MEDICAL SCIENCE MONITOR

MEDICAL TECHNOLOGY

e-ISSN 1643-3750
© Med Sci Monit, 2014; 20: 860-865
DOI: 10.12659/MSM.890769

Received: 2014.03.29
Accepted: 2014.04.16
Published: 2014.05.25

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

Authors' Contribution:
Study Design A
Data Collection B
Statistical Analysis C
Data Interpretation D
Manuscript Preparation E
Literature Search F
Funds Collection G

ABCDEFG 1 **Marcin Mikulewicz**
BCDEF 2 **Paulina Wołowiec**
BCDEF 2 **Izabela Michalak**
ABCDEF 2 **Katarzyna Chojnacka**
EF 3 **Wojciech Czopor**
DEF 4 **Adam Berniczei-Royko**
DEF 5 **Andras Vegh**
DEFG 6 **Thomas Gedrange**

1 Department of Dentofacial Orthopedics and Orthodontics, Division of Facial Abnormalities, Wrocław Medical University, Wrocław, Poland
2 Institute of Inorganic Technology and Mineral Fertilizers, Wrocław University of Technology, Wrocław, Poland
3 Department of Dentofacial Orthopedics and Orthodontics, Division for Facial Esthetics, University of Medical Sciences, Poznań, Poland
4 Department of Orthodontics, University of Szeged, Szeged, Hungary
5 Department of Orthodontics, Heim Pal Children Hospital, Budapest, Hungary
6 Department of Orthodontics, Technische Universität, Dresden, Germany

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

1264 1 2 26

Indexed in: [Current Contents/Clinical Medicine] [SCI Expanded] [ISI Alerting System] [ISI Journals Master List] [Index Medicus/MEDLINE] [EMBASE/Excerpta Medica] [Chemical Abstracts/CAS] [Index Copernicus]

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 progress 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 bioaccumulated 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 Cr_2O_3 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 022, 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 Brücker 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 Cochrane-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

Indexed in: [Current Contents/Clinical Medicine] [SCI Expanded] [ISI Alerting System]
[ISI Journals Master List] [Index Medicus/MEDLINE] [EMBASE/Excerpta Medica]
[Chemical Abstracts/CAS] [Index Copernicus]

