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Corrosive changes and chemical composition of the orthodontic archwires' surface during treatment

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The orthodontic archwires are an integral part of the fixed appliance used for treatment of orthodontic malocclusions. The chemical composition of the surface of three of the most frequently used archwires in orthodontic treatment worldwide and in Bulgaria is investigated, which consist of the following types of metal alloys: chromium-nickel stainless-steel, nickel-titanium, and titanium-molybdenum. The results of XRD, SEM and EDS show that the main element composition of the orthodontic archwires has not been changed for the examined residence time in the patient's mouth, which is an average of 6 and 10 weeks and the complex oral bacterial flora does not influence them.

Key words: orthodontic wires, XRD, SEM, EDX, surface chemical composition.

INTRODUCTION

The orthodontic wires are an integral part of the fixed appliance which is used to treat orthodontic malocclusions. The most frequently used archwires are made of the following alloys: chromium-nickel stainless steel, nickel-titanium, titanium-molybdenum and copper-nickel-titanium. Each of these alloys has its specific characteristics and the corresponding wires made by them possess the typical mechanical properties which enables choice in different treatment phases.

The orthodontic wires, made by stainless steel, classified by AISI (American Iron and Steel Institute) as type 304, are with chemical composition as follows: approximately 71% iron, 18–20% chromium, 8–11% nickel and quantities of carbon, manganese and silicon, respectively not exceeding 0.08%, 2% and 1% [1, 2]. Their mechanical properties are determined by the chemical composition and the microstructure and they are the most frequently used in their austenitic form. They are hard, elastic and have the smoothest surface, which leads to reducing of the friction between the wire and the brackets [3].

Nickel-titanium wires presented by Andreasen and Hilleman [4] in 1970 contain nearly equal amounts of nickel and titanium, respectively, 54–55% and 43-44%, and minimum amount of cobalt – 1.6–3%. They have very low modulus of elasticity and high elastic potential compared to the stainless steel and thus they are able to let out weak and continuous forces, which is desirable during the orthodontic treatment. These first wires are in martensite state and it is believed that they have curved monoclinic, three-clinic or hexagonal crystal structure [5]. They are known as non-super-elastic. The modern orthodontic nickel-titanium wires exist in the austenitic state with cubic crystal structure. They are called super-elastic and are able to undergo stress-induced transformation from austenite to martensite. When subjected to load or activated till elastic deformation they restore their shape approximately 8% of the initial [6].

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Later titanium-molybdenum wires are introduced (β-Ti, or TMA) [7], which are characterized by a high springy effect, low hardness, can be bent and directly soldered. The Element composition of these wires contains: 79% Ti, 11% Mo, 6% Zr and 4% Sn, and the adding of zirconium and zinc contributes to the strength and hardness of the arch. Their major disadvantage is the high friction coefficient.

A new generation of wires is the copper-nickel-titanium arches, which are known as orthodontic wires with shape memory, also called heat-activated. That's because they can be deformed in the martensite state but when increasing their temperature in the oral cavity a phase transformation is induced towards austenite and the form of the arch is returned to the original one [8].

The presented three types of orthodontic wires are used at certain treatment's stages with fixed equipment. They stay in the mouth a certain period, during which they are exposed to the aggressive environment of the oral cavity. The latter is characterized by the presence of complex oral microflora, which together with its bioproducts forms and accumulates plaque around the material [9]. Also the impact of food that the patient used, the type of tooth pastes and the temperature changes occurring in the oral cavity should not be overlooked. All this leads to changes in the surface characteristics of the retrieved orthodontic archwires.

It is established that the surface of the orthodontic wires is covered by the formed intraoral protein coat which covers up their topographic surface to a degree depending on the individual patient's oral circumstances and on the intraoral exposure period. The film's organic components founded on alloy's surface are amide, alcohol and carbonate while the predominant elements are sodium, potassium, chloride, calcium and phosphorus [10].

