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Ion Release and Galvanic Corrosion of Different Orthodontic Brackets and Wires in Artificial Saliva

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ABSTRACT

Introduction: To investigate the galvanic corrosion of brackets manufactured by four different companies coupled with stainless steel (SS) or nickel–titanium (NiTi) wires in an artificial saliva solution.

Materials and methods: A total of 24 mandibular central incisor Roth brackets of four different manufacturers (American Orthodontics, Dentaurum, Shinye, ORJ) were used in this experimental study. These brackets were immersed in artificial saliva along with SS or NiTi orthodontic wires (0.016″, round) for 28 days. The electric potential difference of each bracket/wire coupled with a saturated calomel reference electrode was measured via a voltmeter and recorded constantly. Corrosion rate (CR) was calculated, and release of ions was measured with an atomic absorption spectrometer. Stereomicroscope was used to evaluate all samples. Then, samples with corrosion were further assessed by scanning electron microscope and energy-dispersive X-ray spectroscopy. Two-way analysis of variance was used to analyze data.

Results: Among ions evaluated, release of nickel ions from Shinye brackets was significantly higher than that of other brackets. The mean potential difference was significantly lower in specimens containing a couple of Shinye brackets and SS wire compared with other specimens. No significant difference was observed in the mean CR of various groups ($p > 0.05$). Microscopic evaluation showed corrosion in two samples only: Shinye bracket coupled with SS wire and American Orthodontics bracket coupled with NiTi wire.

Conclusion: Shinye brackets coupled with SS wire showed more susceptibility to galvanic corrosion. There were no significant differences among specimens in terms of the CR or released ions except the release of Ni ions, which was higher in Shinye brackets.

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INTRODUCTION

During orthodontic treatment, wires and brackets remain in the mouth for a long period of time, and so they are subjected to mechanical forces of chewing and wearing and electrochemical reactions.[1]

Orthodontic appliances corrode in the oral cavity and this is one of the challenges clinicians face.[2] An electrochemical reaction between an alloy and the environment is described as corrosion. It causes a complete or relative destruction of material or altered properties.[3] Brackets and wires are made of different types of metals, such as Cr-Co-Ni alloy, nickel–titanium (NiTi) alloy, and stainless steel (SS).[4] Hence, they could be affected by different kinds of corrosion, e.g., galvanic corrosion, pitting corrosion, and general corrosion.[5]

Corrosion can roughen the appliance, increase the friction between archwire and slot, and release metal or alloy ions, which consequently can result in discoloration of enamel and soft tissues, local pains, and allergic reactions in predisposed patient.[6,7] Ni and Cr are considered most important elements among corrosion products due to more side effects.[8]

Corrosion resistance is among the basic principles of biocompatibility and many factors may influence it. It depends on the type of alloy, manufacturing process, and surface features of the materials.[9]

In cases where the corrosion potential difference is high between two metals in contact, electrochemical or galvanic corrosion occurs. Based on the oral conditions, metals properties, and compositions of saliva, this type of corrosion can be considered as the main type of corrosion in wires and brackets.[4,6,10,11]

Galvanic corrosion depends on bracket manufacturing more than bracket composition.[12]

Nowadays, different manufacturers produce various kinds of orthodontic brackets and wires with different prices. As the type of the alloy and the manufacturing process of these products affect their resistance to corrosion, it is necessary to investigate the physical and chemical properties of these brackets and wires. This study aimed at evaluation of the electrochemical corrosion of brackets manufactured by four different companies coupled with SS or NiTi wires in an artificial saliva solution.

MATERIALS AND METHODS

The samples consisted of mandibular central incisor 0.022″ Roth brackets of four different manufacturers: 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). These 24 brackets were coupled with round 0.016″ SS or NiTi wires (American Orthodontics, Wisconsin, USA) in eight groups of three. The electrolyte used was artificial saliva (pH: 6.9) 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.

All brackets and wire segments were immersed in acetone solution for 2 minutes before weighing to clean their surfaces. Then, 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.