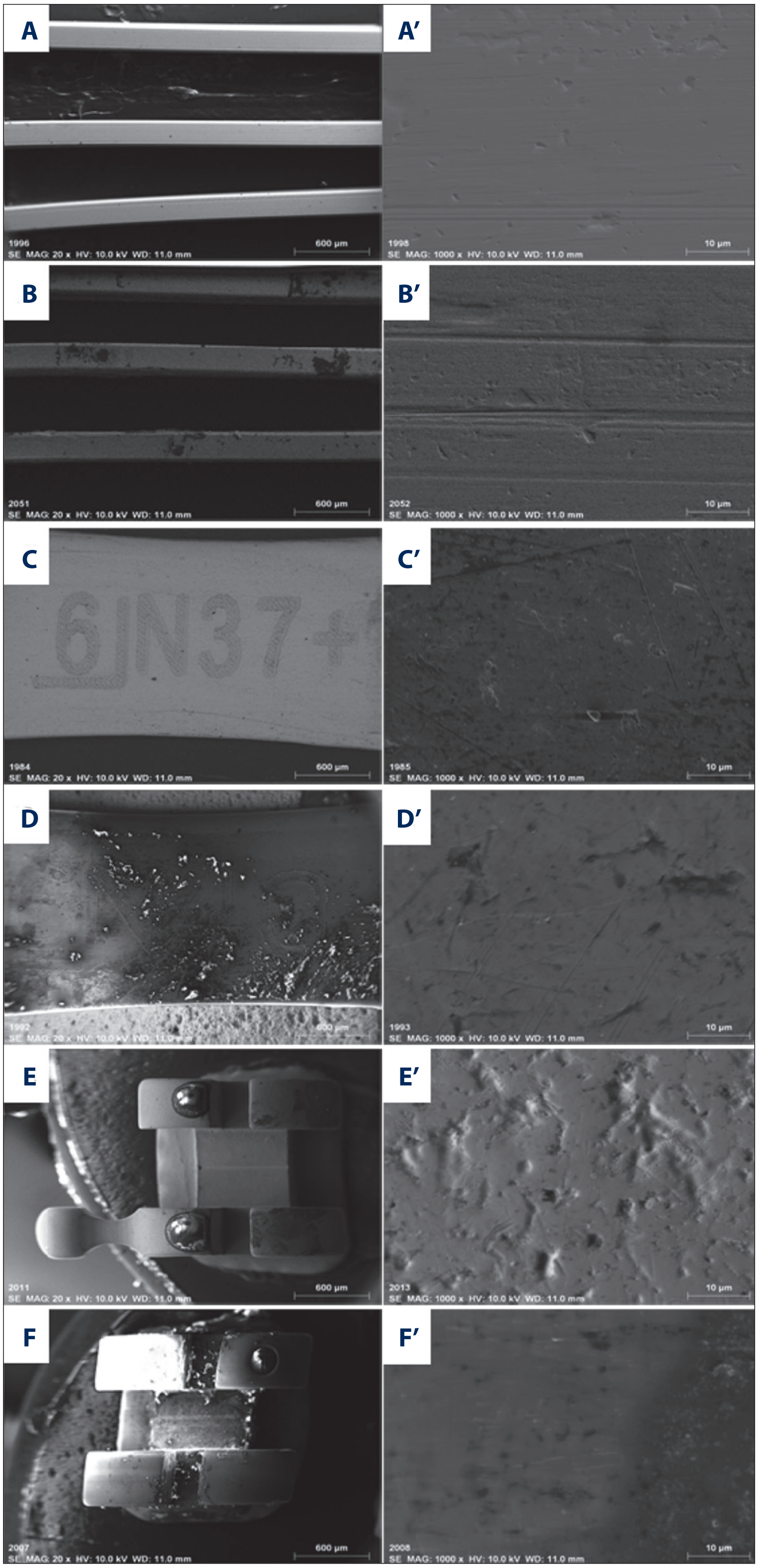

Figure 1. The surface: (**A, A'**) – wires (new); (**B, B'**) – wires (used); (**C, C'**) bands – (new); (**D, D'**) – bands (used); (**E, E'**) – brackets (new); (**F, F'**) – brackets (used); ×20 (**A–D**) and ×1000 (**A'–D'**).

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

Indexed in: [Current Contents/Clinical Medicine] [SCI Expanded] [ISI Alerting System] [ISI Journals Master List] [Index Medicus/MEDLINE] [EMBASE/Excerpta Medica] [Chemical Abstracts/CAS] [Index Copernicus]