In the present study are considered three types (chromium-nickel stainless steel, nickel-titanium, titanium-molybdenum) orthodontic archwires and the changes in the chemical composition of the surface are observed when these wires are used for treatment.

MATERIAL AND METHODOLOGY

The research is on the orthodontic archwires of patients treated in 2012 by researchers – orthodontists. In relation to the study's objectives we provided the tested three main types of orthodontic wires in 3 pieces each, Table 1. The type A wires are with circular cross section 0.016 inches, and the remaining B, and C have a rectangular cross section – 0.016×0.022 inches. These are some of the most commonly used wires as a size and type that are offered by the distributors to the orthodontists in Bulgaria. The treatment of patients with orthodontic malocclusions is carried out with them as at certain treatment's stage the appropriate type and size wires are placed. Two wires are used of each type, which are compared with the corresponding starting wires, called control ones. The selected wires are used for the treatment and stayed in the patient's mouth, respectively 6 and 10 weeks. This period covers the average time of residence of the orthodontic wires at the mouth of the patient in order to perform a certain stage of orthodontic treatment. All wires, after removal from the patient's mouth, they are cleaned with disinfectant and placed in a resealable plastic bag each along with a note in which the following data is recorded: patient's name, his age, wires' type, the size, date of placement, date of removal, the total time of stay in the mouth.

Table 1. Characteristics of investigated orthodontic wires

Type of orthodontic wires	Cross section [inches]	Time of residence in the mouth
A – stainless steel, AISI 304*	0.016	A6 – 6 weeks A10 – 10 weeks
B – nickel-titanium alloys	0.016 × 0.022	B2 – 2 weeks B6 – 6 weeks B10 – 10 weeks
C – beta-titanium alloys	0.016 × 0.022	C6 – 6 weeks C10 – 10 weeks

The studied wires were analyzed by X-ray dispersive analysis (EDS), X-ray powder diffraction and scanning electron microscopy (SEM). Powder X-ray diffraction patterns were collected within the range from 5.3 to 80° 2θ with a constant step 0.02° 2θ on Bruker D8 Advance diffractometer with CuKα radiation and LynxEye position sensitive detector. Phase identification was performed by the program DiffracPlus EVA using ICDDPDF-2 (2009) database. The microstructure of the wires surface was studied by means of Zeiss EVO MA-15 scanning electron microscope (SEM) with LaB_6 cathode on the polished cross-section samples. The chemical composition was determined by the X-ray microanalysis using the energy dispersive spectroscopy (EDS) method and Oxford Instruments INCA Energy system. The qualitative and quantitative analyzes were carried out at an accelerating voltage 20 kV, an optimal condition for these samples.

RESULTS AND DISCUSSION

XRD patterns of the orthodontic archwires from the type A are amorphous, these of type B and C are presented in Figure 1a) and 1b) respectively. On Fig. 1a) it can be seen the peaks of a crystalline phase marked with asterisk. The peaks correspond to the NiTi alloy with composition $Ni_{1.02}Ti_{0.98}$ (ICDDPDF#65-5746) with cubic type structure S.G. Pm-3m and unit cell parameter 3.01Å. For the peaks of the alloy presented in Fig. 1b) the best correspondence was found with a hexagonal phase (Ti_2Sn) with unit cell parameters a = 4. 65 Å and c = 5.7 Å. It is worth nothing that an amorphous hump is seen of the diffraction patterns of arches after prolonged usage for patient treatment. This amorphous part comes not only from corrosion processes on the wires surface but mostly from organic residues. The formed biofilms and calcification layers are well adsorbed to the wire surface and may play protective role towards the alloy surface. It should be mentioned that the presence of such films as well as their thickness and composition do not correlate well with the time of the wires application. The quality of the film is also patient dependant. These differences are mainly related to the nourishing traditions, composition of the saliva and the hygienic habits.

