Galvanic Corrosion of Orthodontic Brackets and Wires in Acidic Artificial Saliva: Part II

[1]Tahereh Sheikh [2]Mohammad Ghorbani [*3]Soodeh Tahmasbi [4]Yadollah Yaghoubnejad

[1]Dentist.
[2]Professor, Dept. of Materials Science & Engineering, Sharif University of Technology, Tehran, Iran.
[*3]Assistant Professor, Dept. of Orthodontics, School of Dentistry, Shahid Beheshti University of Medical Sciences, Tehran, Iran. E-mail: tahmasbisoodeh@gmail.com
[4]PhD Student, Dept. of Materials Science & Engineering, Sharif University of Technology, Tehran, Iran.

Abstract

Objective: Orthodontic wires should have high resistance against corrosion in the oral environment. Since the effect of pH on corrosion has been well recognized, this study sought to assess and compare the electrochemical corrosion of orthodontic brackets and wires of different brands in acidic artificial saliva.

Methods: This *in vitro* experimental study was conducted on 24 mandibular central incisor brackets of 4 manufacturers namely Dentaurum, American Orthodontics, Shinye and ORJ. The brackets were immersed in acidic artificial saliva along with stainless steel (SS) or NiTi 0.016 round wires for 28 days. All specimens were weighed before and after the experiment by a digital scale. After the experiment, the specimens were evaluated under a light stereomicroscope and specimens with corrosion were further assessed by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX). Two-way ANOVA was used for statistical analysis.

Results: The mean corrosion rate (CR) was -1.80, 0.11, 0.05 and -0.93 mpy for Dentaurum, American Orthodontics, Shinye and ORJ brackets, respectively in combination with NiTi wire; these values were 0.46, -0.71, 0.87 and -0.27 mpy, respectively in combination with SS wires; the differences in this regard were not statistically significant ($p>0.05$). Micrographs showed high corrosion in ORJ brackets followed by Shinye brackets. EDX showed that the combination of ORJ bracket with SS wire had the highest iron (Fe) content and the highest CR.

Conclusion: SS brackets manufactured by Shinye and ORJ companies in combination with SS wires showed higher CR in acidic artificial saliva compared to other bracket/wire combinations.

Key words: Acidic artificial saliva, Bracket, Corrosion resistance, Orthodontic wire, Scanning electron microscopy.

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Introduction:

A primary requirement for any metal or alloy to be used in the oral cavity is not to release corrosion products with adverse health effects (1). Orthodontic alloys must have excellent corrosion resistance in the oral environment. This is especially important for better patient compliance to treatment and continuation of orthodontic therapy (2).

Corrosion is an electrochemical reaction between a metal or an alloy and the environment resulting in relative or complete destruction of material or altered properties (3).

Different types of corrosion of metals and alloys occur in the environment. Based on environmental conditions, general corrosion, galvanic corrosion or pitting corrosion may occur. Orthodontic wires, based on the type of metals or alloys in their composition, may show different types of corrosion (1).

Galvanic or electrochemical corrosion is the most common corrosion occurring in the oral environment. This type of corrosion occurs due to the contact of two dissimilar metals. The weaker metal (anode) is corroded in this process. Presence of two dissimilar metals in an electrolyte solution creates a galvanic couple. The electrolyte helps the migration of ions and consequently, corrosion occurs faster. The contact surface of metals is very important in this type of corrosion and the larger the cathode and the smaller the anode area, the more severe the corrosion due to the concentration of corrosion current.

The significance of galvanic corrosion is attributed to increasing the overall corrosion of metals; especially when two metals are in contact with one another. In cases where the corrosion potential difference is high between the two metals in contact with one another, the electrochemical corrosion would be the dominant type. This type of corrosion occurs between the orthodontic brackets and wires in the oral environment and occurs due to the contact of two different alloys in an electrolyte (saliva). Depending on the conditions and characteristics of metals and the composition of saliva, it may comprise a large portion of general corrosion of wires and brackets (4-7).

