Mapping chemical elements on the surface of orthodontic appliance by SEM-EDX

Authors' Contribution:
- Marcin Mikulewicz
- Paulina Wołowiec
- Izabela Michalak
- Katarzyna Chojnacka
- Wojciech Czopor
- Adam Berniczei-Royko
- Andras Vegh
- Thomas Gedrange

Corresponding Author: Marcin Mikulewicz, e-mail: mikulewicz.marcin@gmail.com

Source of support: This research was financially supported by The National Centre for Research and Development in Poland (N R130006 10)

Background: During orthodontic treatment, the various elements that constitute the fixed appliance undergo different processes. As a result of a change of the surface, elution/coverage of metals on the surface can be observed in the process of corrosion/passivation.

Material/Methods: Scanning electron microscopy with an energy-dispersive X-ray analytical system (SEM-EDX) was used to analyze the composition of stainless steel elements of orthodontic fixed appliances (before and after orthodontic treatment), to obtain the composition of the surface of the elements. The analyzed elements were: brackets (Victory Series APC PLUS 022, 3M Unitek, Monrovia, CA, USA); wires (0.017×0.025, 3M Unitek, Monrovia, CA, USA); and bands (37+, 3M Unitek, Monrovia, CA, USA).

Results: The results showed a decrease of chromium and iron contribution to the surface, with increase of oxygen content in used vs. new elements of the appliance.

Conclusions: Our results confirm the formation of oxides (passivation layer) on the surface of stainless steel as a result of the presence of the orthodontic appliance in patients' oral cavities.

MeSH Keywords: Corrosion • Microscopy, Electron, Scanning • Orthodontic Appliances • Stainless Steel

Full-text PDF: http://www.medscimonit.com/download/index/idArt/890769

This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License
Background

During treatment, fixed orthodontic appliances are placed in the oral cavity for around 2–3 years and are exposed to physical and chemical factors that may cause corrosion and passivation [1,2]. As a result of saliva flow, chewing, brushing, and friction between brackets and wires, as well as the effect of acidic drinks, mouthwash, toothpaste, and biofilm formation, the surfaces of the elements of the appliance are modified [3,4]. In stainless steel corrosion, the metals in the alloys undergo dissolution with the formation of ions, which are released into the surrounding environment (saliva) [5]. In passivation, oxides of metals are formed as a layer that protects the alloy from corrosion. As long as the passivation layer is intact, the corrosion does not progress. If the breakdown potential of an alloy is exceeded, the layer of oxides dissolves and corrosion proceeds [6].

Saliva (an electrolyte) provides an environment that supports the corrosion process. Additionally, organic acids produced by microorganisms, as well as enzymes, increase the progression of corrosion in the oral environment [7]. Considering the mechanisms of the process, the following types of corrosion can be distinguished: uniform, pitting, crevice, fretting, intergranular, galvanic, stress, and microbiological [8–10]. As a result of corrosion, metal ions (e.g., nickel and chromium) are released from the surface of orthodontic alloys, whose carcinogenic, mutagenic, cytotoxic, and allergenic impact can cause undesirable effects [11–13]. These metals are also released in tissues [14]. Apart from these biological results, another consequence of metal ion release from the alloy surface is damage to the surface (increase in roughness and the formation of craters and pits), which leads to weakening of the structure’s strength and may result in cracks or fractures of the elements [10,15–17]. The developing anaerobic environment enables the growth of bacteria that reduce sulphates to sulphides, which is accompanied by the formation of dark, insoluble residues [18].

The elements contained in the alloys of stainless steel (e.g., chromium and nickel) are responsible for forming a passivation layer on the elements’ surfaces, consisting of oxides (mainly Cr₂O₃ and NiO) that protect them from corrosion [7].

The method for the analysis of the surface morphology of orthodontic materials often used in the available literature is scanning electron microscopy with an energy-dispersive X-ray analytical system [18–21]. SEM-EDX analyses enable qualitative and quantitative assessments of particular elements in the alloys, and the results are proportional to the weight fractions of these elements in the alloy [22]. It is possible to indirectly estimate the ion release from the nickel, chromium, and iron of the orthodontic alloys [22].

Corrosion causes dissolution and consequent disappearance of metals from the surface of the alloy. Passivation means that metals on the alloy surfaces are covered with oxygen. Consequently, as a result of a change on the surface, elution/coverage of metals on the surface are observed in the process of corrosion/passivation, respectively. The aim of this study was to evaluate changes in the composition of the surfaces of elements for new and used orthodontic appliances by SEM-EDX.

Material and Methods

New and used (after 20 months of treatment) parts of fixed orthodontic appliances were evaluated. Wires, brackets, and bands (5 each in every element) were all made of stainless steel. All the elements were purchased from the following companies: brackets (Victory Series APC PLUS O22, 3M Unitek, Monrovia, CA, USA), wires (0.017 × 0.025, 3M Unitek, Monrovia, CA, USA), and bands (37+, 3M Unitek, Monrovia, CA, USA). Used elements (the same as the new ones) were collected from patients treated in the orthodontic practise. All parts were sent to a specialized laboratory for analysis.

Scanning Electron Microscopy (SEM-EDX)

The surfaces of the parts of fixed orthodontic appliances were evaluated by the SEM-EDX technique before and after orthodontic treatment. Samples were mounted appropriately and were subjected to X-ray microanalysis using Brüker AXS Quantax in conjunction with the software ESPRIT version 1.8.2. The ultrastructure of the examined material was analysed using a scanning electron microscope EVO LS15 ZEISS with an SE1 and CZ BSD detector, operating at EHT=10 kV. For each part of the fixed orthodontic appliances, 10 analyses (on both sides) were performed.