The percentages of various metals presented in each bracket and wire were measured by a quantometer (ARL, Michigan, USA) with 0.01% accuracy. The results were based on weight percentages and are shown in Table 1.

Each sample was inserted in a separate plate with a saturated calomel reference electrode (Ag/AgCl saturated with KCl) (Azmiran, Tehran, Iran); 80 mL of artificial saliva was used as the electrolyte in each plate in accordance with ASTM G71-81 (2003) standard guide for conducting and evaluating galvanic corrosion tests in electrolytes. Specimens were stored in an incubator at 37 ± 0.1°C.

The couple electric potential (EP) difference of each sample with its respective reference electrode was recorded hourly for 28 days using a data gathering device (Data Logger, Mv-02, designed by Sharif University of Technology).

After 28 days, the electrolyte solution was evaluated for the amount of ions released from samples using an Atomic Absorption Spectrometer (GBC Avanta PM, IL, USA), and wires and brackets were washed gently for 30 seconds with deionized water and then air-dried.

All bracket/wire combinations were evaluated under a light stereomicroscope (SZH10, Olympus, Tokyo, Japan). Samples which showed corrosion under stereomicroscopic evaluation were also studied with scanning electron microscope (SEM) (TESCAN-LMU, Brno, Czech Republic), and assessed by energy-dispersive X-ray (EDX) spectroscopy.

For final weighing, the waterproof varnish was wiped off using acetone, and the samples were immersed in 10% sulfuric acid solution for 2 minutes at room temperature followed by another 2 minutes in sulfuric acid solution at 40°C. After final irrigation with deionized water for 1 minute, the samples were air-dried and weighed. The corrosion rate (CR) was calculated using the formula below:

$$CR\ (mg/dm^2/day) = \Delta W/A/T$$

1 mpy= 25.4 (micron/year) where ΔW is the weight loss (mg), A is the surface area of specimen (dm^2), and "T" is the exposure time (days).

Table 1: Weight percentage of different elements in brackets and wires

Element	*Dentaurum bracket*	*American Orthodontics bracket*	*Shinye bracket*	*ORJ bracket*	*NiTi wire*	*SS wire*
Si	0.28	1.05	0.26	0.77	0	0.65
Cr	16.91	15.55	17.83	17.79	0	18.98
Mn	0.63	0.68	1.39	1.25	0	0.99
Fe	67.61	72.16	72.12	71.02	0	70.09
Ni	11.25	6.14	7.60	7.49	53.78	7.67
Cu	0.16	1.61	0.24	0.67	0	0.69
Mo	3.16	2.81	0.56	1.00	0	0.94
Ti	0	0	0	0	46.22	0
Total	100	100	100	100	100	100

Statistical Analysis

Two-way analysis of variance (ANOVA) was applied for the assessment of released ions in different groups. To evaluate the difference among the groups, the proper *post hoc* test [Tukey's highest significant difference (HSD), Tamhane's test] was used.

RESULTS

Ion Evaluation

The mean concentration of released ions from different samples is demonstrated in Table 2. There were not any significant differences in the concentrations of Cu, Fe, and Mo ions between various brackets coupled with NiTi or SS wires ($p > 0.05$).

In terms of the amount of Ni ions released, the wire/bracket interaction and also the interaction between two wires and four brackets based on two-way ANOVA were not significant ($p > 0.05$). However, a significant difference was found between four types of brackets. Based on Tukey's HSD test, the Shinye brackets significantly released more Ni ions than the other brackets (Dentaurum, American Orthodontics, and ORJ) ($p = 0.017$).

The concentration of Ti ions in all the samples was <300 µg/L.

Evaluation of Electric Potential Difference

Repeated measures ANOVA showed that the interaction of wire and bracket was not statistically significant ($p = 0.109$). Furthermore, the type of bracket and wire did not have a significant effect on changes of the potential difference ($p = 1.00$). For NiTi wires, significant differences did not exist in the potential difference of various bracket groups, and this trend was almost similar and ascending (Graph 1). For SS wires, a significant difference existed in the mean potential difference; the trend of alterations in potential difference of Dentaurum, American Orthodontics, and ORJ brackets was almost similar and ascending, but in Shinye bracket, they were descending (Graph 2).

