CORROSION OF ORTHODONTIC BIOMATERIALS - EFFECT OF pH, FLUORIDE AND ACID CONCENTRATION FROM REMINERALIZATION AGENTS ON ELASTIC PROPERTIES OF ORTHODONTIC NICKEL-TITANIUM ARCH WIRES

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ABSTRACT

Aim: To explore the effect of enamel remineralization agents with various concentration of fluorides on the corrosion of orthodontic nickel-titanium arch wires (NiTi).

Materials and methods: Three types of NiTi with dimension of 0.508×0.508 mm were tested: uncoated (NiTi), rhodium-coated (RhNiTi) and with nitrified surface (NNiTi). Ten samples from each type of wire were immersed for 1 hour at 37° into fluoride agents - Mirafluor-k-gel, Elmex, MI Paste Plus and distilled deionized water with no fluorides (dH2O). Acidity in tested solutions and hydrofluoric acid concentrations was assessed. Three-point bend test was used to assess flexibility and resilience in load and unload.

Results: Exposure of NNiTi to fluorides and dH2O induces significant decrease of flexibility in load in comparison to as-received condition ($p<0.001$), but not in unload. Resilience decreases in MiPaste and Mirafluor in load ($p=0.004$), but not in unload. In RhNiTi MiPaste, Mirafluor and dH2O increase flexibility in load in comparison to as-received condition ($p=0.006$), and Mirafluor and dH2O in unload ($p=0.001$). Flexibility of NNiTi does not change due to exposure to fluorides nor dH2O. No correlation between elastic properties and pH or hydrofluoric acid was present. Weak positive linear correlation between fluoride concentration and flexibility and resilience was found only in uncoated NiTi in load ($r=0.341$ and 0.312; $p\leq0.05$).

Conclusion: Commercial fluoride agents with various fluoride concentration do not significantly decrease unloading elastic properties of orthodontic arch wires therefore they will not affect tooth movement, regardless of wire's surface coating. Predictive value of pH, fluoride and hydrofluoric acid concentration is poor.

Key words: corrosion, nickel-titanium alloy, orthodontic wires.

Introduction

Oral cavity is a dynamic environment where electrochemical processes, including electro corrosion, take place. Saliva is an electrolyte, and the dental metal biomaterials are electrodes where ion exchange is performed [1]. Electro corrosion processes in mouth are influenced by physiology and biochemistry of saliva, food, bacterial fermentation products and oral hygiene products.

Electrochemical corrosion in the oral cavity includes oxidation processes of metal, release of electrons and reduction of hydrogen or oxygen by the gain of electrons. Secondary reactions may result in poorly adhering corrosive products propagating further corrosion, or poorly soluble chemical compounds slowing down further corrosion. In dentistry, biomaterials containing titanium (Ti) and nickel (Ni) for prosthetic and implant prosthetic restorations, endodontic instruments and orthodontic wires and springs are often used. In alloys used for elastic orthodontic wires and endodontic instruments, Ni and Ti are represented in roughly equal proportions. Under the influence of corrosion processes nickel ions (Ni^{2+}) are released easier and in greater amount than titanium ions (Ti^{4+}) [2]. The protective passive film on the surface of the material consists mainly of TiO_2 with a small amount of NiO, thus creating a chemical and physical barrier for external influences [3].

There are several forms of corrosion that can occur in dental and orthodontic alloys: general, pitting, pointed or needlelike and galvanic corrosion [4]. General corrosion is the most common type affecting all metals, and it occurs throughout the metal surface. Pitting corrosion penetrates deep into the metal, it is extremely destructive, and only one pit can lead to material fracture. Metals Fe, Ni, Al, Mg, Cu, Zn and their alloys are subject to that type of corrosion. Although materials with high corrosion resistance are used in orthodontics, they can be subject to intense corrosion, usually as localized corrosion damage, under certain environmental conditions. As earlier researches have shown, pitting corrosion on the NiTi surface is mostly manifested in the weak spots of the surface [5, 6].