The information about the change in the surface morphology of the orthodontic wires is obtained by scanning electron microscopy (SEM), Fig 2. The observed change in the surface of the archwires is studied in details through energy dispersion study (EDS). The method used allows quantitative identification of the chemical composition by elements and focuses on the corrosion changes of the alloy rather than commenting on the complex oral flora. In Table 2 are presented the average values of the main components contained in the wires' alloy (Fe, Cr, Ni, Si and Mn) as well as the identified inclusions (P, S, Cl, K, Ca). For comparison are used the data of the studied as-received wires. The results indicate that the presence of the inclusions are as a result of the oral bacterial flora and of the oral hygiene

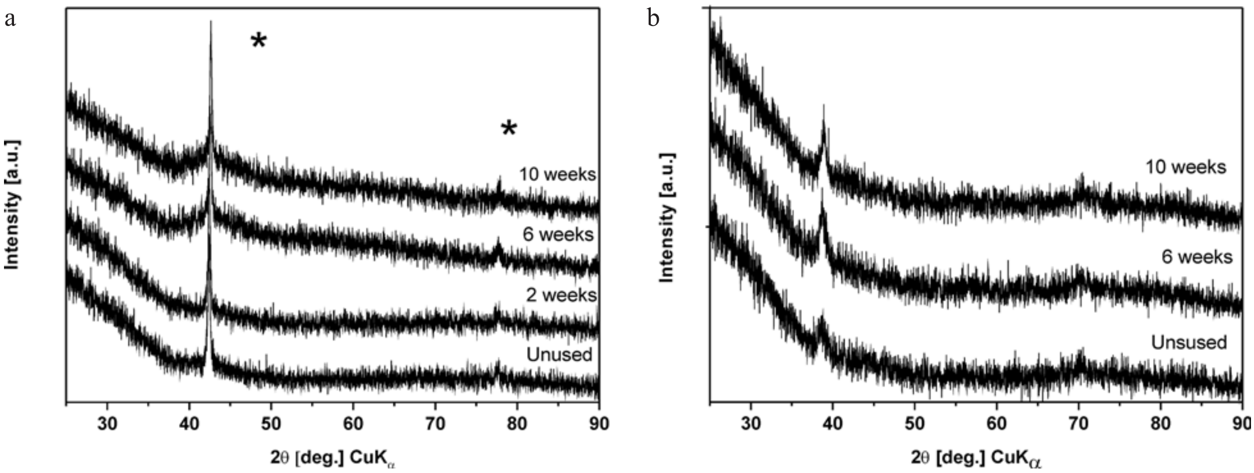

Fig. 1. a) XRD patterns of the orthodontic archwires type B at different stages of treatment; b) XRD patterns of the orthodontic archwires type C at different stages of treatment

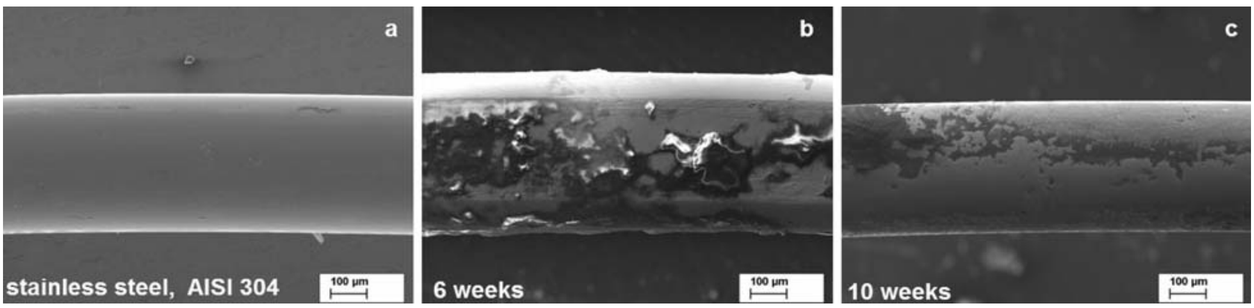

Fig. 2. Scanning electron microscopy images of A-austenitic stainless steel wires with cross section 0.016 inches: a) – as-received (A); b) – 6 weeks retrieved wire (A6) and c) – 10 weeks retrieved wire (A10)