Evaluation of Corrosion Rate

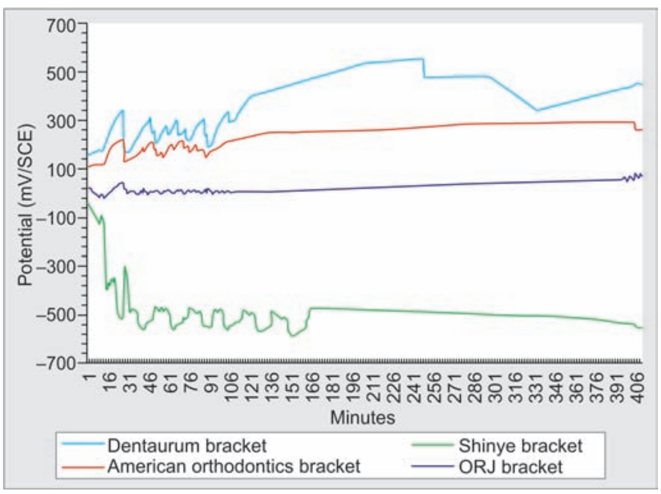
The mean values of CRs are presented in Table 3. Based on two-way ANOVA, no significant difference was observed in the CR of various couplings of brackets with SS or NiTi wires ($p > 0.05$).

Evaluation of Samples under a Light Stereomicroscope

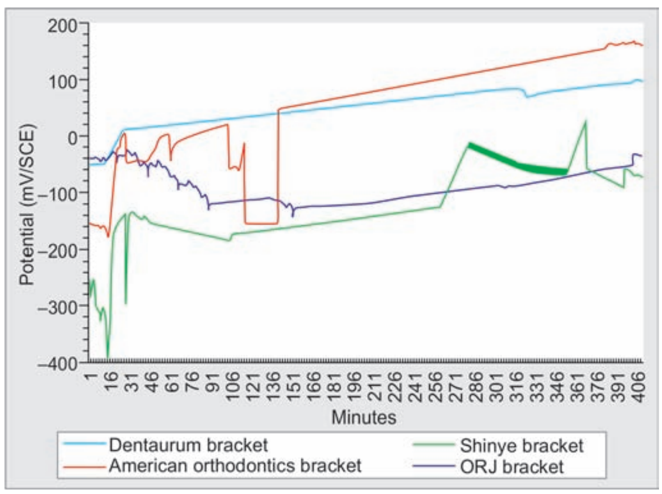
All 24 samples were evaluated under a light stereomicroscope. Two specimens were found to have corrosion.

Table 2: Mean concentrations (in µg) of released ions from various bracket/wire combinations

Wire	Bracket	Cu	Mo	Fe	Cr	Ni
NiTi	Dentaurum	12/33 ± 4/04	133/33 ± 57/73	10/78 ± 17/66	12/66 ± 4/61	28/33 ± 29/19
	American Ortho	27/33 ± 14/01	110 ± 17/32	21/33 ± 8/73	<10 ± 0	17/66 ± 11/59
	Shinye	56/33 ± 3/21	<130 ± 0	14/33 ± 5/33	16/66 ± 11/54	76/66 ± 62/52
	ORJ	31/33 ± 14/97	120 ± 17/32	<10 ± 0	30 ± 0	22 ± 7/54
SS	Dentaurum	46/66 ± 63/50	110 ± 17/32	16 ± 5/29	26 ± 6/92	37 ± 20/042
	American Ortho	0 ± <10	0 ± <100	11 ± 1/73	26 ± 6/92	45 ± 31
	Shinye	0 ± <10	0 ± <100	0 ± <10	15/33 ± 4/61	293/123 ± 365/66
	ORJ	10/66 ± 1/15	110 ± 17/32	<10 ± 0	15/33 ± 4/61	44/66 ± 35/50