The process of corrosion can be limited to specific points on the metal surface and form a pit or a crack or may be evenly distributed on the metal surface and affect the entire surface of metal. Since the occurrence of corrosion requires the dissolution of metal, it occurs on the surface of metals. Therefore, different surface coating techniques can be applied to reduce the corrosion current (8).

The most common type of corrosion that occurs in orthodontic brackets and wires is the crevice and pitting corrosions. The crevice corrosion occurs between two close surfaces or where oxygen exchange cannot occur. This type of corrosion often occurs when non-metal materials are used over metals (i.e. use of elastomers and O rings to hold the brackets). Reduction in pH and increased concentration of chloride ions are important factors responsible for initiation and progression of this type of corrosion. By increased acidity of the environment, the protective layer on the metal surface is ruined and the corrosion is intensified (9, 10).

Pitting corrosion is a type of local corrosion resulting in pitting and cavitation of the surface of specimens and usually occurs in metals containing superficial oxide layers. This type of corrosion has been reported in orthodontic wires and brackets and occurs due to the local loss of superficial protective oxide layer on the metal surfaces. Evidence shows that this type of corrosion occurs in SS, Cr-Co, Ni-Cr, and NiTi arch wires (11).

In addition to the potential difference between two metals, many other factors play a role in galvanic corrosion. Based on the composition of solution, the degree of galvanic corrosion varies (12). Moreover, corrosion is intensified in the acidic environment and thus, commonly used acidic foods and drinks may intensify the process of corrosion (4),

The effect of pH on corrosion has been well investigated. Low pH (in an acidic environment) corrodes many metals and alloys. The same occurs in the oral environment for orthodontic metal wires. At a pH of 4-6, in presence of sodium fluoride and artificial saliva, SS wires and Ni-Ti alloy are subjected to pitting corrosion (1). Corrosion can adversely affect the mechanical properties of brackets and release some compounds with potentially cytotoxic and biological side effects (13).

Metals and alloys are extensively used in orthodontics and restorative dentistry. Considering the high cost of metals and alloys used for dental purposes and the resultant tendency of clinicians to use cheaper products, it is important to assess the corrosion resistance of metals and alloys in the oral environment. This study aimed to assess the electrochemical corrosion of wires and brackets manufactured by 4 different manufacturing companies namely Dentaurum, American Orthodontics, Shinye and ORJ in acidic artificial saliva. The results may help clinicians choose the most suitable orthodontic wires and brackets.

Methods:

In this *in vitro*, experimental study, sample size was calculated to be 3 in each group using PASS software considering 0.05 level of significance and 80% study power. A total of 24 mandibular central slot Roth0.022 brackets from 4 different manufacturers namely Dentaurum (Dentaurum, Ispringen, Germany), American Orthodontics (American Orthodontics, Wisconsin, USA), Shinye (Hangzhou Shinye Orthodontic Products Co., Ltd. China) and ORJ (Hangzhou ORJ Medical Instrument & Material Co., Ltd., Zhejiang, China) in 8 groups were evaluated. Six of each were coupled with round 0.016 SS or NiTi American Orthodontics wires in 8 groups of 3. The electrolyte used was acidic (pH of 4.5) artificial saliva with Fusayama-Meyer formulation (Morvabon, Tehran, Iran). The wire/bracket surface area was considered to be 1:1 and the remaining part of the wire was coated with impermeable nail varnish to prevent the penetration of electrolyte. In each specimen, the wire and bracket were attached using elastomeric ligature (O ring). Study groups are demonstrated in Table 1.

Table 1- Study groups as wire-bracket couples

Wire/Bracket	Dentaurum	American Orthodontics	Shinye	ORJ
NiTi	Group 1	Group 2	Group 3	Group 4
SS	Group 5	Group 6	Group 7	Group 8

All brackets and wire segments were immersed in acetone solution for 2 minutes before weighing to clean their surfaces. Next, the wires and brackets were separately weighed using a digital scale (XS204, Mettler Toledo, Columbus, OH, USA) with an accuracy of 0.1 mg. The values were recorded in grams.