Table 2. Elements content in new wire type A-stainless steel and used ones after 6 and 10 weeks

Elements, weight %	Si	Cr	Mn	Fe	Ni	P, S, Cl, K, Ca
Initial components content (new wire)	0.67	19.48	1.4	70.19	8.26	–
Mean components content after 6 weeks treatment	0.86	19.51	1.51	69.63	8.39	1.75
Mean components content after 10 weeks treatment	0.85	19.44	1.49	69.70	8.38	2.89

of the patient, while the main element composition of the orthodontic archwires from the stainless steel does not change for the examined period of treatment (6 and 10 weeks).

The second type of studied orthodontic wires is composed of nickel and titanium in almost equal amounts. Figure 3 shows the structure (3a) and the spectrum of the performed integral analysis of the element content by EDS (3b) of the as-received wires. The analysis confirms the two-component composition of nickel (54.67 wt.%) and titanium (45.38 wt.%).

After the usage of the wires correspondingly 6 and 10 weeks, which is shown in Figure 4, again changes of the surface are observed, which are associated with the presence of oral plaque. The presented scanning microscopical pictures are of selected areas of the wires' surface, where a point element analysis is made. The average values of the element composition are shown in Table 3. The quantity of nickel and titanium is not changed during the time of use. On the wires' surface that has stayed in for 10 weeks are observed surface irregularities, Figure 4c, which we assume, are as

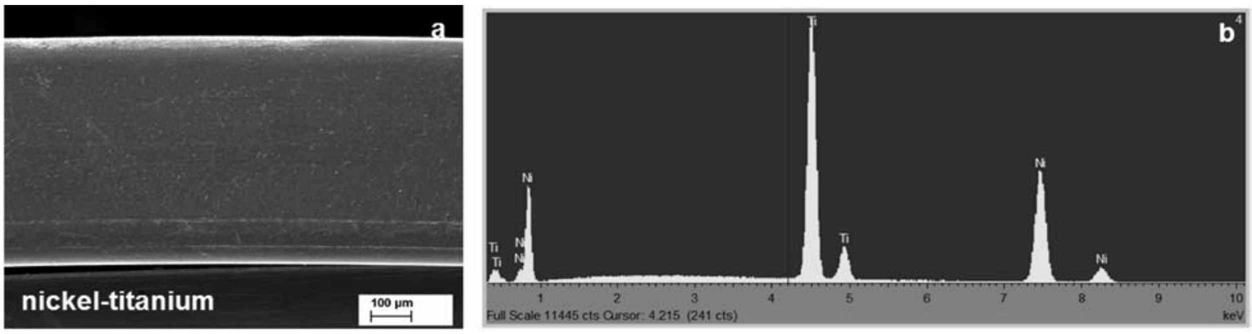

Fig. 3. Scanning electron microscopy images of as-received nickel-titanium wire and EDS spectrum of wire