Low pH values, found in dental plaque, and fluoride ions released from antiseptics or enamel remineralization agents may propagate corrosion [7-9]. Fluorides in acidified solution induce the formation of a hydrofluoric acid which interacts with titanium oxides on the surface of NiTi alloy creating Ti-F complexes and titanium oxyfluoride, thereby reducing the protective titanium oxide layer [10]. Corrosion could be manifested in changes of the elastic properties of NiTi alloys.

The aim of this study was to explore the effect of fluoride agents with various concentration of fluorides on the corrosion of orthodontic NiTi wires with various coatings in terms of changes of elastic properties. It was hypothesized that corrosion is seen as deterioration of flexibility and resilience, more in unloading than loading. Elasticity will probably be more influenced by hydrofluoric acid concentration than pH or fluoride concentration in enamel remineralization agents. Coating of the arch wire will probably influence corrosion with nitrification improving resistance while rhodium coating causing susceptibility to corrosion.

Materials and methods

Three types of nickel-titanium orthodontic arc wires (Ni=50.4%; Ti=49.6%) with dimension of 0.508×0.508 mm were tested: uncoated (NiTi), rhodium-coated (RhNiTi) and with nitrified surface (NNiTi) (Bioforce Sentalloy, Dentsply GAC Int, Bohemia, USA).

Experimental solutions included Mirafluor-k-gel (Hager&Werken, Duisburg, Germany) – 6150 ppm of fluorides (NaF), Elmex (Gaba, Loerrach, Germany) – 12500 ppm of fluorides (NaF and amine fluoride), MI Paste Plus (GC, Tokyo, Japan) – 900 ppm of fluorides (NaF) with casein phosphopeptide-amorphous calcium phosphate, and distilled deionized water with no fluorides (dH_2O). Measurement of pH in tested solutions was conducted at temperature 37°C by using pH-meter MP 220 (Mettler Toledo Int., Greifensee, Switzerland). For the calculation of hydrofluoric acid (HF) concentrations in solutions the following formula was used: $[HF]=[F^-]/10^{pH-pKa}$, where $[F^-]$ is the fluoride concentration and pKa is the constant of dissociation of hydrofluoric acid 3.17 [11].

Ten samples (25 mm long) were taken from each type of wire and immersed for 1 hour at 37° in order to simulate total exposure to fluoride agents in duration of 5 min per week during 12 week period. After that they were rinsed with dH_20.

For testing the elastic properties three-point bend test on a universal machine (Instron 1125/5500, Instron, Norwood, USA) were done. The supporting span of Texture Analyzer TA.HD.plus (Stable Micro Systems, Godalming, UK) was set to 12 mm and loaded with a low force (5 kg, factory calibrated). During the measurement, the temperature in the thermal chamber was set at 37° C. Each sample was deflected to 3.1 mm and then unloaded to 0 mm at a crosshead speed of 0.0167 mm/s. Force (N) and deflection (mm) were recorded every 5 ms for each sample in both loading and unloading, using Texture Exponent software (Stable Micro System, Godalming, UK). Force-deflection curves were generated. From data on elastic modulus (E) and yield strength (YS) in load and unload springback ratio as a measure of flexibility (YS/E) and modulus of resilience as a measure of resilience (YS2/2E) were calculated. Decrease of both values indicated a deterioration of elastic properties. As-received was used as an absolute control, while exposed to dH_2O as a negative control.

Differences in elastic properties between exposed and unexposed arch wires was tested by using analysis of variance (ANOVA) with Student-Newman-Keuls post hoc. Pearson correlation was used to explore relationship between elastic properties and concentration of fluorides, hydrofluoric acid and pH of solution. Commercial software IBM SPSS 22 (IBM Corp, Armonk, USA) was used.

Results

Data on concentration of pH, fluorides and hydrofluoric acid is presented in **Table 1**.

Exposure of uncoated NiTi to fluorides and dH_2O induces significant decrease of flexibility in load in comparison to as-received condition ($p<0.001$), but not in unload (**Figure 1**). Resilience decreases in MiPaste and Mirafluor in load ($p=0.004$), but not in unload. MiPaste and Mirafluor have decreased flexibility and resilience in unload in comparison to Elmex ($p \leqslant 0.012$), but not to unexposed wire nor dH_20.