Statistical methods

The results were analyzed statistically by Statistica version 10.0 and descriptive statistics (means, standard deviations) are reported. Normality in the distribution of experimental results was assessed by the Shapiro-Wilk test. On this basis, a statistical test was selected, which was used to investigate the significance of differences between the groups. The differences between the groups were investigated using the Mann-Whitney U test, t-test, or Cochran-Cox test. Results were considered significantly different when p<0.05 and p<0.1.

Results

Micrographs of the components of the orthodontic appliances before and after the orthodontic treatment (magnification...
20 and 1000 times) are shown in Figure 1. Maps of the distribution of elements on the surface of the analysed elements magnified by 1000 are shown in Figure 2. Table 1 presents the atomic content of the elements on the examined surfaces. Pictures were taken and mapping of the atomic density of the elements was performed. During the analysis of
the surface composition of the tested elements at a magnification of 1000, a decrease in the content of Cr and Fe was observed on the surface of the brackets, bands, and wires (Table 1).

Table 1. Atomic concentration of elements (% of all detected elements) on the surface of wires, bands and brackets, n=10.

|       | Wire       | Bands      | Brackets   |
|-------|------------|------------|------------|
|       | New       | Used       | p          | New       | Used       | p          | New       | Used       | p          |
| Fe    | 68.87±1.03 | 58.83±9.09 | <0.05*     | 69.31±7.70 | 59.31±7.70 | <0.05*     | 68.83±4.52 | 63.31±4.52 | <0.05*     |
| Cr    | 18.46±0.73 | 17.40±2.29 | ns         | 17.25±0.35 | 16.56±1.71 | ns         | 17.25±0.83 | 16.56±1.71 | <0.05**    |
| Ni    | 10.22±0.97 | 11.41±1.81 | <0.05*     | 13.01±0.05 | 13.24±0.79 | <0.05*     | 10.22±0.97 | 11.41±1.81 | ns         |
| O     | <0.01     | 3.94±2.86  | <0.05*     | <0.01     | 0.08±0.05  | <0.05*     | <0.01     | 0.08±0.05  | 0.80±0.85  |

Atomic concentration of other elements (Mn, Al, Ti, Na, Ca, Mg, K, C, S, N, P, Cl) were below 1%. * U Mann-Whitney test; ** Student’s t-test; ns – not statistically significant.
**Discussion**

The surface composition of the wires, bands, and brackets changed after 20 months of orthodontic treatment. In all the elements, the percentage contribution of Fe and Cr decreased (in wires: Fe 15%, Cr 6%; in bands: Fe 8%, Cr 4%; in brackets: Fe 2.5%, Cr 8%) and Ni and O increased (in wires: Ni 12%, O from below LLD (lower limit of detection) to 3.4%; in bands: Ni 1%, O from below LLD to 0.08%; in brackets: Ni 35%, O decreased 46%). This could suggest solubilization of Fe and Cr and passivation by oxides.

Stainless steel, containing Fe and Cr, is classified as a corrosion-resistant alloy. However, according to published reports, 316L stainless steel (of which orthodontic brackets are made) possesses a corrosion potential (release of Ni). The resistance to corrosion of stainless steel is related to the Cr content, which spontaneously forms oxides and thus a passivation layer. Acidity and chlorides cause destruction of the passivation layer. The passivation layer, besides Cr, also contains other metals – Fe, Ni, and Mo [8].

The products of stainless steel passivation consist mainly of iron (48.82%), chromium (17.9%), nickel (4.73%), and oxygen (19.56%) [22]. These can be Fe₂O₃ (or hydrated forms), Fe₅O₇, FePO₄, Fe(OH)₃, or Cr(OH)₃ [18,23–25]. Similar results were obtained by Menezes et al. during a study of bracket surfaces made of stainless steel after 60-day incubation in a physiological saline solution [22]. Using a magnification of 1000, the atomic density mapping of the elements was analysed. Areas with the highest density of O were found, which suggests that oxides were present in the examined surfaces.

We observed that an organic layer containing Na, P, S, Cl, K, and Ca was present on the wires [26]. The research also showed that there was significantly more residue on the wire surface. In brackets, the largest amount of residue was observed between the wings, yet the wing surfaces, as well as the areas that adjoined the wires, were relatively free of biofilm. The accumulation of residue in the above-mentioned areas on the wires and bracket surfaces is a result of difficulties in access during tooth brushing.

**Conclusions**

The analysis of the surface composition showed a decrease in the content of chromium and iron on the surface of the components of fixed orthodontic appliances, which showed the contribution of passivation and corrosion.
23. Escriva-Cerdan C, Blasco-Tamarit E, Garcia-Garcia DM et al: Temperature Effect on the Corrosion Behaviour of Alloy 31 in polluted H3PO4 and Analysis of the Corrosion Products by Laser Raman Microscope. Int. J Electrochem Sci, 2012; 7: 5754–64

24. Huttunen-Saarivirta E, Honkanen M, Lepisto T et al: Microbiologically influenced corrosion (MIC) in stainless steel heat exchanger. App Surf Sci, 2012; 258: 6512–26

25. Kocijan A, Milosev I: The influence of complexing agent and proteins on the corrosion of stainless steels and their metal components. J Mater Sci-Mater Med, 2003; 14: 69–77

26. Edie JW, Andreasen GF, Zaytoun MP: Surface Corrosion of Nitinol and Stainless Steel Under Clinical Conditions. Angle Orthod, 1981; 51: 319–24