Each of the prepared specimens was placed in a separate container with a saturated calomel reference electrode (saturated Ag/AgCl with KCl, Azmiran laboratory equipment, Tehran, Iran). Each specimen and the reference electrode were attached to a voltmeter with connecting wires; 80cc of acidic artificial saliva was added to each container as electrolyte (according to ASTM G71-81 standard)(14) and the circuit was completed. The specimens were stored at 37±0.1°C. After 28 days, the circuit was opened and the wires and brackets were individually washed with distilled water gently for 30 seconds and dried.

All bracket and wire specimens were evaluated under a light stereomicroscope (Olympus Optical Co., Ltd., Tokyo, Japan)before further washing. Images were obtained of the specimens, and the corroded samples (3 brackets) were subjected to SEM (Mira II LMU, Tescan, Brno, Czech Republic) assessment before and after washing. The remaining specimens were washed as described below for final weighing:

The O ring was removed to separate the wire and bracket. The varnish coating was removed using acetone. Bracket and wire specimens were immersed in 10% sulfuric acid for 2 minutes at room temperature and then rinsed with distilled water to remove any residues. Specimens were then immersed in sulfuric acid at 40°C for 2 minutes and after final rinsing with distilled water for one minute, they were dried and weighed. Final weights were recorded. Specimens sent for SEM analysis were also washed and weighed as such. Acid washing was performed to clean the corrosion products accumulated on the surface of specimens.

The results were compared using two-way ANOVA and based on the results of this test, pairwise comparisons were carried out using the appropriate post hoc test of Tukey's HSD, t-test or Tamhane's test.

Results:

Results of CR:

To calculate the CR, the difference between the baseline and final weight of wires and brackets was measured and the CR was calculated using the equation below:

$$CR=\frac{534\times AM}{D\times T\times A}(mpy)$$

1mpy=25.4 (microns/year)

Where W is weight in g/cm^2, D is density in g/cm^2, A is the surface in square inch and T is time in hours. Since corrosion only occurred in brackets and the wires were free of corrosion, the CR was only calculated for brackets and the obtained values are shown in Table 2.

Two-way ANOVA revealed that the interaction effect of wire and bracket on CR was not significant either for the brackets or for the wire ($p>0.05$).

Table 2- The mean CR of brackets based on the type of bracket and wire

Type of wire	Type of bracket	Mpy (SD)	Microns/year (SD)
NiTi	Dentaurum	-1.80 (1.66)	-45.90 (42.23)
	American Orthodontics	0.11 (0.84)	2.80 (21.57)
	Shinye	0.05 (0.36)	1.47 (9.21)
	ORJ	-0.93 (1.81)	-23.82 (46.11)
SS	Dentaurum	0.46 (0.62)	11.82 (15.76)
	American Orthodontics	-0.71 (0.81)	-18.21 (20.73)
	Shinye	0.87 (1.21)	22.12 (30.97)
	ORJ	-0.27 (0.50)	-7.00 (12.84)

Assessment of corroded specimens under a light stereomicroscope:

After opening the set up and before washing with acid, all specimens were evaluated in terms of corrosion using a light stereomicroscope. Three specimens were found to have corrosion as follows:

1. Third specimen from group 4 (ORJ bracket with NiTi wire, specimen #12).
2. First specimen from group 7 (Shinye bracket with SS wire, specimen # 19)
3. Third specimen from group 8 (ORJ bracket with SS wire, specimen #24)

Evaluation of the three corroded specimens under light stereomicroscope revealed the followings:

1. Third specimen from group 4 (ORJ bracket with NiTi wire, specimen #12):

No corrosion was detected in the wire. In the bracket, green deposits were observed below the wing. Acid washing revealed corrosion beneath the deposits (Figure 1).