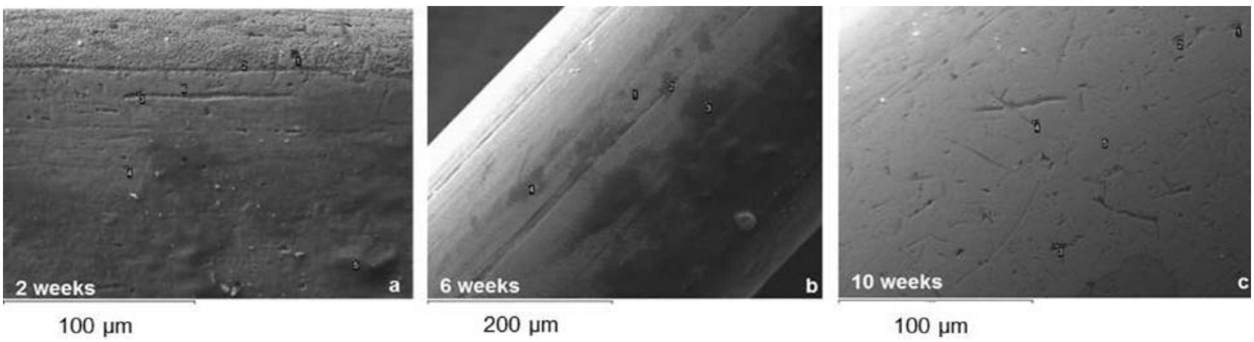

Fig. 4. Scanning electron microscopy images of retrieved nickel-titanium wires: a) – 2 weeks retrieved wire (B2); b) – 6 weeks retrieved wire (B6) and c) – 10 weeks retrieved wire (B10)

Table 3. Elements content in new wire type B – nickel-titanium alloys and used ones after 2, 6 and 10 weeks

Elements, weight %	Ni	Ti	Al, P, S, Cl, K, Ca
Initial components content (new wire)	54.67	45.38	–
Mean components content after 2 weeks treatment	54.85	45.16	2.06
Mean components content after 6 weeks treatment	54.33	45.48	1.48
Mean components content after 10 weeks treatment	54.74	45.30	0.22

a result of mechanical action. According to some authors [11] such surface alterations may be caused by loads during chewing. It is difficult to trace and investigate the corrosion according to the treatment's time stage and the wires' residence in the mouth due to the individuality of each patient (type of food, hygiene, age, gender, etc.). As an example we will point out the carried out analysis of nickel - titanium archwires used only for 2 weeks (B2), in which there is a large percentage of accumulated plaque on the surface in comparison with those used for 6 and 10 weeks, Fig. 4a, Table 3. From the analysis it appears that the coating deposits cannot be regarded as foci of corrosive change in wires. In-depth research on the mechanical resistance is about to be made.

Figure 5 shows the structures of titanium-molybdenum orthodontic archwires, respectively, 5a – as-received, 5b – after 6 weeks, and 5c, after 10 weeks of use. The determined chemical composition by EDS analysis is presented in Table 4. The trend to maintain the main components of the alloy (Ti, Mo, Zr, and Sn) is also observed in this type of orthodontic wires. The element study of the wires surface's changes indicate the presence of Na, Ca, Cl, which is associated with biofilm formation and

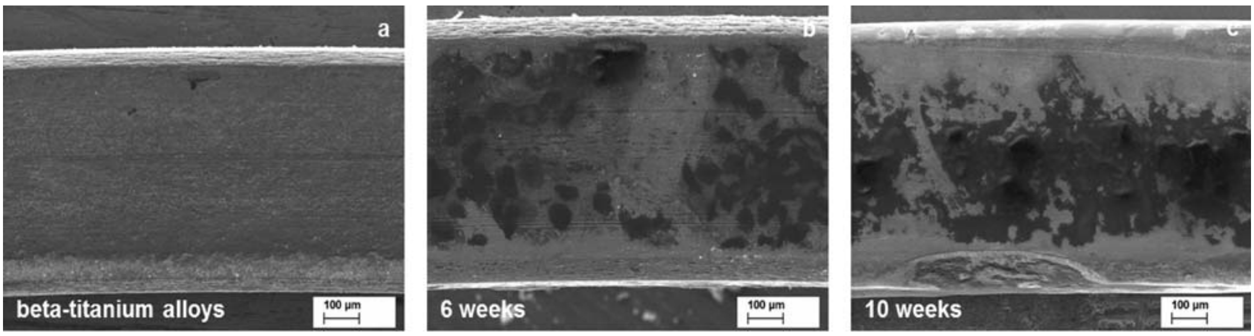

Fig. 5. Scanning electron microscopy images of retrieved beta-titanium wires with cross section 0.016×0.022 inches: a) – as-received (C); b) – 6 weeks retrieved wire (C6) and c) – 10 weeks retrieved wire (C10)