In rhodium coated NiTi MiPaste, Mirafluor and dH_2O increase flexibility in load in comparison to as-received condition ($p=0.006$), and Mirafluor and dH2O in unload ($p=0.001$). Resilience increases only dH_20 in unload ($p=0.008$), but not in load.

Flexibility of nitrified NiTi does not change due to exposure to fluorides nor dH2O. Elmex induced higher resilience than Mirafluor and MiPaste in load ($p=0.015$), and Mirafluor in unload ($p=0.022$). Resilience does not change in comparison to unexposed wires.

When analyzing only arch wires exposed to fluoride agents and dH_2O no correlation between elastic properties and pH or hydrofluoric acid was

Media	pH	F (ppm)	HF (ppm)
MI Paste Plus	6.6	900	0.33
Mirafluor	5.1	6150	72.26
Elmex	5.5	12500	58.47
dH_2O	6.1	0	0.00

Table 1.
Data on concentration of pH, fluorides and hydrofluoric acid

Wire	Variable		pH	F	HF
NiTi	springback ratio load	r	-0.178	0.342*	0.198
		p	0.271	0.031	0.222
	springback ratio unload	r	-0.067	0.266	0.047
		p	0.682	0.097	0.773
	modulus resilience load	r	-0.125	0.312*	0.102
		p	0.444	0.050	0.533
	modulus resilience unload	r	-0.055	0.286	0.023
		p	0.737	0.073	0.889
RhNiTi	springback ratio load	r	-0.020	-0.152	-0.005
		p	0.900	0.350	0.974
	springback ratio unload	r	-0.007	-0.216	-0.114
		p	0.963	0.180	0.483
	modulus resilience load	r	-0.171	-0.031	0.081
		p	0.290	0.847	0.619
	modulus resilience unload	r	-0.074	-0.171	-0.074
		p	0.651	0.291	0.652
NNiTi	springback ratio load	r	-0.021	0.161	0.017
		p	0.897	0.322	0.918
	springback ratio unload	r	-0.063	0.278	0.072
		p	0.698	0.083	0.658
	modulus resilience load	r	-0.029	0.273	0.022
		p	0.860	0.089	0.893
	modulus resilience unload	r	-0.046	0.297	0.060
		p	0.776	0.063	0.715

Table 2. Pearson correlations between elastic properties, pH and concentration of fluorides and hydrofluoric acid