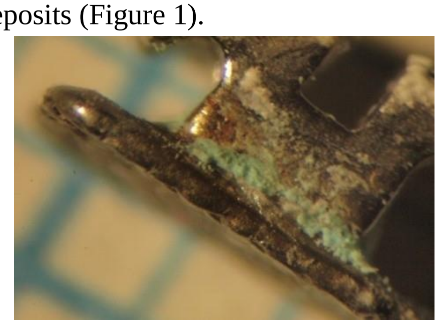

Figure 1- Bracket of the third specimen from group 4 at 6X magnification

2. First specimen from group 7 (Shinye bracket with SS wire, specimen # 19):

No corrosion was noted on the wire surface. On the bracket surface, green deposits were seen at the site of O ring. Acid washing revealed crevice corrosion beneath the O ring and corrosion products (Figure 2).

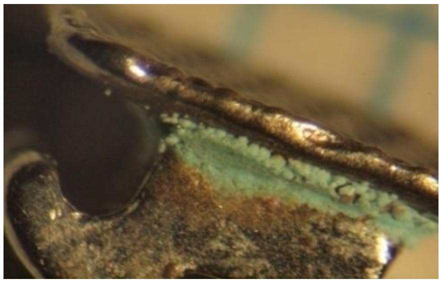

Figure 2- Bracket of the first specimen from group 7 at 7X magnification

3. Third specimen from group 8 (ORJ bracket with SS wire, specimen #24):

No corrosion was noted on the surface of wire. Deposits were noted on the bracket surface. Pitting corrosion was noted beneath the deposits and crevice corrosion was noted at the interface of O ring and bracket (based on the appearance, the corrosion was severe in this specimen) (Figure 3).

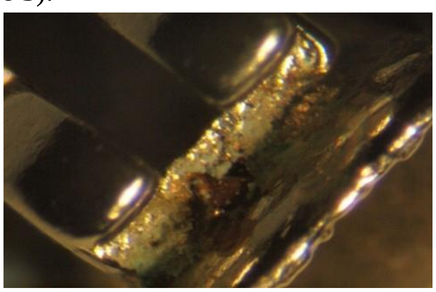

Figure 3- Bracket of the third specimen from group 8 at 7X magnification

Results of SEM analysis of corroded specimens:

1. Third specimen from group 4 (ORJ bracket with NiTi wire, specimen #12):

Micrographs before acid washing:

Figure 4a- SEM micrograph of ORJ bracket surface after the experiment and before washing at 1000X magnification

As seen in Figure 4a, the diameter of deposits was 20-40 μm and 80-100 μm. Deposits had high density and were interrupted and spherical in shape.

Micrographs after acid washing: Electrochemical corrosion products were also noted on the surface of ORJ brackets coupled with NiTi wire in the electrolyte. These products appeared green under the light microscope. After testing, on the surface of ORJ bracket coupled with NiTi wire, deposits, crevice corrosion, pitting corrosion, surface corrosion and many defects were noted in order of frequency.

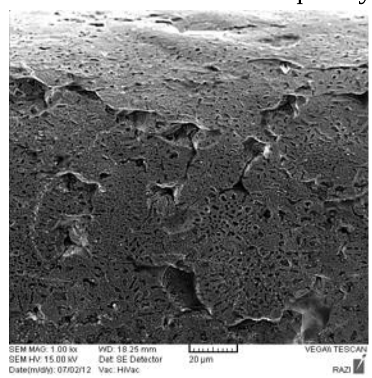

Figure 4b- SEM micrograph of ORJ bracket surface after testing and washing at 1000X magnification

2. First specimen from group 7 (Shinye bracket and SS wire, specimen #19):

Micrographs before acid washing:

As seen in Figure 5a, deposits had a diameter of 50-60 μm. Deposits had high density and were interrupted and spherical in shape on the bracket surface.

