity in orthodontic patients: a meta-analysis. *Am J Orthod Dentofacial Orthop* 2008; 134: 722.e1-722.e12.
- 22) Kwon YH, Cheon YD, Seol HJ, Lee JH, Kim HI. Changes on NiTi orthodontic wires due to acidic fluoride solution. *Dent Mater J* 2004; 23: 557-565.
- 23) Mirjalili M, Momeni M, Ebrahimi N, Moayed MH. Comparative study on corrosion behaviour of Nitinol and stainless steel orthodontic wires in simulated saliva solution in presence of fluoride ions. *Mater Sci Eng C Mater Biol Appl* 2013; 33: 2084-2093.
- 24) Nakagawa M, Matsuya S, Shiraishi T, Ohta M. Effect of fluoride concentration and pH on corrosion behavior of titanium for dental use. *J Dent Res* 1999; 78: 1568-1572.
- 25) Filipović I, Lipanović S. Opća i anorganska kemija II. dio. Zagreb: Školska knjiga; 1995, str. 658-659.
- 26) Marek M, Topfl E. Electrolytes for corrosion testing of dental alloys. *J Dent Res* 1986; 65: 301.
- 27) Lin HY, Bowers B, Wolan JT, Cai Z, Bumgardner JD. Metallurgical, surface, and corrosion analysis of Ni-Cr dental casting alloys before and after porcelain firing. *Dent Mater* 2008; 24: 378-385.
- 28) Bollen AM, Cunha-Cruz J, Bakko DW, Huang GJ, Hujoel PP. The effects of orthodontic therapy on periodontal health: a systematic review of controlled evidence. *J Am Dent Assoc* 2008; 139: 413-422.
- 29) Chang HS, Walsh LJ, Freer TJ. The effect of orthodontic treatment on salivary flow, pH, buffer capacity, and levels of mutans streptococci and lactobacilli. *Aust Orthod J* 1999; 15: 229-234.
- 30) Arndt M, Bruck A, Scully T, Jager A, Bourauel C. Nickel ion release from orthodontic NiTi wires under simulation of realistic in situ conditions. *J Mater Sci* 2005; 40: 3659-3667.
- 31) Tylka DF, Stewart GP. Comparison of acidulated phosphate fluoride gel and hydrofluoric acid etchants for porcelain-composite repair. *J Prosthet Dent* 1994; 72: 121-127.
- 32) Mujeeb A, Mansuri S, Hussain SA, Ramaswamy K. In vitro evaluation of topical fluoride pH and their effect on surface hardness of composite resin-based restorative materials. *J Contemp Dent Pract* 2014; 15: 190-194.
- 33) Walsh FC, Ponce de León C, Kerr C, Court S, Barker BD. Electrochemical characterisation of the porosity and corrosion resistance of electrochemically deposited metal coatings. *Surf Coat Tech* 2008; 202: 5092-5102.
- 34) Ermolli M, Menne C, Pozzi G, Serra MA, Clerici LA. Nickel, cobalt and chromium-induced cytotoxicity and intracellular accumulation in human haec keratinocytes. *Toxicology* 2001; 159: 23-31.
- 35) Gursoy UK, Sokucu O, Uitto VJ, Aydin A, Demirer S, Toker H. The role of nickel accumulation and epithelial cell proliferation in orthodontic treatment-induced gingival overgrowth. *Eur J Orthod* 2007; 29: 555-558.
- 36) D'Antò V, Valletta R, Amato M, Schweikl H, Simeone M, Paduano S, Rengo S, Spagnuolo G. Effect of nickel chloride on cell proliferation. *Open Dent J* 2012; 6: 177-181.
- 37) Rezić I, Čurković L, Ujević M. Metal ion release from electric guitar strings in artificial sweat. *Corros Sci* 2009; 51: 1985-1989.
- 38) Nielsen GD, Søderberg U, Jørgensen PJ, Templeton DM, Rasmussen SN, Andersen KE, Grandjean P. Absorption and retention of nickel from drinking water in relation to food intake and nickel sensitivity. *Toxicol Appl Pharmacol* 1999; 154: 67-75.
- 39) Fors R, Stenberg B, Stenlund H, Persson M. Nickel allergy in relation to piercing and orthodontic appliances—a population study. *Contact Derm* 2012; 67: 342-350.
- 40) Fage SW, Muris J, Jakobsen SS, Thyssen JP. Titanium: a review on exposure, release, penetration, allergy, epidemiology, and clinical reactivity. *Contact Derm* 2016; 74: 323-345.
- 41) Peitsch T, Klocke A, Kahl-Nieke B, Prymak O, Epple M. The release of nickel from orthodontic NiTi wires is increased by dynamic mechanical loading but not constrained by surface nitridation. *J Biomed Mater Res A* 2007; 82: 731-739.
- 42) Fragou S, Eliades T. Effect of topical fluoride application on titanium alloys: a review of effects and clinical implications. *Pediatr Dent* 2010; 32: 99-105.