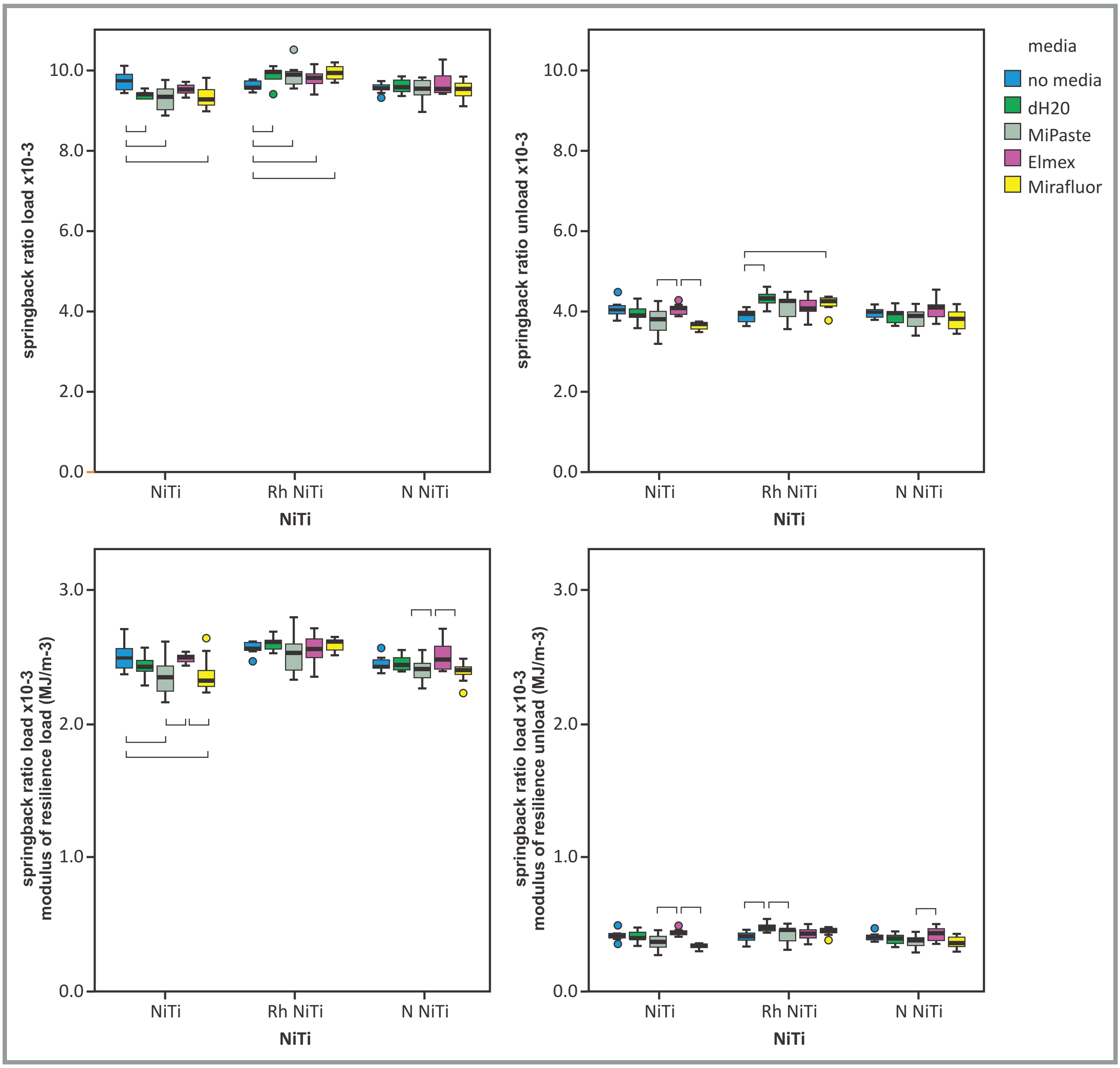

Figure 1. Influence of fluorides on elastic properties of NiTi archwires

present (**Table 2**). Correlation with concentration of fluorides was not present in NNiTi nor RhNiTi. A weak positive linear correlation between fluoride concentration and flexibility and resilience was found only in uncoated NiTi in load (r=0.341 and 0.312; p<0.05).

Discussion

Present study demonstrates that enamel remineralization agents induce corrosion of orthodontic biomaterials to some extent. It is seen in changes in elastic properties of some orthodontic NiTi arch wires.

It was hypothesized that corrosion would be seen as deterioration of flexibility and resilience of NiTi arch wires, more in unloading than loading. However that was not the case. In fact, in uncoated NiTi alloy agents with lower fluoride content (MiPaste and Mirafluor), decrease of elastic properties occurs only in loading but not in unloading phase. And unloading phase is the one used to move teeth during orthodontic treatment. So it will not affect orthodontic biomechanics, duration of treatment nor provoke high forces and damage of periodontal ligament, cementum or alveolar bone. Opposite is reported previously, but it depends on the type of NiTi arch wire [12,13].

Our hypothesis that coating of the arch wire will probably influence corrosion with nitrification improving resistance while rhodium coating causing susceptibility to corrosion was only partially confirmed. So, fluorides have the lowest influence on NNiTi, lower than uncoated alloy. Agents with higher fluoride content even have tendency to improve elasticity of RhNiTi arch wires.

To reduce corrosion and improve esthetics, the surface of biomaterials is coated with various coatings. Nitrification is one of the most important methods of thermochemical treatment of the surface. It is based on nitrogen implantation on the surface layer forming a TiN coating increases the hardness and resistance to both wear and corrosion [14].

Research indicates that nitrification of surface slows down corrosion of NiTi alloys in saliva or makes the alloy more resistant to general corrosion, but does not make it more resistant to localized corrosion [15, 16]. Rhodium coating increases the tendency towards general and localized corrosion [15]. By applying a thin layer of rhodium on wire better esthetics is achieved, but obviously not higher corrosion resistance. The cause of increased corrosion is the occurrence of galvanic couple between noble coating and non-noble NiTi base due to coating breakdown, whereby the coating becomes a cathode and the base alloy anode. The corrosion process is carried out locally, in areas where the coating is porous [17]. However, the coating does not behave equally in all environmental conditions, it modifies the influence of oral agents on NiTi alloy [18]. It was found that commercially available coatings are not homogeneous, therefore do not bring a significant improvement of corrosion properties compared to uncoated wires [19].