Figure 5a- SEM micrograph of Shinye bracket surface after the experiment and before washing at 1000X magnification

Micrographs after acid washing:

Electrochemical corrosion products were noted on the surface of Shinye brackets coupled with SS wire. These brackets were appeared yellow and green under light microscope.

After the experiment, on the surface of Shinye brackets coupled with NiTi wire, crevice corrosion, pitting corrosion, surface corrosion and many defects were noted in order of frequency.

Figure 5b- SEM micrograph of Shinye bracket surface after the experiment and washing at 814X magnification

<u>3. Third specimen from group 8 (ORJ bracket coupled with SS wire, specimen #24):</u>

Micrographs before acid washing:

As seen in Figure 6a, the diameter of deposits was 20-30µm. Deposits had high density and were interrupted and spherical in shape on the bracket surface.

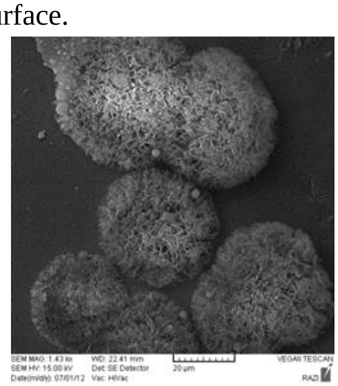

Figure 6a- SEM micrograph of ORJ bracket after the experiment and testing at 1430X magnification

Micrographs after acid washing:

Electrochemical corrosion products were noted on the surface of ORJ brackets coupled with SS wire in the electrolyte. These brackets were appeared yellow, brown and green under light microscope. After the experiment, on the surface of ORJ brackets coupled with SS wire, deposits, crevice corrosion, pitting corrosion, surface corrosion and many defects were noted in order of frequency.

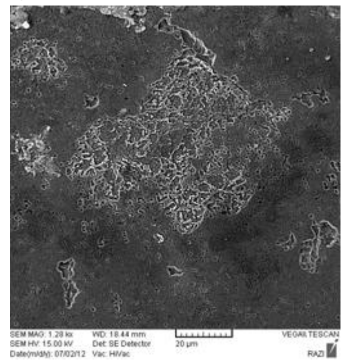

Figure 6b.SEM micrograph of ORJ bracket surface after the experiment and washing at 1280X magnification

Chemical analysis of corroded spots on the surface of brackets using EDX:

In this method, some points were randomly chosen on the surface of brackets. Under electron microscope, X ray was irradiated to determine the amount of elements in the spots. The results are reported in EDX Table. In SEM micrographs (Figures 7-9), the area marked with circle shows crevice corrosion at the interface of bracket and O ring.

<u>1. Third specimen from group 4(ORJ bracket with NiTi wire, specimen #12):</u>

Figure 7 shows ORJ bracket under EDX analysis. Analysis of the specified points (points A, B, C and D) was carried out.

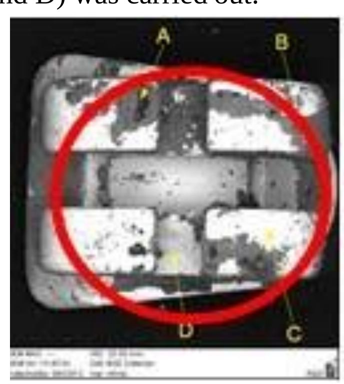

Figure 7- The surface of ORJ bracket after the experiment and before washing

Based on the results for the third bracket from group 4, the C, Fe, Cr and Ni contents were the highest in A, B, D and C points, respectively. O_2, P, and Ca were the highest in point B.

2. First specimen from group 7 (Shinye bracket with SS wire, specimen #19):

Figure 8 shows the Shinye bracket. Analysis of elements in points A, B and C showed that in the first bracket from group 7, the Fe, Cr and Ni contents in point B, Ag and Sn in point C and Cu, C and P in point A were the highest.

