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INFLUENCE OF FLUORINE-CONTAING MOUTHWASHES ON NiTi ALLOY CORROSION

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Abstract: *Evaluation of NiTi alloy corrosion behaviour in fluorine-containing media still remains a great characterization challenge. Such characterization is commonly simplified by using aggressive media with a high concentration of fluorine. Accordingly, the difficulties in the characterization of material changes on a nano-level are avoided. However, these results do not sufficiently resemble the real situation. Therefore, the motivation of this work was to perform a non-accelerated corrosion test, characterize the nano topographic changes, and to evaluate the obtained results by statistical methods. In this study, we examined the behaviour of NiTi alloy archwires exposed for 21 days to artificial saliva and fluorine-containing mouthwash Aquafresh My Big teeth®. Atomic force microscope (AFM) Veeco CP-II, and scanning electron microscope (SEM) Hitachi TM3030, were employed for characterization of changes in surface topography, on the areas of 80x80 and 10x10 µm. Before and after the corrosion tests specimens were evaluated at 5 locations of 80x80 µm. Topographic images were analysed by image analysis software (Spip 6.2.0) and surface roughness parameters (Sa and S10z) were calculated. The changes in chemical composition were evaluated by energy-dispersive X-ray spectroscopy (EDS). Paired T-test and one-way ANOVA statistical analysis were employed for the evaluation of the changes observed in surface roughness parameters and chemical composition. Changes in surface topography observed in AFM and SEM images (80x80 µm) are negligible for both specimens. Analysis of AFM topographic images (10x10 µm) revealed that only specimen exposed to Aquafresh My Big teeth® exhibited nano changes in surface topography. For artificial saliva negligible changes were observed, while Aquafresh My Big teeth® exhibited notable changes in Sa and S10z parameters. Statistical analysis of data revealed that changes in roughness parameters are significant only for specimens exposed to Aquafresh My Big teeth® ®. This indicates that the presence of fluorine in mouthwash increases the NiTi corrosion. Statistical analysis methods and AFM have been proven as a valuable tool in the characterization of nano topographic changes caused by corrosion in real conditions.*

Keywords: *biomaterial, NiTi, corrosion, AFM, nano topography, ANOVA, paired T-test.*

1. INTRODUCTION

Ni-Ti alloy is a biomaterial that is widely applied for dental application due to its good corrosion resistance and special mechanical properties [1].

During orthodontic treatment with NiTi alloy appliances, practitioners recommend

their patients to use fluoride mouthwashes to prevent dental caries and enamel [2]. However, application of fluoridated mouthwashes could lead to corrosion and release of metal ions into the body [3]. The release of metal ions from dental alloys may have an adverse biological effect, depending on the ion species and their concentrations [4]. It has been shown that Ni ion release caused by corrosion process lead to allergenicity, toxicity and carcinogenicity [2,5]. Additionally, ion release inevitably induces NiTi material corrosion, degradation of its surface (topography) and tribological characteristics [6,7]. Therefore, the characterization and quantification of topographic changes induced by the corrosion processes is very important for reduction of their effect on patient health and improvement of material performance in application [1,4,6,7].

Investigations with electrochemical [2,8], and non-electrochemical tests with higher fluoride concentration (> 1400 ppm) [9,10], revealed a significant decrease of NiTi corrosion resistance in commercially available mouthwashes. By employing accelerated tests, with support of electricity or concentrated corrosive media, difficulties in the characterization of nanostructures and nano topographic changes of the surface are avoided. However, these tests do not sufficiently resemble the real situations.

Therefore, the aim of this work was to perform a non-accelerated corrosion tests of NiTi wires in artificial saliva and commercially available fluoride mouthwash, with a goal to characterize and quantify the changes that occur in surface topography and chemical composition.

2. MATERIALS AND METHODS

The corrosion performance of NiTi orthodontic wires (Denataurum, Germany) was evaluated in this study. Two prismatic specimens were prepared of the wire in as-received condition. In order to easily locate the same area after the tests, 5 scan locations on each specimen were marked by scratches on the surface before the corrosion tests. Each specimen was exposed to corrosive media for duration of 21.5 day at room temperature. The specimen denotations and corresponding corrosive media used in test are presented in Table 1.

Table 1. Specimen's denotations and the employed medium.