It was expected that elasticity will be more influenced by hydrofluoric acid concentration than pH or fluoride concentration in enamel remineralization agents. However, predictive value of pH, fluoride and hydrofluoric acid concentration is poor, particularly with unloading elastic properties regardless of the wire's surface coating. In fact, no correlation between elastic properties and pH or hydrofluoric acid concentration was detected. Fluorides weakly correlated only in loading and only in uncoated NiTi. Still, our previous research demonstrates that concentration of hydrofluoric acid from enamel remineralization agents predict release of nickel and titanium ions from NiTi alloys more than pH or concentration of fluorides solely [11].

Corrosion of orthodontic biomaterials has numerous implications, beside their impact on working properties of arch wires which can directly alter orthodontic biomechanics. Continuous release of low doses of nickel ions from orthodontic appliances can initiate gingival hyperplasia by increasing proliferation of epithelial cells [20]. It can also induce IV hypersensitivity reactions, i.e. cell-mediated delayed hypersensitivity [21]. The prevalence of nickel allergy is the most common metal allergy affecting up to 30% of the population, being three times more common in women [22]. Oral clinical signs and symptoms of nickel allergy may include burning mouth sensation, gingival hyperplasia, lichenoid reaction, labial desquamation, angular chelitis, erythema multiforme, periodontitis, stomatitis with mild to severe erythema, papular perioral rash, loss of taste or metal taste, tenderness, ulceration on the tongue, and less often edema of the lips [23]. It was found that the most important risk factors for nickel allergy is number of piercings and time exposed to the jewelry. Orthodontic treatment before wearing earrings reduces the risk for nickel allergy [24].

Adhesive consistency of prophylactic agents allows a prolonged contact with teeth as well as orthodontic appliances, which can cause changes in working properties and corrosion resistance of appliances. Present study demonstrated that commercially available caries preventive agents affect the change in working performance of nickel-titanium wires to a lower extent, depending on the composition of their surface. Generally, they do not reduce the elasticity of the wire during unloading, which is the working phase in which the teeth are moved. Therefore, it is unlikely that it will disrupt the course and duration of orthodontic treatment. The problem of surface corrosion induced by fluorides and low pH appears not to be clinically significant, as long as no more than a 1500 ppm fluoride concentration agents are used [25]. Clinically, the use of fluoride varnishes at specific, caries-risk sites may provide protection while minimizing the potential risk of adverse effects [26].

Conclusion

Commercial fluoride agents with various fluoride concentration do not significantly decrease elastic properties of orthodontic arch wires in unloading that moves teeth, regardless of wire's surface coating.

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Declaration of interest

No conflict of interest.