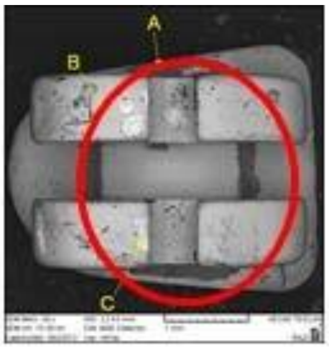

Figure 8- Shinye bracket surface after the experiment and before washing

3. Third specimen from group 8 (ORJ bracket and SS wire, specimen #24):

Figure 9 shows the ORJ bracket. Analysis of points A, B and C revealed that in the third bracket from group 8, Fe, Cr, and Ni contents in point A, P and Cu in point B and Ag in point C were the highest.

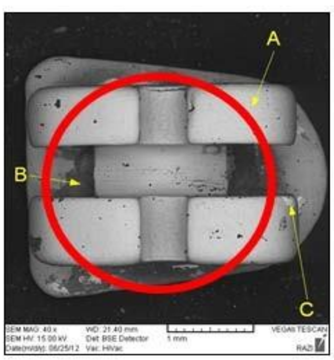

Figure 9.SEM micrograph of the surface of ORJ bracket after the experiment and before washing at 40X magnification

Presence of Fe indicated the occurrence of corrosion on the bracket surface. This element was higher in point B in Figures 7 and 8 (72.85 and 71.81 atomic percent, respectively) and point A in Figure 9 (73.31 atomic percent). This indicates that in these brackets, the mentioned points had the highest CR compared to other points. Also, it can be concluded that the third specimen from group 8 (ORJ bracket with SS wire, specimen #24) with 73.31 atomic percent of Fe had the highest CR compared to other specimens.

Discussion:

Metals and alloys are at risk of corrosion in the oral environment. Also, at present, a wide range of orthodontic products in terms of quality and price are available in the Iranian dental market. These factors along with an increased demand for orthodontic treatment necessitate evaluating the corrosion resistance of different brackets and wires. Several methods are available for the assessment of CR. In the current study, the CR was assessed based on weight reduction in wires and brackets, assessment of corroded specimens under stereomicroscope and SEM, and chemical analysis of some points on the corroded surfaces using EDX.

Orthodontic products are widely variable in the Iranian market and low quality, cheap products made in China are highly popular particularly among general dentists.

Although a passive layer is present on the alloy surface, different ions can be released from the metal bracket surface into the acidic oral environment and thus, the corrosion occurs (13). In electrochemical corrosion, a galvanic couple forms due to the contact of 2 metals with different corrosion potentials. Clinically, a galvanic couple commonly forms in the oral cavity of patients with orthodontic appliances due to the contact of bracket metal with orthodontic wire (6).

The electrochemical properties of saliva depend on the concentration of its constituents, pH, surface tension and buffering capacity (2). On the other hand, consumption of acidic food and drinks by the patient during orthodontic treatment results in drop in saliva pH and exacerbation of the process of corrosion (4). Different factors are responsible for the differences in the corrosion of brackets such as the type of alloy used in different parts of a bracket, type of alloy used for soldering, nobility of metal and phases of bracket fabrication. Also, several important factors are available in the oral environment such as the pH of saliva, presence of microorganisms, and nutrition that play arole in corrosion (13).

In the assessment of CR, specimens did not show significant differences. This finding is in contrastto the results of Masoud Rad, *et al*. in 2012 that used fluoridated mouthrinse as electrolyte (15). In their study, the CR of brackets coupled with NiTi wire was significantly higher than that of brackets coupled with SS wire (15).

Assessment of specimens with light and electron microscopes showed that the CR of Shinye and ORJ brackets was higher than that of Dentaurum and American Orthodontics and the surface changes on the surface of Shinye and ORJ brackets were significantly greater than those on the surface of Dentaurum and American Orthodontics. Difference in the surface roughness of SS brackets does not necessarily result in different susceptibility to corrosion (5). Different CR of brackets of different manufacturers can be attributed to stresses applied during the manufacturing process of these products and the alloys used (4, 5).