Specimen	Corrosive medium
Specimen 1	Artificial Saliva (pH 7.1)
Specimen 2	Aquafresh My Big teeth® (GSK Consumer Healthcare) 0.05 % (250 ppm) NaF

Corrosion was characterized by means of changes in surface topography. For these purposes, each specimen was analysed in 5 predefined locations, before and after the corrosion test, by employing atomic force microscopy (AFM) (CP-II di, Veeco) and scanning electron microscopy (SEM) (TM 3030, Hitachi, Japan). AFM measurements were performed in contact mode, using symmetrically etched Silicon-Nitride tip. The scanning parameters were as follows: fast scanning direction X-axis, scanning area 100 x 100 µm, setpoint 225 nN, scanning rate 0.5 Hz and gain 0.5.

Imperfections in the probe movement mechanism caused a mismatch in scanning location, before and after the test. Therefore, in order to evaluate the effects of corrosion on exactly the same location, the areas of 80x80 and 10x10 µm were extracted from original measurements, and further analysed.

Scanning Probe Image Processor (SPIP) image analysis software was employed for the analysis of topographic images, extracting areas of 80x80 µm and 10x10 µm and the calculation of surface roughness parameters.

X-ray energy dispersive spectroscopy analysis (EDS) (TM 3030, Hitachi, Japan) was employed for the analysis of chemical composition of specimens.

After the corrosion tests, the change in observed surface roughness parameters and

comparison of difference in change of roughness parameters were analysed using paired T-test (T-test) and one-way ANOVA,

respectively. All statistics analyses were performed with Minitab 16 software at a significance level of 5%.