Graph 1: Changes in potential difference during the experiment in different brackets coupled with NiTi wire in artificial saliva at 37°C



Graph 2: Changes in potential difference during the experiment in different brackets coupled with SS wire in artificial saliva at 37°C

Table 3: The mean CR of brackets based on the type of bracket and wire

Type of wire	*Type of bracket*	*mpy ± SD*	*±SD*
NiTi	Dentaurum	0/641 ± 0/0138	0/3519 ± 1/6281
	American Orthodontics	0/0256 ± 0/0443	0/6502 ± 1/1262
	Shinye	0 ± 0/0536	1/3614 ± 0
	ORJ	−0/0595 ± 0/0820	−1/5129 ± 2/0849
SS	Dentaurum	0/0320 ± 0/0555	0/8144 ± 1/4107
	American Orthodontics	0/0147 ± 0/0085	0/2167 ± 0/3754
	Shinye	0/0709 ± 0/0268	1/8024 ± 0/6815
	ORJ	−0/01780 ± 0/0147	−0/4318 ± 0/3739

In one of the American Orthodontics brackets coupled with NiTi wire, corrosion products were observed at the intersection of wire and O-ring with yellow discoloration on the bracket slot. No corrosion was detected on the wire.

One sample of coupling Shinye bracket with SS wire showed thick continuous deposits at the site of O-ring. Acid washing revealed little corrosion on the bracket.

Scanning Electron Microscopy Analysis of Samples

Among all the evaluated samples, two brackets (American Orthodontics bracket coupled with NiTi wire and Shinye bracket coupled with SS wire**)** which showed apparent changes were selected for SEM analysis. The evaluation revealed deposits, surface corrosion, and several defects on the brackets.

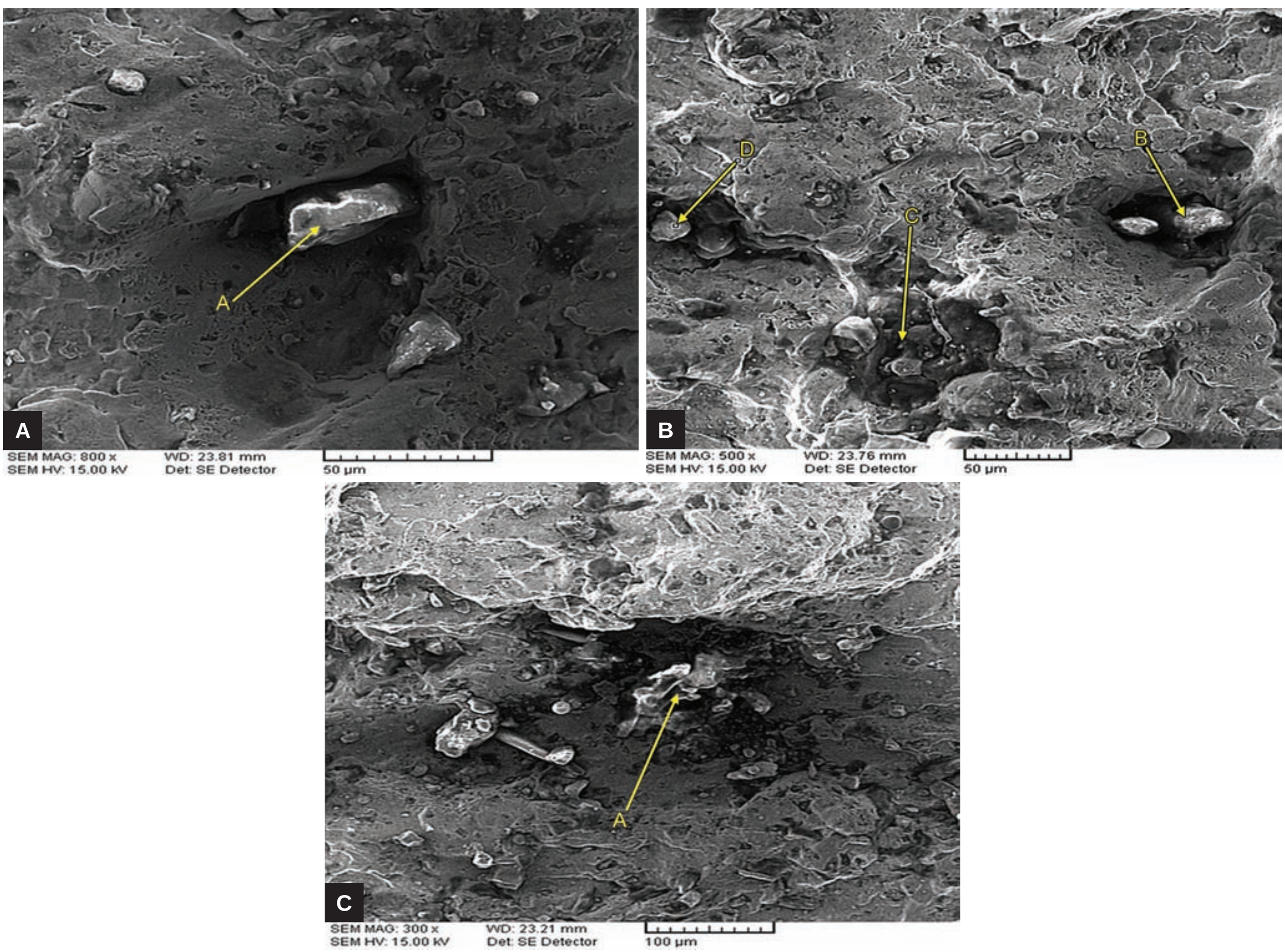
The above-mentioned brackets were further assessed by EDX spectroscopy.