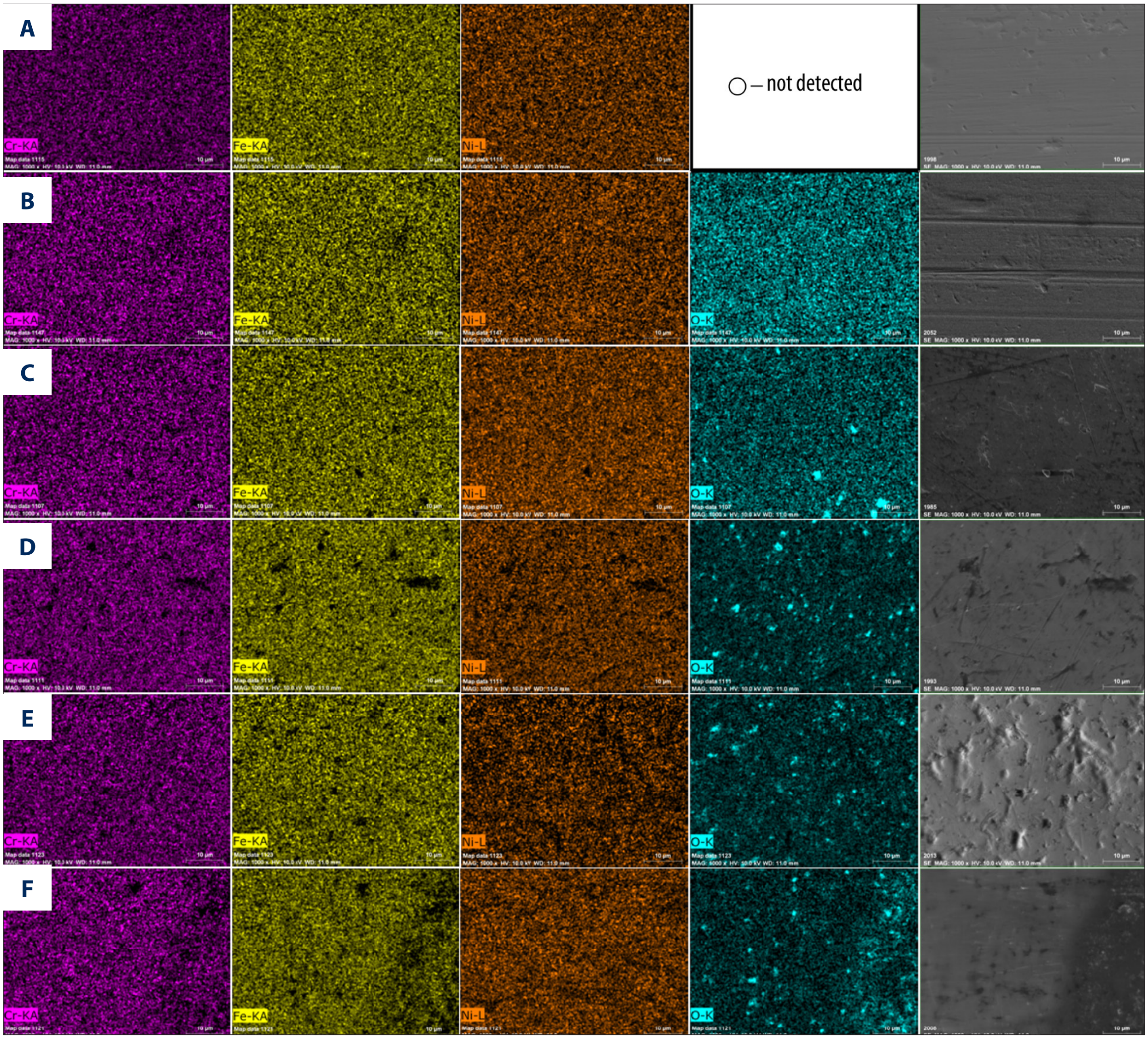

Figure 2. Maps of distribution of elements on the surface – (**A**) wires (new); (**B**) wires (used); (**C**) bands (new); (**D**) bands (used); (**E**) brackets (new); (**F**) brackets (used), ×1000.

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*	64.64±0.99	59.31±7.70	<0.05*	70.11±3.00	68.39±4.52	ns
Cr	18.46±0.73	17.40±2.29	ns	17.25±0.35	16.56±1.71	ns	16.55±0.58	15.24±0.83	<0.05**
Ni	10.22±0.97	11.41±0.81	<0.05*	13.01±1.05	13.24±0.79	<0.05*	7.03±1.66	9.46±2.07	<0.05**
O	<0.01	3.39±2.86	<0.05*	<0.01	0.08±0.05	<0.05*	0.80±0.85	0.43±0.46	ns

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

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 used (Table 1).

Indexed in: [Current Contents/Clinical Medicine] [SCI Expanded] [ISI Alerting System] [ISI Journals Master List] [Index Medicus/MEDLINE] [EMBASE/Excerpta Medica] [Chemical Abstracts/CAS] [Index Copernicus]

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 Fe_2O_3 (or hydrated forms), Fe_3O_4, $FePO_4$, $Fe(OH)_3$, 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.

References:

1. Sfondrini MF, Cacciafesta V, Maffia E et al: Chromium release from new stainless steel, recycled and nickel-free orthodontic brackets. Angle Orthod, 2009; 79: 361–67
2. Fernandez-Minano E, Ortiz C, Vincente A et al: Metallic ion content and damage to the DNA in oral mucosa cells of children with fixed orthodontic appliances. Biometals, 2011; 24: 935–41
3. Harzer W, Schröter A, Gedrange T, Muschter F: Sensitivity of titanium brackets to the corrosive influence of fluoride-containing toothpaste and tea. Angle Orthod, 2001; 71: 318–23
4. Amini F, Rakhshan V, Mesgarzadeh N: Effects of long-term fixed orthodontic treatment on salivary nickel and chromium levels: a 1-year prospective cohort study. Biol Trace Elem Res, 2012; 150: 15–20
5. Mikulewicz M, Chojnacka K, Wozniak B, Downarowicz P: Release of Metal Ions from Orthodontic Appliances: An *In Vitro* Study. Biol Trace Elem Res, 2012; 146: 272–80
6. Kim H, Johnson JW: Corrosion of stainless steel, nickel-titanium, coated nickel-titanium, and titanium orthodontic wires. Angle Orthod, 1999; 69: 39–44
7. Amini F, Borzabadi Farahani A, Jafari A, Rabbani M: *In vivo* study of metal content of oral mucosa cells in patients with and without fixed orthodontic appliances. Orthod Craniofac Res, 2008; 11: 51–56
8. Eliades T, Athanasiou AE: *In Vivo* Aging of Orthodontic Alloys: Implications for Corrosion Potential, Nickel Release, and Biocompatibility. Angle Orthod, 2002; 72: 222–37
9. House K, Sernetz F, Dymock D et al: Corrosion of orthodontic appliances – should we care? Am J Orthod Dentofacial Orthop, 2008; 133: 584–92
10. Chaturvedi TP, Upadhayay SN: An overview of orthodontic material degradation in oral cavity. Indian J Dent Res, 2010; 21: 275–84
11. Gedrange T, Kuhn UD, Walter B et al: Effects of 28-day mechanical and chewing stress on content of bound and diffusible ions in muscles of mastication. Exp Toxicol Pathol, 2001; 53: 207–13
12. Hafez HS, Selmi EMN, Eid FHK et al: Cytotoxicity, genotoxicity, and metal release in patients with fixed orthodontic appliances: a longitudinal *in-vivo* study. Am J Orthod Dentofac Orthop, 2011; 140: 298–308
13. Mikulewicz M, Chojnacka K, Wołowiec P: Release of metal ions from fixed orthodontic appliance an *in vitro* study in continuous flow system. Angle Orthod, 2014; 84: 140–48
14. Mikulewicz M, Chojnacka K, Zielinska A, Michalak I: Exposure to metals from orthodontic appliances by hair mineral analysis. Environ Toxicol Phar, 2011; 32: 10–16
15. Kao CT, Ding SJ, Chen YC, Huang TH: The anticorrosion ability of titanium nitride (TiN) plating on an orthodontic metal bracket and its biocompatibility. J Biomed Mater Res (Appl Biomater), 2002; 63: 786–92
16. Kao CT, Ding SJ, He H et al: Cytotoxicity of orthodontic wire corroded in fluoride solution *in vitro*. Angle Orthod, 2007; 77: 349–54
17. Luft S, Keilig L, Jager A, Bourauel C: *In-vitro* evaluation of the corrosion behavior of orthodontic brackets. Orthod Craniofac Res, 2009; 12: 43–51
18. Bagatin CR, Ito IY, Andrucioli MCD et al: Corrosion in Haas expanders with and without use of an antimicrobial agent: an *in situ* study. J Appl Oral Sci, 2011; 19: 662–67
19. Gedrange T, Mai R, Richter G et al: X-ray microanalysis of elements in the masticatory muscle after paresis of the right masseter. J Dent Res, 2005; 84: 1026–30
20. Fjeld M, Ogaard B: Scanning electron microscopic evaluation of enamel surfaces exposed to 3 orthodontic bonding systems. Am J Orthod Dentofacial Orthop, 2006; 130: 575–81
21. Amini F, Rakhsahan V, Pousti M et al: Variations in surface roughness of seven orthodontic archwires: an SEM-profilometry study. Korean J Orthod, 2012; 42: 129–37
22. Menezes LM, Souza RM, Dolci GS, Dedavid BA: Analysis of biodegradation of orthodontic brackets using scanning electron microscopy. Dental Press J Orthod, 2010; 15: 48–51

Indexed in: [Current Contents/Clinical Medicine] [SCI Expanded] [ISI Alerting System]
[ISI Journals Master List] [Index Medicus/MEDLINE] [EMBASE/Excerpta Medica]
[Chemical Abstracts/CAS] [Index Copernicus]

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

Indexed in: [Current Contents/Clinical Medicine] [SCI Expanded] [ISI Alerting System] [ISI Journals Master List] [Index Medicus/MEDLINE] [EMBASE/Excerpta Medica] [Chemical Abstracts/CAS] [Index Copernicus]