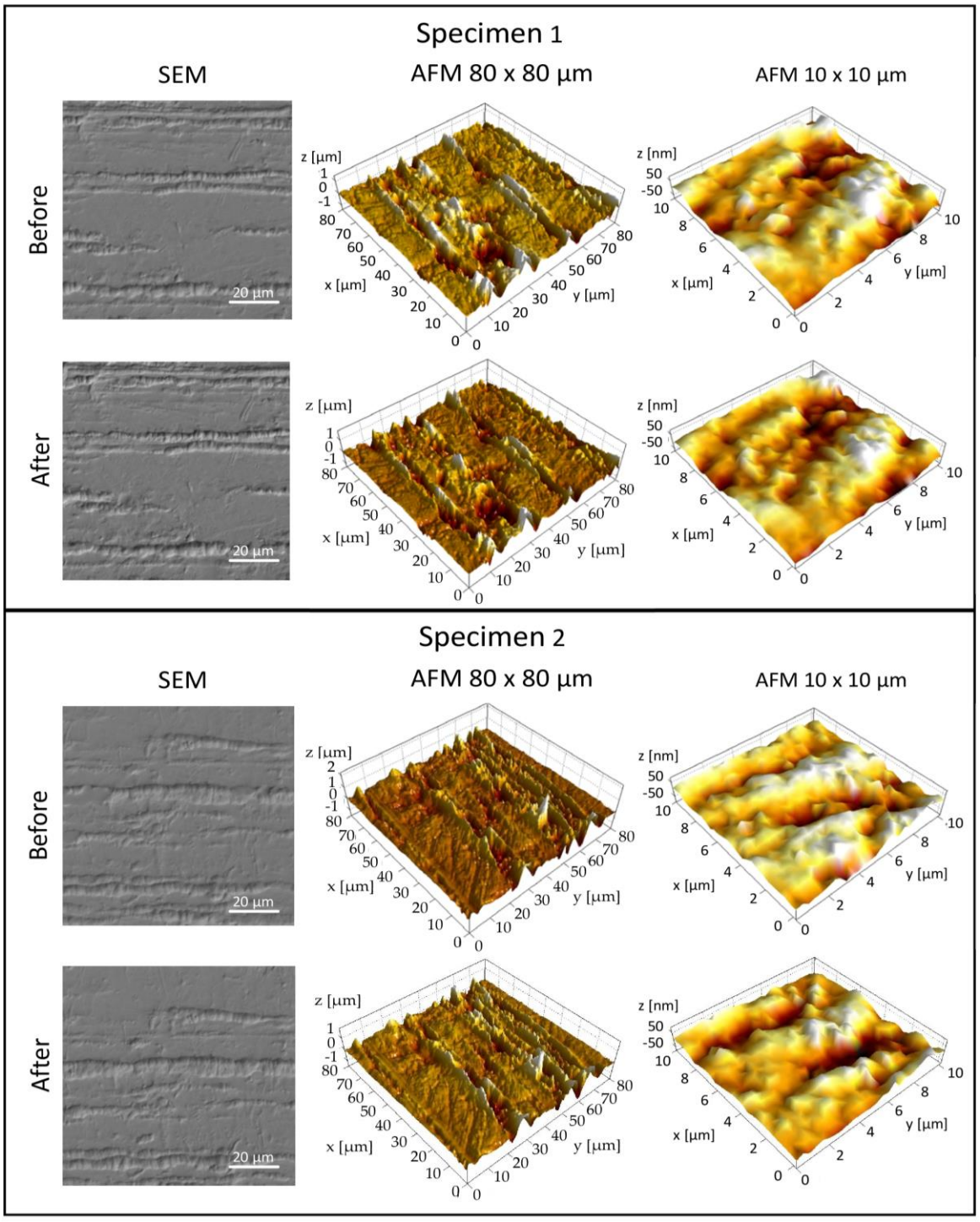

Figure 1. Representative AFM (80 x 80 µm and 10 x 10 µm) and SEM(80 x 80 µm) images for Specimen 1 and 2, before and after corrosion test

3. RESULTS

Representative SEM and AFM images of specimen surfaces before and after the corrosion tests are given in Figure 1. The initial surfaces of the specimens are characterized by relatively parallel deep grooves. The area between the grooves is much smoother. When comparison is made between the SEM and AFM images of 80 x 80 µm areas (Figure 1), of surfaces before and after the corrosion tests, differences in topography cannot be noticed.

However, when the small areas (10 x 10 µm) between the grooves of Specimen 2 (Figure 1) are compared, changes in nano-topography induced by corrosion are evident.

The specimen's chemical composition was investigated by EDS. The initial specimen chemical composition comprises of averagely 40 % of Ti and 60 % of Ni. Results of ANOVA revealed that chemical composition of all specimens after the test did not change significantly.

Table 1 presents the average values of Sa and S10z parameters, determined on the areas of 80 x 80 µm before and after the tests, for all investigated specimens. Although all specimens were produced of a same archwire, differences in the initial surface roughness parameters, of ~ 20 %, are observed. Also, it must be noted that the values of confidence interval after the corrosion tests, exhibited only a minor change.

Table 1. Values of surface roughness parameters Sa and S10z, before and after corrosion test, of surface areas 80x80 µm areas. Note: Values in brackets are confidence intervals.

Element	Surface roughness parameters			
	Sa_{before} [nm]	Sa_{after} [nm]	$S10z_{before}$ [µm]	$S10z_{after}$ [µm]
Specimen 1	136 (56.7)	129.7 (38.3)	1.957 (1.17)	1.781 (0.63)
Specimen 2	133.5 (74.1)	125.7 (66.3)	2.065 (1.010)	2.668 (0.907)

Results of T-test and ANOVA revealed an insignificant change, and difference in change of surface roughness parameters determined for the areas of 80 x 80 µm. These results indicate that all investigated corrosive media did not impose a significant change of specimens' Sa and S10z parameters on these "large" evaluated areas.

Table 2 presents the average values of Sa and S10z parameters of 10 x 10 µm areas, determined before and after the corrosion tests, for all investigated specimens. A variation of ~ 25% in the initial surface roughness parameters, determined for the areas of 10 x 10 µm, is noticeable. A small change in the average values of parameters Sa and S10z can be observed. It can be noticed that trend of change for both roughness parameters is the same. It also can be noticed that values of confidence intervals suffered only a negligible change after the corrosion tests.

Table 2. Values of surface roughness parameters Sa and S10z, before and after corrosion test, of surface areas 10x10 µm areas. Note: Values in brackets are confidence intervals.

Element	Surface roughness parameters			
	Sa_{before} [nm]	Sa_{after} [nm]	$S10z_{before}$ [nm]	$S10z_{after}$ [nm]
Specimen 1	14.5 (6.9)	14.2 (6)	88 (37.4)	88 (37.3)
Specimen 2	15.1 (3.3)	20.2 (5.8)	109 (23.9)	142 (29.3)

Results of T-tests performed on Sa and S10z parameters, determined for 10 x 10 µm areas, are presented in Table 3. The specimen treated with artificial saliva (Specimen 1) again did not show a significant change in the observed surface roughness parameter. On the other side, specimens treated with fluoride containing mouthwash (Specimen 2) significantly changed the value of both surface roughness parameters ($p < 0.05$).