Figures 1A to C show American Orthodontics bracket under EDX analysis. Analysis of the specified points (points A, B, C, and D) showed that the Fe and Ti contents were the highest in point D. Carbon (C) and O_2 contents were the highest in point C.

Shinye bracket under EDX analysis is illustrated in Graph 2. Analysis of the specified point (points A) demonstrated that C and O_2 were the mostly found elements in this point.

DISCUSSION

Metallic orthodontic appliances are prone to corrosion. We evaluated the galvanic corrosion of different bracket/



Figs 1A to C: (A, B) SEM micrograph of American orthodontics bracket (respectively x800 and x500); and (C) SEM micrograph of Shinye bracket (x300) wire combinations through released ions measurement, CR calculation, EP difference recording, and microscopic assessment.

The thermal, ionic, enzymatic, and microbiological properties of the oral cavity make it a suitable environment for corrosion of metals. For example, release of metal ions increases with decreasing saliva pH.[13] To simulate the ordinary oral environment, we used artificial saliva with pH of 6.9 as the electrolyte and the samples were incubated at 37°C.

The rate and speed of galvanic corrosion also depend on the surface area ratio of the two different alloys in contact.[14] A small anode next to a large cathode will increase CR, while a large anode next to a small cathode will have the reverse effect.[12] To eliminate the effect of this confounding factor, we prepared the samples with bracket/wire surface area of 1:1.

Results of several investigations have indicated that the amount of metal ions released from the fixed orthodontic appliances reaches its maximum in 7 days and will be completed in about 4 weeks.[15-18] In this study, bracket and wire specimens were kept in artificial saliva for 28 days. Then, the amount of copper, nickel, chrome, molybdenum, titanium, and iron ions released from the samples was investigated. From a statistical point of view, Shinye brackets released higher nickel ions than the other brackets. The results are consistent with previous studies that show the increased amount of Ni release from this bracket in fluoride mouthwash and acidic artificial saliva.[19,20] It has been known that there is no proportional relation between the release of nickel ions and the nickel content of orthodontic brackets and wires.[6] The results confirm this finding, as the Ni content of Shinye bracket is less than that of Dentaurum bracket and is close to ORJ and American Orthodontics brackets (Table 1). Nickel causes more allergic reactions than any other metal existing in orthodontic appliances. If absorption of nickel ion exceeds 2.5 μg/kg body weight, allergic symptoms will occur.[11] Compared with this, the amount of nickel ion released in this study is significantly lower.