The surface of ORJ brackets showed significant changes under a light microscope indicating the staining of these brackets in acidic artificial saliva. This corrosion results in release of corrosion products into the oral cavity. It increases the friction between the wire and bracket and negatively affects the service of these products in the oral cavity and the treatment course of patients (2). This situation was noted in coupling of these brackets with both SS and NiTi wires. Jahanbin, *et al*. in 2009 (13)studied the amount of released Ni ions and the site of corrosion in different brackets available in the Iranian mark, *et al.* one (no coupling with wire). The corrosion of brackets manufactured in China was found to be greater than that of other brackets such as Dentaurum. These results confirm our findings. In the study by Masoud Rad in 2012 (15), greater corrosion was noted in Shinye and ORJ brackets compared to Dentaurum and American Orthodontics brackets. Light microscopic images of Shinye bracket revealed that the surface of this bracket especially at the site of O ring attachment had marked green discoloration, attributed to $FeCl_3$ (16). Such discoloration on the bracket surface may be attributed to staining of brackets. Electron micrographs of ORJ brackets showed severe corrosion at the site of O ring attachment in the form of green and yellow-brown discolorations. The green color was attributed to the presence of $FeCl_3$ and the yellow-brown discoloration was attributed to α-FeOOH (16). This corrosion, considering its location, was of crevice type due to the close contact of two surfaces with one another and lack of oxygen significantly reinforcing the corrosion on the surface of SS brackets resulting in the formation of salt on the bracket surface and release of Fe, Cr, and Ni from the metal. Bracket surface defects may be due to the phases of manufacturing such as milling and electro-polishing (4, 9, 10).

In a study by Masoud Rad in 2012 (15), the corrosion on the surface of Dentaurum bracket wing was of uniform type. Also, electron micrographs of ORJ brackets revealed severe corrosion at the location of O ring, which was of crevice type.

In a study by Jahanbin in 2009 (13), corrosion was found to be in the form of hallow pits, which were brown in color in some points and were more commonly seen on the bracket base and between wings.

Based on the results of EDX Table, release of Fe ions resulted in corrosion of products. Release of Fe, Ni and Cr means destruction of the superficial chromium oxide layer on the SS surface and anodic degradation of elements on the electrode surface and their release into the solution. Considering the standard potential of each metal, it can be predicted, to some extent, that metals with more negative potential have higher solubility in the solution or in other words, have higher potential for corrosion. Other elements such as C, O2 and P are the corrosion products.

Shinye and ORJ brackets in this study did not show similar behavior in contrast to Dentaurum brackets and this resulted in the dispersion of CRs. This finding indicates the lower quality of these products compared to Dentaurum and American Orthodontics brackets. However, further studies are still required on this topic.

The current study had an *in vitro* design and showed the CR of specimens under controlled laboratory conditions. However, the results may change in the dynamic oral environment. Due to limited budget, we could not increase the sample size. In evaluation of electrochemical corrosion, the surface ratio of coupled wire to bracket is very important. In this study, only 1:1 ratio of wire to bracket was evaluated while this ratio is often different in the oral cavity.

Future studies are required to assess the CR of brackets and wires in conditions similar to the oral environment. Also, corrosion of brackets and wires in artificial saliva with variable pH values must be investigated.

Conclusion:

In terms of CR, the understudy wire-bracket couples did not show significant differences. Light and electron microscopic assessments revealed that ORJ followed by Shinye brackets had the highest surface changes in terms of corrosion. Chemical analysis of the corroded points on the surface using EDX revealed that the third specimen from group 8 (ORJ bracket with SS wire, specimen #24) with 73.31 atomic percent of Fe had the highest CR compared to other specimens.

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Conflict of Interest: "None Declared"

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