Table 4. Elements content in new wire type C beta – titanium alloys and used ones after 6 and 10 weeks

Elements, weight %	Ti	Zr	Mo	Sn	Na, Cl, Ca
Initial components content	76.90	6.36	11.87	4.86	–
Mean components content after 6 weeks treatment	76.80	7.11	11.45	4.65	0.52
Mean components content after 10 weeks treatment	77.09	6.54	12.4	3.95	4.27

does not contribute to a change of the initial wires' chemical composition.

CONCLUSION

The studied orthodontic archwires made of stainless steel, nickel-titanium and titanium-molybdenum is essential in orthodontic treatment. The analyses made and the achieved results show chemical resistance of all three wires. The orthodontic archwires are under continuous influence of the saliva, which is different from patient to patient and depends on the age, the hygiene of meal, the individual oral hygiene, which determines the plaque quality in the oral cavity, the presence of different diseases. From the carried out tests it is established that the complex oral flora, regardless of the changes it is subjected to according to the above described factors, it does not alter the major components of the alloys, which make them biocompatibility to the patient.

REFERENCES

1. R. S. de Biasi, A. C. O Ruela, C. N. Elias, O. Chevitarese, *J. Mater. Res*., **3**, 97 (2000).
2. W. A. Brantley, Orthodontic materials: scientific and clinical aspects, Stuttgart, New York, Thieme, 2001.
3. T. Eliades, et al., *Europ. J. Orthod*., **22**, 317 (2000).
4. G. F. Andreasen, T. B. Hilleman, *J. Am Dent. Assoc*., **82**, 1373 (1971).
5. R. P. Kusy, *Angle Orthod*., **67**, 197 (1997).
6. S. A. Thompson, *Int Endod J*., **33**, 297 (2000).
7. A. J. Goldberg, C.J. Burstone, *J. Dent. Res*., **58**, 593 (1979).
8. D. K. Pun, D. W. Berzins, *Dent. Mater.*, **24**, 221 (2008).
9. G. Eliades, T. Eliades, M. Vavuranakis, General aspects of biomaterials' surface alterations following exposure to biological fluids, D. C. Watts (ed.), Chicago, Quintessence, 2003.
10. T. Eliades, C. Bourauel, *Am J Orthod Dentofacial Orthop*., **127**, 403 (2005).
11. O. Prymak, A. Klocke, B. Kahl-Nieke, M. Epple, *Mater Sci Eng A*., **378**, 110 (2004).

КОРОЗИОННИ ПРОМЕНИ В ХИМИЧНИЯ СЪСТАВ НА ПОВЪРХНОСТТА НА ОРТОДОНТСКИ ДЪГИ ПРИ ИЗПОЛЗВАНЕТО ИМ ЗА ЛЕЧЕНИЕ

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(Резюме)

Ортодонтските дъги са неразделен елемент от фиксираната техника, използвана за лечение на ортодонтските деформации. Изследван е химичния състав на повърхността на три от най-използваните дъги за лечение в България, състоящи се от следните видове метални сплави: хром-никелова неръждаема стомана, никел-титан, титан-молибден и мед-никел-титан. Всяка една от тези сплави има своите специфични характеристики и направените от тях съответни дъги притежават характерни химични и механични свойства, давайки възможност за избор при употребата им в различните етапи от лечението. Резултатите от направените рентгенови и морфологични повърхностни изследвания показват, че основният химичен състав на ортодонските дъги не се променя в периода на лечение, който е между 2, 6 и 10 седмици. Наличието на химични примеси и отлагания се свързва с индивидуалната бактериална микрофлора в устната кухина на всеки пациентит.