While the amount of released ions is significantly lower than the mean dietary intake and much less than the toxic concentration,[21,22] it is worth mentioning that it may have some adverse effects on the oral mucosa cells, including changes in deoxyribonucleic acid synthesis and in enzyme activity and suppression of the chemotaxis of leukocytes.[23] According to previous studies, the amount of nickel ions that existed in patients' mucosa who use fixed orthodontic appliances is more than in the control group.[24]

In case of released copper, iron, molybdenum, and titanium ions, no significant difference was detected between various wire/bracket combinations. When released ions from these bracket/wire combinations were assessed in fluoride mouth wash,[19] besides Ni, there were significant differences between groups in terms of Cu and Fe. This conflict addresses the importance of electrolyte composition in corrosion behavior of metals.

In addition, other studies[4,19,25] have demonstrated that when SS brackets are coupled with NiTi, wires show more corrosion, compared with not being coupled with SS wires. This finding is in contrast to our results which can be attributed to the difference in study design and the used solution. In the study launched by Bakhtari et al[12] galvanic current and charge of couples did not significantly differ by wire type: NiTi, beta-titanium, and SS. Furthermore, Heravi et al[26] found no significant differences in galvanic corrosion of different combination of orthodontic archwires and SS brackets. This finding was in accord with the results of Kim's study, which evaluated the corrosion resistance of different archwires in a normal saline solution.[27]

The mean of potential difference, which was recorded constantly for 28 days, was significantly lower in specimens containing couple of Shinye brackets and SS wire compared with the other specimens. This had been recorded as negative and descending EP difference throughout the experiment. These results show a good agreement with the study of Tahmasbi et al[19], which showed that the potential difference of coupling Shinye brackets with SS or NiTi wires had been significantly lower than the other combinations. Evaluating these bracket/wire combinations in acidic artificial saliva[20] resulted in the same finding that the potential difference of Shinye brackets coupled with SS wire remained negative throughout the study. Negative potential difference indicates higher galvanic activity and, therefore, higher susceptibility to corrosion.

Corrosion rate based on the weight loss of specimens showed no significant difference between groups. Using acidic, artificial saliva as the electrolyte resulted in the same findings.[14,28] However, this finding differs from the results of the previous study in which the corrosion was evaluated in fluoride mouthwash and showed more CR in specimens coupling SS brackets with NiTi wire rather than SS wire.[19] This may reveal the destructive influence of fluoride ion on resistance of alloys to corrosion, which results in different behaviors.

Microscopic evaluation under light stereomicroscope and SEM showed no corrosion in wires and among the brackets just in two samples: One American Orthodontics bracket coupled with NiTi wire and one coupling of Shinye bracket with SS wire. In experiments where acidic saliva[28] or fluoride mouthwash[19] was utilized as the electrolyte, ORJ brackets also demonstrated corrosion under microscopic assessment, which further confirms the effect of environment on corrosion behavior of brackets.

All these findings show the difference in corrosion resistance of various brackets. This could be largely due to the manufacturing process of the brackets. Bakhtari et al[12] showed that the galvanic corrosion of the brazed bracket coupled with wires was significantly higher than that of the metal injection-molded (MIM) brackets. In the study of Nayak et al,[29] on comparison of galvanic currents generated between different combinations of orthodontic brackets and archwires, the highest mean current was recorded in MIM bracket when used with heat-activated NiTi archwire, while the lowest mean current was recorded in laser-cut bracket when used with beta-titanium archwire.

CONCLUSION

The results of this study showed that:

- Shinye brackets released significantly higher nickel ions than the other brackets.
- There were no significant differences in the CR and concentrations of released Cu, Fe, and Mo ions between various brackets coupled with NiTi or SS wires.
- The mean of potential difference was significantly lower in specimens containing couple of Shinye brackets and SS wire compared with other combinations.

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