Table 3. Results of T-test for comparisons of roughness parameters before and after exposure.

Specimen/Results of paired T-test (P-Value)	Results of Paired T-test (P-Value)	
	Sa	S10z
Specimen 1	0.451	0.884
Specimen 2	0.036	0.041

Results of ANOVA for comparison of the differences in change of surface roughness parameters revealed that the difference in change of parameters between Specimen 1 and 2 is significant.

4. DISCUSSION

The analysis performed in this study revealed that nano topographic changes of

NiTi induced by corrosion processes can be successfully revealed by AFM.

Analysis of AFM and SEM images, surface roughness parameters, and chemical composition of Specimen 1, before and after the corrosion test in artificial saliva, indicates an insignificant change of topography. This means that artificial saliva with pH 7.1 during the period of 21.5 days, do not induce observable corrosion of NiTi, by means of changes in surface roughness. This agrees with finding of Huan et al. [11], who found, that artificial saliva with pH value as high as 7.1 does not induce corrosion of Ni-Ti alloy.

An insignificant change of roughness parameters, topography and chemical composition, evaluated for areas of 80 x 80 μm, indicate that the medium employed for testing of Specimen 2 did not cause corrosion effects. However, the corrosion effects of the employed medium on specimen 2 are evident for the area of 10 x 10 μm. We assume that this discrepancy is caused by large variations in roughness of specimen at areas of 80 x 80 μm. These variations act as a noise in signal and overlap the nano topographic changes caused by corrosion processes. Results for specimen 2 indicate that a medium with 0.05 % NaF (250 ppm fluoride) causes the corrosion effects of NiTi which are observable on a nano scale. This finding was also confirmed in previous investigation [2,6], with electrochemical tests, where is reported that similar concentration of fluoride in medium causes a decrease of corrosion resistance and induces corrosion effects on the surface.

Changes that occurred on the surfaces indicate that the employed medium for specimen 2 causes material loss from the surface. This type of change causes a significant increase in concerned surface roughness parameters. These results lead us to the following findings. First, the increase of surface roughness (Sa) of the specimen is caused dominantly by material loss beneath the surface mean plane. Second, an increase of surface roughness parameter (S10z) indicates that the employed medium causes deepening of the existing grooves. Third, despite the fact that this investigation used medium with considerably lower concentration of fluoride than the one used in investigation [9], the same trend of change was observed. This indicates that the reduced fluoride concentration in medium did not cause a significant change of the operating corrosion mechanism. Fourth, we assume that a significant change in parameter Sa is not linked with an increase in depth of deepest grooves and its lower sensitivity to these changes. But, to the uniform changes that occur beneath the mean plane. Minor changes in values of confidence intervals are indications of uniform changes in specimen nano topography. Kassab et al [12] came to the same finding that fluoride containing media cause formation of evenly distributed pits on the surface (uniform corrosion).

The results of ANOVA (10 x 10 μm) can be an indication that the presence of NaF in mouthwash leads to corrosion effects. Again, this confirms the previous findings of Huang et al. [8], that the presence of NaF in solution leads to the increased corrosion effects of NiTi.

It is reported that exceeding the allowable mass loss limit of 0.5 μg / cm^2 / week of Ni ion release leads to allergenicity, toxicity, and carcinogenicity [2,5]. Change in the surface topography can be used for approximation of material loss caused by corrosion. The material loss that occurred on the surface can be approximated by employing the Sa parameter. Multiplying the difference of Sa parameter (Sa_{before}-Sa_{after}) with the area of the examined location will give an approximate value of a change in a volume. If we assume that all change in volume was caused only by release of Ni ions, a mass loss of 0.15 μg/ cm^2 / week can be approximated. Observing the approximation in material loss it can be noticed that it does not exceed the allowable mass loss limit. Although the observed changes do not exceed the limit, the occurred material loss is an order of magnitude of allowable limits. Therefore, the application of this mouthwash should be used in recommended dosage.