References

1. Upadhyay D, Panchal MA, Dubey RS, Srivastava VK. Corrosion of alloys used in dentistry: A review. Mater Sci Eng A 2006;432(1):1–11.
2. Iijima M, Endo K, Ohno H, Yonekura Y, Mizoguchi I. Corrosion behavior and surface structure of orthodontic Ni-Ti alloy wires. Dent Mater J 2001;20(1):103-113.
3. Huang HH. Surface characterizations and corrosion resistance of nickel-titanium orthodontic archwires in artificial saliva of various degrees of acidity. J Biomed Mater Res A 2005;74(4):629-639.
4. Eliades T, Athanasiou AE. In vivo aging of orthodontic alloys: implications for corrosion potential, nickel release, and biocompatibility. Angle Orthod 2002;72(3):222-237.
5. Hu T, Xin XC, Wu SL, Chu CI, Lu J, Cuan I, et al. Corrosion behavior on orthopedic NiTi alloy with nanocrystalline/amorphous surface. Mater Chem Phys 2011;126:102-107.
6. Mirjalili M, Momeni M, Ebrahimi N, Moayed MH. Comparative study on corrosion behavior 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(4):2084-2093.
7. Igrashi K, Lee IK, Schachtele CF. Effect of dental plaque age and bacterial composition on the pH of artificial fissures in human volunteers. Caries Res 1990;24(1):52-58.
8. Huang HH, Chiu YH, Lee TH, Wu SC, Yang Hw, Su KH, et al. Ion release from NiTi orthodontic wires in artificial saliva with various acidities. Biomaterials 2003;24(2):3585-3592.
9. Schiff N, Grosgogeat B, Lissac M, Dalard F. Influence of fluoridated mouthwashes on corrosion resistance of orthodontics wires. Biomaterials 2004;25(19):4535-4542.
10. Boere G. Influence of fluoride on titanium in an acidic environment measured by polarization resistance technique. J Appl Biomater 1995;6(4):283-8.
11. Katic V, Curkovic L, Bosnjak MU, Peros K, Mandic D, Spalj S. Effect of pH, fluoride and hydrofluoric acid concentration on ion release from NiTi wires with various coatings. Dent Mater J 2017;36(2):149-156.
12. Walker MP, White RJ, Kula KS. Effect of fluoride prophylactic agents on the mechanical properties of nickel-titanium-based orthodontic wires. Am J Orthod Dentofacial Orthop 2005;127(6):662-669.

13. Ramalingam A, Kailasam V, Padmanabhan S, Chitharanjan A. The effect of topical fluoride agents on the physical and mechanical properties of NiTi and copper NiTi archwires. An in vivo study. Aust Orthod J 2008;24(1):26-31.
14. Al Jabbari YS, Fehrman J, Barnes AC, Zapf AM, Zinelis S, Berzins DW. Titanium nitride and nitrogen ion implanted coated dental materials. Coatings 2012;2(3):160-178.
15. Katić V, Curković HO, Semenski D, Baršić G, Marušić K, Spalj S. Influence of surface layer on mechanical and corrosion properties of nickel-titanium orthodontic wires. Angle Orthod 2014;84(6):1041-1048.
16. Kim H, Johnson JW. Corroson of stainless steel, nickel-titanium, coated nickel-titanium and titanium orthodontic wires. Angle Orthod 1999;69(1):39-44.
17. Zohdi H, Emami M, Shahverdi HR. Galvanic corrosion behavior of dental alloys. Environmental and industrial corrosion- practical and theoretical aspects. Rijeka: In Tech; 2012.
18. Katić V, Mandić V, Ježek D, Baršić G, Špalj S. Influence of various fluoride agents on working properties and surface characteristics of uncoated, rhodium coated and nitrified nickel-titanium orthodontic wires. Acta Odontol Scand 2015;73(4):241-249.
19. 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(1):53-58.
20. Gursoy UK, Sokucu O, Uitto VJ, Aydin A, Demirer S, Toker H et al.. The role of nickel accumulation and epithelial cell proliferation in orthodontic treatment-induced gingival overgrowth. Eur J Orthod 2007;29(6):555-558.
21. Bass JK, Fine H, Cisneros GJ. Nickel hypersensitivity in the orthodontic patient. Am J Orthod Dentofacial Orthop 1993;103(3):280-285.
22. Peternel S, Saint-Georges V, Kaštelan M, Katić V, Pavlić A, Špalj S. Sensitivity to nickel – orthodontic implications. Acta Stomatol Croat. 2017;51(2):169.
23. Schultz JC, Connelly E, Glesne L, Warshaw EM. Cutaneous and oral eruption from oral exposure to nickel in dental braces. Dermatitis 2004;15(3):154-157.
24. Gölz L, Papageorgiou SN, Jäger A. Nickel hypersensitivity and orthodontic treatment: a systematic review and meta-analysis. Contact Dermatitis 2015;73(1):1-14.
25. Perinetti G, Contardo L, Ceschi M, Antoniolli F, Franchi L, Baccetti T, et al. Surface corrosion and fracture resistance of two nickel-titanium-based archwires induced by fluoride, pH, and thermocycling. An in vitro comparative study. Eur J Orthod. 2012;34(1):1-9.
26. Fragou S, Eliades T. Effect of topical fluoride application on titanium alloys: a review of effects and clinical implications. Pediatr Dent. 2010;32(2):99-105.