5. CONCLUSIONS

The corrosion behaviour of NiTi alloy in artificial saliva and fluoride containing mouthwash was investigated. Analysis of the obtained results leads us to the following conclusions:

- The changes in surface topography, that are induced by corrosion processes in non-accelerated tests, can be observed only on micro-areas such as 10 x 10 µm.
- Artificial saliva with pH 7.1 does not cause a change of NiTi alloy surface topography nor its chemical composition.
- Fluoride containing mouthwash (Aquafresh My Big teeth®) with the concentration of 0.05% NaF (250 ppm) causes a uniform corrosion of the surface which manifests with increase in surface roughness.
- According to the approximation of volume loss calculation, the application of Aquafresh My Big teeth® did not exceed the allowable limit of Ni ion release.
- Statistical analysis methods and AFM have been proven as a valuable tool in the characterization of nano topographic changes induced by corrosive media present in oral environment and health.

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REFERENCES

[1] T. W. Duerig, A. R. Pelton, and D. Stöckel: The utility of superelasticity in medicine., Biomed. Mater. Eng., vol. 6, no. 4, pp. 255–266, 1996.

[2] N. Schiff, B. Grosgogeat, M. Lissac, and F. Dalard: Influence of fluoridated mouthwashes on corrosion resistance of orthodontics wires, Biomaterials, vol. 25, no. 19, pp. 4535–4542, 2004.

[3] P. Močnik, T. Kosec, J. Kovač, M. Bizjak, The effect of pH, fluoride and tribocorrosion on the surface properties of dental archwires, Mater. Sci. Eng. C. 78 (2017) 682–689. Mater. Biol. Appl., vol. 78, pp. 682–689, Sep. 2017.

[4] M. R. Grimsdottir, A. Hensten-Pettersen, and A. Kullmann: Cytotoxic effect of orthodontic appliances, Eur. J. Orthod., vol. 14, no. 1, pp. 47–53, 1992.

[5] R. Köster, D. Vieluf, M. Kiehn, M. Sommerauer, J. Kahler, S. Baldus, T. Meinertz, C.W. Hamm: Nickel and molybdenum contact allergies in patients with coronary in-stent restenosis, Lancet, vol. 356, no. 9245, pp. 1895–1897, Dec. 2000.

[6] H. H. Huang: Variation in surface topography of different NiTi orthodontic archwires in various commercial fluoride-containing environments, Dent. Mater., vol. 23, no. 1, pp. 24–33, 2007.

[7] A. Geramy, T. Hooshmand, T. Etezadi: Effect of Sodium Fluoride Mouthwash on the Frictional Resistance of Orthodontic Wires., J. Dent. (Tehran)., vol. 14, no. 5, pp. 254–258, 2017.

[8] H. H. Huang, T. H. Lee, T. K. Huang, S. Y. Lin, L. K. Chen, and M. Y. Chou: Corrosion resistance of different nickel-titanium archwires in acidic fluoride-containing artificial saliva, Angle Orthod., vol. 80, no. 3, pp. 547–553, 2010.

[9] C.M. Ogawa, K. Faltin, F.A. Maeda, C.L.F. Ortolani, R.O. Guaré, C.A.B. Cardoso, A.L.F. Costa: In vivo assessment of the corrosion of nickel–titanium orthodontic archwires by using scanning electron microscopy and atomic force microscopy, Microsc. Res. Tech., vol. 83, no. 8, pp. 928–936, 2020.

[10] G. Perinetti, L. Contardo, M. Ceschi, F. Antoniolli, L. Franchi, T. Baccetti, R. Di Lenarda: 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., vol. 34, no. 1, pp. 1–9, 2012.

[11] H.H. Huang, Y.H. Chiu, T.H. Lee, S.C. Wu, H.W. Yang, K.H. Su, C.C. Hsu: Ion release from NiTi orthodontic wires in artificial saliva with various acidities, Biomaterials, vol. 24, no. 20, pp. 3585–3592, 2003.
[12] E. J. Kassab and J. P. Gomes: Assessment of nickel titanium and beta titanium corrosion resistance behavior in fluoride and chloride environments, Angle Orthod., vol. 83, no. 5, pp. 864–869, Sep. 2013.
[13] Directive EU, 2004/96/EC: Amending Council Directive 76/769/EEC as Regards Restrictions on the Marketing and Use of Nickel for Piercing Post Assemblies for the Purpose of Adapting its Annex I to Technical Progress.